

On the wetting behavior of copper

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*„Der Sinn des Lebens besteht nicht darin ein erfolgreicher Mensch zu sein,
sondern ein wertvoller.“*

- Albert Einstein

Zusammenfassung

Benetzungsphänomene begleiten nicht nur unseren Alltag, sie beeinflussen maßgeblich verschiedenste Disziplinen der Materialforschung und Werkstofftechnik. Ein grundlegendes Verständnis der Beziehung zwischen Materialeigenschaften, Oberflächenchemie, Topographie und Benetzungsverhalten ist unabdingbar, um technische Oberflächen mit definierten Benetzungseigenschaften zu designen. Die vorliegende Dissertation verfolgt dabei einen systematischen Ansatz, wobei Kupfer aufgrund seiner vielseitigen Einsatzmöglichkeiten als Modellwerkstoff dient. Die Charakterisierung von Benetzungseigenschaften mittels statischer Kontaktwinkelmessungen erwies sich hingegen der weit verbreiteten Meinung als komplexe Analyse. Die zeitabhängige Adsorption organischer Verbindungen hat sich dabei als Schlüsselfaktor herauskristallisiert, da Materialeigenschaften wie das Gefüge oder Oxidschichten durch Adsorbatfilme maskiert werden. Topographisch modifizierte Oberflächen z.B. durch direkte Laser-Interferenz-Strukturierung können in Verbindung mit einer adäquaten Oberflächenchemie ihr Potenzial entfalten und extreme Benetzungseigenschaften herbeiführen, wobei selbst kleinste topographische Abweichungen maßgeblich das resultierende Benetzungsverhalten beeinflussen können. Die vorliegende Dissertation liefert tiefe Einblicke in die komplexe Welt der Benetzung und leistet einen entscheidenden Beitrag zum grundlegenden Verständnis von Benetzungsvorgängen auf technischen Kupferoberflächen.

Abstract

Wetting phenomena do not only accompany our daily lives but also significantly affect various disciplines in the field of materials science and engineering. In order to design technical surfaces with defined wetting properties, fundamental knowledge of the interplay between material's properties, surface chemistry, topography and wetting behavior is indispensable.

This dissertation follows a systematic approach where copper serves as the model material due to its versatile application possibilities. Contrary to the widespread belief, characterization of wetting properties via static contact angle measurements proved to be a complex analysis. Time-dependent adsorption of organic compounds was identified as a crucial parameter as adsorption films mask material properties like microstructure or oxide layers. Topographically modified surfaces e.g., by direct laser interference patterning can show their potential to shift the wetting properties to extremes if combined with adequate surface chemistry while even the slightest deviation in topography can have a significant impact on the resulting wetting behavior.

This dissertation provides deep insight into the complex world of wetting and contributes significantly to the fundamental understanding of wetting processes on technical copper surfaces.

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Abbreviations and Symbols

Abbreviations

SCA	Static contact angle
XPS	X-ray Photoelectron Spectroscopy
CB	Cassie-Baxter
DLIP	Direct Laser Interference Patterning
ACA	Advancing Contact Angle
RCA	Receding Contact Angle
SEM	Scanning Electron Microscopy
PFAS	Per- and Polyfluoroalkyl Substances
SP	Short-pulsed
USP	Ultra-short-pulsed
DLW	Direct Laser Writing
LIPSS	Laser Induced Periodic Substructures
LSFL	Low Spatial Frequency LIPSS
HSFL	High Spatial Frequency LIPSS
PVD	Physical Vapor Deposition
LSM	Laser Scanning Microscopy
WLI	Wight Light Interferometry
EDS	Energy Dispersive X-Ray Spectroscopy
FIB	Focused Ion Beam
WLI	Wight Light Interferometry
TOF-SIMS	Time of Flight – Secondary Ion Mass Spectrometry
EBS	Electron Backscatter Diffraction
XRD	X-ray Diffraction
AFM	Atomic Force Microscopy

Symbols

θ_Y	Contact angle according to Young
γ_{SV}	Interfacial tension between solid and vapor phase / Surface energy of a solid in contact with a vapor phase
γ_{LV}	Interfacial tension between liquid and vapor phase / Surface energy of a liquid in contact with a vapor phase
γ_{SL}	Interfacial tension between solid and liquid phase / Surface energy of a solid in contact with a liquid phase
r	Roughness factor (Wenzel)
θ_W	Contact angle according to Wenzel
θ_{CB}	Contact angle according to Cassie and Baxter
f	Wetted area fraction according to the Cassie-Baxter-Model
$\Delta\theta$	Contact angle hysteresis
γ	Surface energy
γ^p	Polar components of the surface energy
γ^d	Dispersive components of the surface energy
τ_P	Laser pulse duration
τ_L	Lattice heating time
τ_e	Cooling time of electrons
p	Periodicity of laser pattern
λ	Wavelength
2α	Angle between laser beams

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1 Motivation

Wetting is a scientific phenomenon which we encounter daily – also as non-scientists: If you look outside the window on a rainy day, you may find water droplets rolling down your window while they won't stick to your freshly waxed car. A closer look in your garden will reveal water droplets beading up on rose petals and rolling off lotus leaves even cleaning the petal by transporting dirt from the surface. You might even have purchased certain coated sanitary equipment or cleaning agents promising to leave the surfaces with a self-cleaning behavior. After finishing your first cup of coffee in the morning you will see residues running down the side of your cup. And, since the corona pandemic at the latest, we've all become familiar with the problem of our vision becoming cloudy because our glasses fog up from the moisture in our breath while wearing a mask. All these phenomena can be traced back to the wetting of a surface which can be understood as its likelihood of interacting with certain fluids determined by the energy of the surface and the interaction forces with the liquid. In general, surfaces with a high affinity to water and a resulting strong wettability show spreading of water on the surface and are referred to as hydrophilic (greek: hydro = water, philic from philos = to love). In contrast, a surface is classified as hydrophobic when droplets of water are repelled by the surface (greek: hydro = water, phobos = fear).

From a scientific point of view, there are even more phenomena which are influenced by the wettability of the surface, such as:

- ❖ The altering of wetting properties is applied to tune **heat transfer** of surfaces, often considering copper surfaces due to their inherently high thermal conductivity [1–3].
- ❖ The **corrosion resistance** can be adjusted by altering the wettability of a surface e.g., by coating with highly hydrophobic films [4–6].
- ❖ Adhesion, wetting and spreading of lubricants in tribological contact zones directly influences the **tribological performance** of a material [7,8].
- ❖ The **adhesion of coatings** becomes important in printing processes and is strongly connected to a surface's energy and therewith wettability [9,10]. But also in joining processes, e.g., soldering, wettability is a crucial factor to achieve durable material connections [11,12].
- ❖ Wetting properties of materials can qualify them to act as **filter media** for different substances, typically the separation of oil from water is widely discussed [13–15].
- ❖ Alteration of surfaces to not only achieve extreme wetting behavior but also to suppress **ice formation** has created an own research field around water-surface interactions [16–18].
- ❖ **Self-cleaning behavior** of technical surfaces is highly dependent on the wettability of the surface and its interaction forces with the particles to be removed [19,20].
- ❖ Wettability is also investigated on much smaller scales e.g., in nanochannels as it greatly influences the **flow friction** and therewith **transport of fluids** through the channels [21] but also affects **heat transfer in nanochannels** [22,23].

- ❖ The **antimicrobial activity**, which is inherent especially to copper containing alloys [24], is influenced by the wettability of a surface, which was found to affect e.g., interaction forces as well as mechanical bacteria-surface interactions [25–29].
- ❖ Wetting also shows an impact on **cell responses** to a surface: cell proliferation, guidance or differentiation, especially important for e.g., implants can be influenced by wetting [30–32].

Apparently, the wettability of the surface is crucial for many scientific and technological issues. The characterization of the wetting behavior poses a challenge in different ways: In recent years, researchers became more aware of dynamic changes from hydrophilic to hydrophobic wetting behavior of metallic surfaces over time due to the adsorption of volatile carbonaceous compounds from the atmosphere [33–36]. This time-dependent wetting behavior asks for strictly controlled experimental procedures to ensure comparable sample conditions. Still, often there is a lack of detailed information on procedures and sample conditions, complicating comparability of different studies. Different approaches in literature can be found to accelerate the wetting transition from hydrophilic to hydrophobic e.g., low temperature annealing [37–40] or storage in a vacuum chamber [17,41,42]. The adsorption processes not only induce a time dependency of the wetting behavior but also directly affect the chemical composition of the surface under investigation. While some researchers apply coatings to achieve stable wetting states [43–45], others use the adsorption and desorption dynamics of volatile organic compounds to create switchable wetting states [38,40]. As topography is known to greatly alter the wetting behavior of freshly prepared as well as aged or coated samples, different approaches can be found in literature to roughen surfaces ranging from etching and electrodeposition [45,46], to lithography [47,48] to laser treatments [36,49–51] among others. Laser treatment is conducted either with a single beam or in more complex multi-beam interference-based patterning setups favoring hierarchical surface patterns. Due to the above-described dynamic changes in surface chemistry upon exposure to the atmosphere, the effect of topography needs to be investigated by considering surface chemistry as well. Especially laser-based patterning techniques do not only form multiscale hierarchical topographies but also cause process-induced changes in surface chemistry due to oxidation, usually leaving the surface superhydrophilic right after laser processing but rendering it increasingly hydrophobic upon exposure to volatile organic compounds [25,33,36,49–52]. Thus, it becomes evident that for a detailed assessment of wetting properties of technical surfaces a multitude of different effects (surface chemistry, surface topography, age, storage conditions, measurement conditions etc.) need to be considered. Especially time dependent changes in surface chemistry due to the contact to volatile organic species and their impact on the development of wetting behavior are crucial for a fundamental understanding of the role of chemistry and topography in wetting analysis of technical surfaces. It is also still under debate, if the chemical composition of the base material influences the species of adsorbed volatile organic molecules [53], which can only be investigated if samples are subjected to identical storage conditions during the aging process and not equalized by chemical coatings right after preparation. With careful design of the conducted experiments as portrayed in this thesis, the

understanding of occurring wetting phenomena becomes possible. This knowledge forms the basis for the transfer into applications with a design of technical surfaces depicting the desired wettability for the tailored application.

This thesis therefore aims at not only creating a general deeper understanding of the influence of surface topography and surface chemistry on the wetting behavior of metallic surfaces by empirical alteration but to follow a systematic approach instead. This approach is based on fundamental investigations of the sample material and the experimental setup for wetting analysis. Furthermore, this evolves into advanced investigations of the effects of intrinsic material properties on time-dependent wetting behavior. Finally, a multi-scale study incorporates the effect of surface chemistry and different surface topographies into the assessment of wetting behavior. The following chapter provides a brief overview of the research questions addressed in this thesis.

2 Research Objectives

In order to precisely determine the role of surface chemistry and surface topography on the water wettability of technical surfaces, a systematic investigation is necessary. A study on the effect of topography and chemistry on water wettability conceptualized and initiated by Dr. Philipp Grützmacher was conducted on stainless steel and acted as an experimental pre-work and motivation to formulate the research questions. For the core investigations conducted in this thesis to address the presented research objectives, copper was chosen as a model material. Copper finds a wide application in scientific as well as industrial sectors [54] and its wetting behavior is of the utmost importance e.g., for its antimicrobial properties [25,28], the assessment of its corrosion behavior [4,6], its self-cleaning properties [55], heat transfer capabilities [1,2,56] and many more. Oxide formation of pure copper is well known [57] and Cu_2O and CuO seem to form the main components of oxidic reaction layers after laser treatment [52]. Oxygen-free copper (CW008A, $\text{Cu} \geq 99.95\%$) was therefore chosen as a model material for the main studies to address the research objectives summarized in Figure 1.

The presented research objectives were compiled during the work on the DFG project 435334669 [58] which dealt with the topographical and chemical influences on the wetting behavior of laser-patterned metallic surfaces.

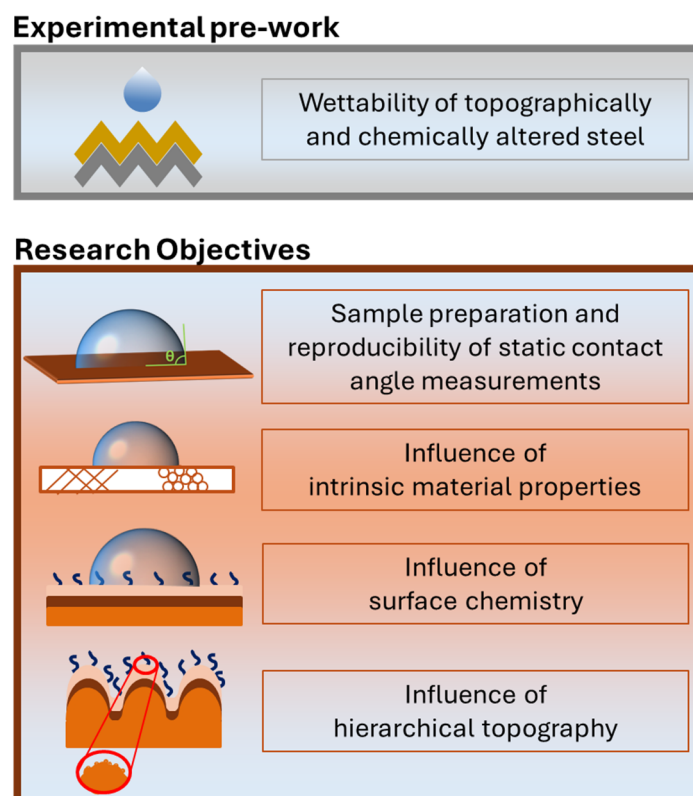


Figure 1: Overview of the structure of research objectives within this thesis.

Research Objective 1: Copper sample preparation and influences on the reproducibility of static contact angle measurements

Metallographic sample preparation is a basis for any subsequent characterization and sample processing steps which were applied throughout this thesis. Therefore, the first aim of this research objective evolves around the investigation of the metallographic preparation of copper surfaces, and the removal of preparation induced deformation layers by electropolishing. The preparation of flat copper surfaces with a high-quality finish made the foundation for the main focus of this research objective, namely the investigation of classical static contact angle (SCA) measurements under consideration of different influencing parameters taking into account wetting changes due to dynamic adsorption processes of volatile organic species. The identification of parameters possibly influencing the reproducibility of static contact angle (SCA) measurements was pursued to allow for better control of SCA measurements.

Research Objective 2: Influence of intrinsic material properties on the wetting behavior

The main focus of the second research objective is the evaluation of the influence of microstructure on the time dependent development of the wetting behavior of copper. In order to investigate complex influences on the wetting behavior of copper by topographical and/or chemical surface treatments, fundamental investigations on material properties influencing the surface water interaction are necessary. Three different microstructure states were created by sample preparation based on the results of research objective 1 and investigated in regards of the dynamics of the adsorption of volatile organic compounds and the resulting wetting behavior.

Research Objective 3: Influence of surface chemistry on the wetting behavior

Topographic alteration usually is accompanied by chemical alteration as well, either due to process oxide formation e.g., during laser patterning of the surface or due to subsequent formation of adventitious carbon due to adsorption. In order to assess the influence of surface chemistry on the long-term wettability of technical copper surfaces, this research objective focuses on the detailed characterization of adsorbed carbonaceous species on the one hand. The depth distribution of adventitious carbon is investigated via advanced XPS (x-ray photoelectron spectroscopy) measurement techniques. On the other hand, influence of oxidic surface termination of flat copper samples is to be investigated in the framework of research objective 3. The influence of the nature of copper oxide state prior to sample aging is investigated by magnetron sputtering of Cu, CuO and Cu₂O on flat copper substrates. Therewith, the influence of surface chemistry can be determined vastly independent of surface topography.

Research Objective 4: Influence of hierarchical surface topography on the wetting behavior

Research objective 4 of this thesis deals with the influence of surface topography on the long-term wetting behavior of copper surfaces. With regards to the results of research objective 4, two different categories of surface topography are investigated. A statistical isotropic topography is applied by one-beam laser roughening. Directional anisotropic topography is created by direct laser interference patterning (DLIP) with fs and ps pulse durations. Induced variations in primary topography features (aspect-ratio) were investigated as well as the effect of varying subpattern characteristics while maintaining the primary topography.

3 Theoretical Background and State of the art

This chapter will give a brief overview of the fundamentals of wetting analysis, theoretical models on wetting phenomena on ideal and real technical surfaces, different measurement techniques currently applied to determine the wettability of a surface and an overview of chemical and topographical surface treatments to alter the wetting behavior of surfaces.

3.1 Wetting Analysis – The foundation stone

More than 200 years ago, in 1805, Dr. Thomas Young reported “that for each combination of a solid and a fluid, there is an appropriate angle of contact between the surfaces of the fluid, exposed to the air, and to the solid” [59]. This so called “angle of contact” evolved to be a key parameter to determine the wettability of a surface.

In his essay, Dr. Young described the contact angle in an ideal equilibrium system θ_Y to be dependent on interfacial tensions between the solid and the vapor phase γ_{SV} , the interfacial tension between the liquid and the vapor γ_{LV} and between solid and liquid γ_{SL} according to equation (1). A schematic illustration of this equation is presented in Figure 2. It should be noted that more recent literature concludes that instead of a mechanical / force-based interpretation of equation (1) in terms of surface tensions, the energetic interpretation based on surface energies is more appropriate [60], where details are out of scope of this work. Surface energies of solids or liquids in contact with vapor differ from theoretical values in vacuum by a term often referred to as spreading pressure. This term usually is neglected which appears reasonable for contact angles $> 0^\circ$ [61–63].

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

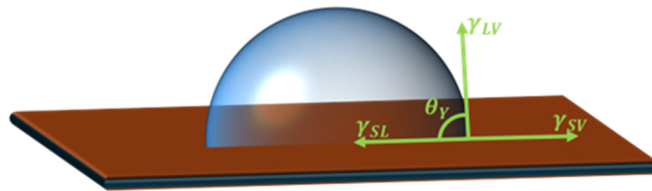


Figure 2: Schematic illustration of the definition of the contact angle according to Young in ref. [59] showing a droplet of a liquid in equilibrium with its contacting solid and surrounding vapor phase.

A prerequisite to an ideal system is chemical and topographical homogeneity of the contacting phases as well as full inertness avoiding changes in the interaction forces [61]. This already indicates that while Young was able to set the fundamental rules for the definition of a contact angle, other models were necessary to describe the wetting behavior of surfaces prone to chemical as well as topographical

irregularities. The wetting community has agreed on defining a surface as hydrophilic once its θ_Y is below 90° and as hydrophobic once it increases to or above 90° [64,65].

Quick summary

In the early 19th century, Dr. Thomas Young derived the basic theories around the contact angle, which arises when a liquid comes in contact with a solid surface under ideal conditions.

3.2 From the ideal to the real world

While in theory a surface can be assumed as atomically flat and chemical homogeneous and therewith deserves to be deemed as “ideal”, such a surface does not exist in nature. After Young published the essay on the contact angle of ideal surfaces in 1805 [59], it took another 130 years until Wenzel published an article on the contact angle of rough surfaces [66] arguing that an increased surface area induced by roughness influences the surface energy per unit area and therewith the wetting behavior of a solid. To describe his observation mathematically, he introduced the “roughness factor” r defined as the quotient of the actual (rough) surface by the projected surface area (geometric surface). He found the contact angle on a rough surface θ_W to be proportional to the contact angle on an ideal surface of the same material as described in equation (2).

$$\cos \theta_W = r * \cos \theta_Y \quad (2)$$

This model assumes complete wetting of the surface topography by the liquid. For an ideal surface, $r = 1$ and equation (2) transforms into the Young equation (1). Wenzel concludes that roughness enhances the existing wetting behavior. With increasing droplet size compared to the size of the topographic features, the Wenzel equation appears to become more reliable [67]. In 1944, Cassie and Baxter extended the theory of Wenzel to rough (porous) surfaces [68] where the liquid forms air inclusions with the solid. Figure 3 shows a schematic illustration of a droplet in the Wenzel state, wetting the substrate roughness and, in the Cassie-Baxter (CB) state, with the droplet forming air inclusions with the surface topography.

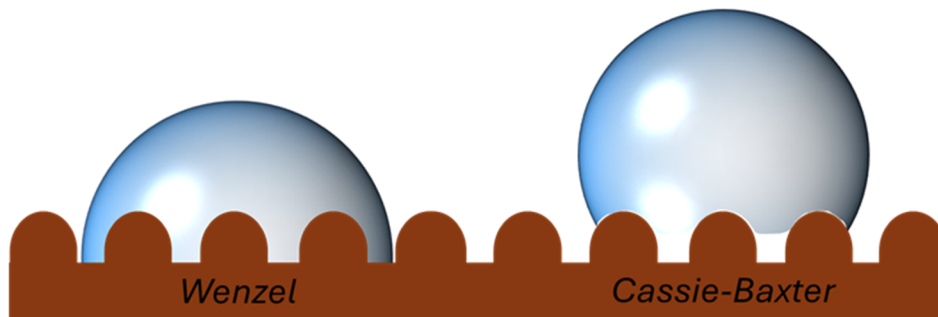


Figure 3: Schematic showing a droplet wetting the roughness in the Wenzel wetting state or encapsulating air bubbles with the solid surface in the Cassie-Baxter wetting state.

The resulting contact angle θ_{CB} is defined according to equation (3) where f_1 is the total area between solid and liquid and f_2 between liquid and air per projected unit area.

$$\cos \theta_{CB} = f_1 * \cos \theta_Y + f_2 \quad (3)$$

In their original publication [68], Cassie and Baxter refer to advancing (ACA) and receding contact angles (RCA) in equation (3). These terms refer to the highest and lowest measurable apparent contact angle [64] and will be discussed in more detail in the next chapter. Milne et Amirfazli report in reference [69] on a work of Johnson and Dettre [70] (source was not accessible) who reevaluated equation (3) based on thermodynamic principles and showed that the contact angles refer to the equilibrium angles. In another work, Cassie [71] introduced a more general term for equation (3) taking into account chemically heterogeneous surfaces of different materials (material 1 and 2):

$$\cos \theta_{CB} = f_1 * \cos \theta_{Y1} + f_2 * \cos \theta_{Y2} \quad (4)$$

For air as material 2, θ_{Y2} equals 180° and therefore $\cos \theta_{Y2} = -1$ and equation (4) transforms into equation (3). Again, this approximation is better fulfilled with increasing drop volume [67,69,72]. In literature, different forms of the Cassie-Baxter equation are applied, where equation (5) is a commonly applied simplification and defines f as the wetted area fraction in terms of the projection of the solid-liquid interface per projected unit area [69].

$$\cos \theta_{CB} = f * \cos \theta_Y - (1 - f) \quad (5)$$

It allows for a simplified approximation of f and ignores any penetration of the droplet into the roughness – Milne et Amirfazli recommend using the original definition of the equation due to inaccuracies associated with equation (5) [69]. Though Wenzel as well as Cassie and Baxter took criteria for real surfaces like roughness or chemical heterogeneity into consideration, not all wetting phenomena can be explained by their models. Often, transition states exist from the energetic higher metastable Cassie-Baxter state to the stable Wenzel state where the transition mechanism depends on topography and chemistry of the surface [73,74]. Not only properties of the surface but also of the droplet, e.g., volume, can heavily influence the transition [75]. Figure 3 displays a rather simple topography in the form of non-hierarchical periodic patterns spreading homogeneously over the surface. In the case of hierarchical topographies, where the main pattern is decorated with additional features as often found on laser treated surfaces [43,52,76], additional definitions derived from the classical Wenzel and Cassie-Baxter wetting can be found in the literature. Bhushan and Nosonovsky [77] for example defined nine wetting states with different combinations of filled micro- and nanostructure respectively primary and secondary topography. A well-known wetting state thereby refers to the lotus leaf with a highly hydrophobic behavior of the leaf combined with low water adhesion resulting in a self-cleaning effect of the plant. They attribute this behavior to a droplet sitting on top of the topography without impregnating either the primary or the secondary pattern. Details on the outstanding wetting properties of lotus leaves can be found in a work by Ensikat et al [78]. A rose petal behavior with highly hydrophobic surface properties but a strong water adhesion is achieved by the liquid penetrating the primary but not the secondary

topography according to Bhushan and Nosonivksy [77]. This wetting state is also deemed as Cassie impregnating wetting state in literature [79]. Both wetting dynamics were also already successfully mimicked by laser surface treatment and thereby transferred to technical surfaces [43,51,80].

Quick summary

- *As ideal surfaces do not exist in nature, Wenzel as well as Cassie and Baxter derived models to describe the wetting behavior of rough surfaces. Wenzel describes the contact angle of surfaces where the liquid fully penetrates the roughness features while Cassie and Baxter take air inclusions between the liquid and the solid into account.*
- *Different forms of the Cassie-Baxter equation exist, where especially the determination of the wetted area fraction poses a challenge.*
- *Both models are commonly used in literature to approximate observed wetting phenomena.*
- *Researchers have defined evolved wetting states on rough surfaces taking hierarchical topography into account*

3.3 The challenge of wetting characterization

If a droplet is applied to a solid surface and the apparent contact angle is measured under static conditions (no movement of the baseline) after droplet deposition, this contact angle is called static contact angle [81]. Usually, the droplet is applied by a microliter syringe, and the needle is retracted from the droplet before the drop is captured. A goniometer is used which captures the side view of the droplet and the shape is fitted (e.g. by an elliptical or a polynomial fit) to calculate the angle the droplet forms on the surface.

As literature often portrays a variety of different SCA results for the very same material [34,61], researchers try to find reasons for the scattering of the reported angles on the one hand and suggestions for improvement of reproducibility in the wetting analysis on the other hand [61]. While dynamic changes in surface chemistry due to adsorption of volatile organic compounds from the atmosphere gain growing recognition, there are also theoretical energetic considerations to explain scattering contact angle values as described in the following paragraph.

The Gibbs' energy curve for non-ideal chemically or topographically inhomogeneous surfaces might depict multiple metastable equilibrium states along the lowest, most stable state which seems not accessible via experiments with currently available measurement techniques (see Figure 4). Some researchers question the reproducibility and significance of static contact angles since the result could portray any local (metastable) equilibrium state between the maximum (advancing contact angle) and the minimum metastable contact angle (receding contact angle) [61,64,67,81–84]. On rough surfaces,

the lowest energetic apparent contact angle is represented by the models of Wenzel and Cassie and Baxter [64,69,70].

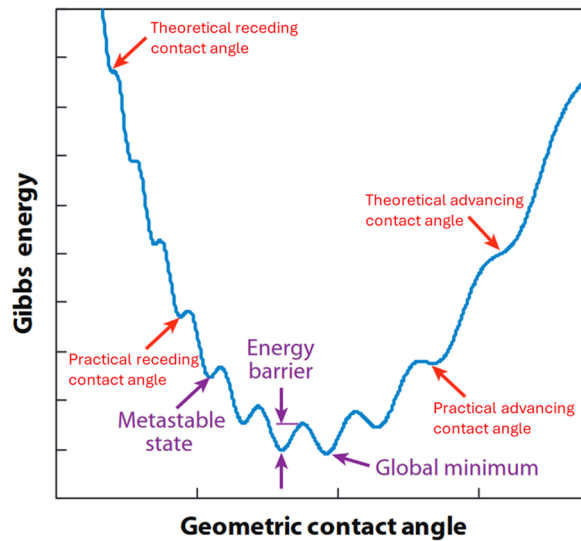


Figure 4: Definitions of contact angles based on the Gibbs energy over the geometric contact angle. For (metastable) equilibrium states, the geometric contact angle corresponds to the apparent (experimental measured) contact angle. Reproduced and adapted from [67].

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Some researchers prefer the measurement of ACA and RCA over the measurement of static contact angles and associate them with a greater reproducibility [61,64,67,81–83]. In the sessile drop setup, ACA and RCA are usually measured by slowly adding or rejecting liquid from the droplet. Slow dosing speeds are pursued to avoid dynamic effects, ACA and RCA are therefore deemed as “quasi-static” [83]. Volume enlargement / volume reduction leads to an increase / decrease in the measured contact angles until the baseline starts to move and ACA / RCA is reached - protocols can be found in the literature [81,83]. Another technique relies on the tilting of the surface after a droplet was applied, although ACA and RCA are not necessarily determined correctly in this setup [83]. As the static contact angle, these two contact angles can be influenced by measurement conditions. Naturally occurring vibrations in a laboratory can cause a shift from the theoretical values of the minimum and maximum metastable apparent contact angle to the practical (measured) values as depicted in Figure 4 because they “overcome some magnitude of a potential barrier” [67]. Especially the measurement of RCA seems challenging, e.g., due to problems in the movement of the receding contact line and great dependencies on the initial droplet volume [85]. On rough or patterned surfaces ACA and RCA measurement can be accompanied by pinning of the contact line and an observed stick and slip behavior [86]. The contact angle hysteresis $\Delta\theta$ is defined as ACA-RCA and serves as a measure for droplet mobility but does not have a clear physical interpretation [61,85]. If a surface depicts high ACA ($> 150^\circ$) and low $\Delta\theta$ ($< 10^\circ$) with a small roll-off angle, it is called superhydrophobic [64].

Despite this high complexity of ACA/RCA measurements compared to SCA analysis and the

vulnerability towards environmental influences, SCA measurements are often associated with a poorer reproducibility [61,82,83]. Therefore, it was of interest in this thesis – especially within the investigations in research objective 1 – to identify possible sample as well as measurement induced influences on static contact angles and to increase reproducibility with a strong control of the identified parameters. SCA still is one of the most common methods for wetting characterization and attractive due to its alleged simplicity, where other measurement techniques should be understood as complementary but not as substitutional – SCAs for example do not provide information on droplet mobility [84]. Though researchers are aware of potentially influencing factors like droplet size, surface rigidity, surface roughness, chemical adsorbents, surface impurities, sample cleaning, measurement liquid or humidity [84,87,88], approaches for the measurement of SCA vary strongly. With so many possible influencing factors, it is no surprise that reported SCA values often lack comparability despite earlier discussed possible thermodynamic reasons. Especially surface contamination by contact with the atmosphere and adsorption of carbonaceous species often is neglected in the discussion of contact angles [34] as well as measurement techniques. The above explanations show that measured contact angles highly depend on the measurement technique, environmental effects and sample state and that reproducibility currently is a great challenge for the wetting community. For any contact angle measurement, researchers need to consider that theoretical values are not necessarily met and therefore models like the Young equation or Wenzel and Cassie-Baxter equations can only “be regarded as tools in aiding the wettability characterization” [84]. Next to the measurement technique itself, sample state and surface condition need to be evaluated in detail in order to allow for a correct interpretation of the measured angles. This point often is neglected in the discussion of the quality of measurement techniques – not all differences observed on the same material necessarily arise through inappropriate measurement but rather due to a lack of sample state observation. In order to refine the measurement of SCAs towards greater reproducibility and more precise interpretation, detailed investigations of measurement as well as sample induced influences are needed, taking into account different chemical sample states through dynamic adsorption processes, which will be explained in more detail in the following chapter.

Quick summary

- *The measurement of the wetting behavior of technical surfaces poses a challenge when it comes to reproducibility.*
- *SCA measurements are a popular and widespread measurement technique but often deliver varying contact angles on the same material. Some researchers prefer to measure the advancing and receding contact angles instead, but again results may differ depending on the applied measurement technique or environmental influences where especially the receding contact angle often cannot be determined correctly.*

- *Besides the existence of several metastable thermodynamic states, various additional factors can affect the SCA results. Therefore, a thorough investigation of measurement as well as sample induced influences is needed to assess the reproducibility of SCA measurements in detail.*
- *The influence of sample state and especially of dynamic changes in surface chemistry due to atmospheric contact needs particular investigation.*

3.4 From theory to practice

While inconsistencies in the measurement technique and thermodynamic insecurities might be one reason for a scattering of measured contact angles, an important factor is often neglected: Dynamic changes in surface chemistry due to the adsorption of adventitious carbon groups leading to significant changes of the wetting response depending on sample age and storage conditions. Especially the role of dynamic chemical alterations of technical surfaces rendering them hydrophobic upon atmospheric contact should be taken into account in any measurement and discussion of contact angle measurements. Therefore, the next chapter provides profound insight into the influence of surface polarity and energy minimization by adsorption of volatile organic molecules on technical surfaces.

Surface chemistry influenced by natural contamination shows to majorly affect the wetting characterization of a material. Volatile organic compounds are present in the air and cause the accumulation of thin carbonaceous layers (adventitious carbon) on technical surfaces in contact with the surrounding atmosphere [89]. Literature from the 1980's [88] already pointed out a strong scattering of contact angles measured e.g., on copper due to surface contamination, sample preparation or sample cleaning. Finding the real contact angle of copper still occupies researches 40 years later as shown by the work of Korczeniewski et al. [34]. They found clean copper surfaces to be hydrophilic while the exact value seems to depend on the crystallographic orientation - contact to air induced an increase of the SCA towards the hydrophobic regime. Hydrocarbon contamination also affected evaporation and ice-formation. Gim et al. [90] showed that clean surfaces of noble materials are superhydrophilic with a SCA = 0° and suggest that deviations from this observation are a result of surface contamination or oxidation, e.g., a chemical alteration of the surface. This is in agreement with the findings by Schrader [91]. The accumulation of adventitious carbon lowers the surface energy of the solid [36,62]. The surface tension / energy can be divided into polar components γ^p and dispersive components γ^d according to equation (6). The dispersive component constitutes long-ranged Lifshitz-van der Waals forces as sum of Debye, Keesom and London interactions. The second term forms the polar component of the interaction force and is typically resembled by hydrogen bonds [61,62,92,93].

$$\gamma = \gamma^d + \gamma^p \quad (6)$$

If the liquid and the solid are similar in the composition of polar and dispersive components, small contact angles and high water adhesion are expected [94]. Reference [61] provides a detailed overview of the historical development of various models describing forces and energies connected with wettability, which are out of scope of this thesis. Due to the concept of energy minimization, high energetic surfaces like metals or oxides adsorb volatile organic compounds if available in the vicinity of the surface upon storage in an aging process. Therewith, they terminate their surface with nonpolar groups introducing a change from an initially hydrophilic to a growing hydrophobic behavior until the contact angle stabilizes [33,34,36]. This termination directly influences the interactions with liquids and therewith the resulting wettability.

In an article from J.E. Castle [95] a schematic of a metal surface with the reaction layers forming in atmospheric contact on top of the metallic base material is given. It was originally introduced by Eirich et al. [96] in 1968, but this primary source was not accessible.

It shows a system consisting of different layers:

- a metallic base
- a growing oxidic reaction layer with possible impurities / alloying elements
- a hydroxylated layer due to the reaction of the oxide layer with water molecules from the atmosphere
- polar organic molecules which adhere to the hydroxylates and
- non-polar organic compounds which terminate the surface.

It proves that already more than 50 years ago, scientists were aware of the complex reaction layers forming on metals that exceed the classical approach of a simple oxidation layer as surface passivation. Still, up to today, some researchers do not acknowledge the formation of these airborne carbonaceous species strongly affecting the wetting behavior and rather rule deoxidation processes responsible [97]. The oxidation process naturally occurs as soon as the metal surface is in contact with atmospheric oxygen and leaves the surface in a polar state due to unsaturated metal as well as oxygen ions [42]. The hydroxylation process rendering the oxidic surface with OH⁻-groups is believed to happen very fast due to the reaction of the non-equilibrium oxidic metallic surface with atmospheric water vapor. A possible theory for the development of hydrophobic surfaces with the non-polar organic termination is the subsequent reaction of the hydroxide groups with atmospheric carboxylates. Due to the chemisorption process, the non-polar chains of the organic groups stick outwards [36,38,41,42,98–100]. Especially the formation of a hydroxylation layer is believed to be a crucial prerequisite for the adsorption of carbonaceous species as reactive adsorption sites are formed and it seems to depend on the chemical nature of the metallic substrate and the negative charge density in the oxidic reaction layer [101]. The amount of available water molecules in the atmosphere which can be measured by the relative humidity also seems to significantly influence the entire aging process. While aging in very dry environments might suppress hydroxylation and therefore strongly limit the chemisorption of organic compounds,

high relative humidity might favor the formation of hydrogen bonds and hinder the adsorption of organic compounds [17,41,42,99–101]. Long et al. [33,98] were able to show that atmospheres rich in organic compounds favor hydrophobization while storage in pure oxygen, CO₂ or nitrogen maintained hydrophilicity.

Grey et al. [89] found that about one quarter of the analyzed adsorbed adventitious carbonaceous molecules shows bonds to oxygen, which can be found in ketones, aldehydes, ethers, alcohols, esters and carboxylic acids while the majority shows an aliphatic nature. This goes well with the broadly accepted effect of aliphatic hydrocarbons rendering the surface hydrophobic after aging. The exact chemical composition of adsorbed adventitious carbon groups might strongly depend on the chemistry of the volatile organic compounds available in the atmosphere which can differ depending on the location, while a dependence on the bulk material could not be detected by Grey et al. [89]. In contrast, Heier et al. [53] found an impact of the substrate material on contamination layers induced by different sample treatments. In order to induce a wetting transition, simulation in a work by Korczeniewski et al. [34] suggest that the formation of one monolayer of adsorbed hydrocarbons is decisive for the wetting transition. Rafiee et al. [102] showed that monolayers of graphene on top of copper do not impact the Van der Waals-dominated copper-water-interaction and reported on a gradual change of the SCA with a growing number of graphene layers.

It becomes apparent, that not only the mechanism of surface passivation with a non-polar termination is a very complex process which needs to be further investigated but also the chemical nature of the adsorbed organic molecules is still under discussion. Depending on the atmospheric conditions, the time needed for the wetting transition from hydrophilic to hydrophobic might greatly differ. Different approaches exist in order to accelerate the wetting transitions induced by the adsorption of hydrocarbons. Storage in atmospheres rich in organic matter e.g., by introducing grease in the atmosphere can accelerate the adsorption of volatile organic species [33]. Also vacuum conditions can show a similar effect due to oil pollution released into the atmosphere [17,33,41,42], which lead to a rather uncontrolled adsorption of organic species and might be highly dependent on previous chamber use [17]. Also a combination of vacuum storage with slightly elevated temperatures [38] can be beneficial for the reduction of the required storage time. Low temperature annealing in atmospheric conditions is also applied in order to accelerate the adsorption of volatile organic compounds [37,39] since annealing at higher temperatures holds the potential to desorb organic species and to reactivate initial hydrophilicity [33]. Similar effects could be achieved by IR-irradiation [38]. Not only the storage atmosphere, also packaging of the surfaces under investigation might influence the hydrophobization process as shown by Cardoso et al. [99] for laser-patterned aluminum samples, e.g. in the form of restriction of adventitious carbon by polystyrene sample boxes. Though the adsorption and desorption of volatile organic species by atmospheric contact is gaining growing attention in the research community, information on sample storage and especially packaging often remains vague. Therefore, systematic investigations on the aging of technical surfaces are needed including a detailed chemical

analysis of the adsorbed organic species to allow for a comprehensive interpretation of the wetting analyses. These dynamic changes in surface chemistry need to be taken into account for the interpretation of any wetting analyses. They might show the potential to be responsible for the great scattering of reported static contact angles in literature where instead, often the measurement technique itself is criticized. Detailed investigations of the measurement of static contact angles including measurement induced influences as well as sample induced influences like aging or storage are highly needed. Another possible factor is the solubility of adventitious carbon groups in the applied water droplet over time which is why droplets should be observed not only for a few seconds, but for prolonged times. Climate chambers usually allow for a saturation of the atmosphere with water before application of the droplet where also suggestions for self-built climate chambers exist in the literature, e.g. in the form of a glass cell isolated from the laboratory atmosphere [81]. As discussed above, storage of samples in high humidity or even water-saturated atmospheres might affect the adsorption layer and also shows the potential to form water films on the surfaces [103].

But not only the chemical surface termination, also topographical as well as morphological surface properties can influence the surface energy [104], [66]. Surface defects like dislocations as well as grain boundaries increase surface energy and make preferred adsorption sites [104–106]. As in reality, a complex interplay of different factors is usually expected to influence the wetting behavior of a solid surface, the following chapter aims at providing a brief overview of such possible influences and how their effects on the wetting behavior of metallic surfaces are investigated currently in literature.

Quick summary

- *Freshly prepared metallic surfaces are characterized by high surface energy which is minimized by the adsorption of volatile organic species forming thin layers of adventitious carbon on the surfaces, which are believed to be dominated by nonpolar hydrocarbons [89] upon contact with the atmosphere.*
These dynamic changes in surface chemistry induce a transition from initial (super)hydrophilic to a growing (super)hydrophobic wetting behavior over time.
- *The influence of the developed sample state cannot be neglected in the discussion of measurement techniques and the received wetting results.*
- *The underlying mechanisms of hydrocarbon adsorption are highly complex, and more research is needed in order to investigate the processes as well as the chemical nature of the adsorbed carbonaceous species with a possible dependency on the base material and their impact on the resulting wettability.*

3.5 Techniques for wetting control

As outlined in chapter 1, wetting is relevant for a broad variety of applications in the industrial as well as scientific and health sector. Therefore, control of wetting properties by manipulating surface chemistry and / or topography finds growing attention in the research community. This chapter provides a brief overview of different techniques portrayed in literature to tune the wetting response of the surface under investigation. Due to the focus of this thesis on metallic substrates represented by a detailed investigation of the wetting properties of copper surfaces, this chapter also concentrates on the wetting control of metallic surfaces.

Nature provides a wide range of examples for outstanding wetting properties including the self-cleaning behavior of the lotus leaf or the high water adhesion of rose petals [43]. In their review, Liu et al. [107] divide naturally occurring extreme wetting phenomena into different categories: superhydrophobicity in combination with low water adhesion and self-cleaning properties can be represented by different plant leaves like the lotus leaf; a high hydrophobicity with a high water adhesion is shown by rose petals as water droplets usually stick to them; the ability to collect water which can be found on a special beetle's back; and superhydrophobic plant leaves which even show the potential to restore superhydrophobicity which was lost due to leaf injury. Nature usually achieves such extreme wetting states by a combination of distinct topography in the micrometer and nanometer scale and coatings stimulating surface energy [107]. More extreme wetting states which can be found in nature are summarized in a review by Liu et al. [108]. Usually, researchers aim at mimicking these natural structures and surface terminations by different topographical as well as chemical treatments. Figure 5 a) shows a water droplet on a lotus leaf rolling to the center of the leaf and forming a water bead as a result of self-cleaning superhydrophobic behavior. Images b)-c) show SEM (scanning electron microscopy) scans of the top side of the leaf depicting a hierarchical topography consisting of papillae and wax tubules. They cover the surface with wax and lower the surface free energy. The SEM scan in Figure 5 d) shows the leaf after critical-point drying revealing the stomata as the wax tubules were dissolved by the treatment. Figure 5 e) reveals the underside of the leaf after the same drying process with convex cells [78]. Long et al. [43] mimicked the wetting behavior of a lotus leaf by a combination of femtosecond laser treatment with chemical surface modification of copper samples. Figure 5 f) and g) show the created microstructure as a result of the copper-laser-interaction. They found that by varying the scanning speed of the laser, the wetting behavior can be changed to rose-petal behavior due to changes in the achieved topography. Researchers do not only apply laser-based techniques to mimic the lotus-leaf wetting behavior. Latthe et al. [109] applied dip and spray coating of hydrophobic silica nanoparticles on various substrates to achieve a self-cleaning behavior while vastly maintaining the optical appearance of the surfaces. The extraordinary wettability of the lotus leaf is only one example of naturally occurring wetting phenomena which inspire scientists all over the world to apply different techniques to achieve extreme wetting scenarios and even create wetting properties which exceed the ones found in nature.

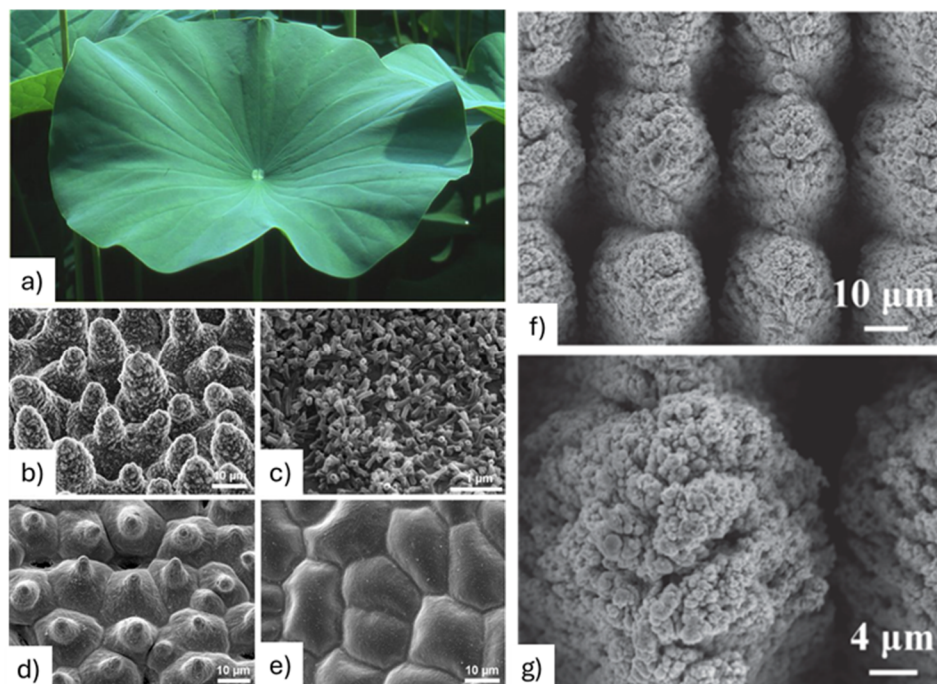


Figure 5: a) – e) Analysis of the micro- and nanostructure of the lotus leaf revealing a hierarchical topography with a wax coating on the surface resulting in the self-cleaning superhydrophobic surface properties. (a) Image of a lotus leaf, (b) SEM image of the top surface of the leaf, (c) SEM image of the top surface of the leaf showing the wax tubules, (d) top surface of the leaf after dissolution of the wax tubules, stomata become visible, (e) bottom side of the leaf after the same post-processing [78].

Images reproduced from “Superhydrophobicity in perfection: the outstanding properties of the lotus leaf, Hans J. Ensikat, Petra Ditsche-Kuru, Christoph Neinhuis and Wilhelm Barthlott, *Beilstein J. Nanotechnol.* **2011**, 2, 152–161. <https://doi.org/10.3762/bjnano.2.19>” published under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/2.0>).

f) – g) SEM images of a laser-patterned copper surface mimicking the wetting behavior of the lotus leaf [43]. Adapted with permission from “Superhydrophobic Surfaces Fabricated by Femtosecond Laser with Tunable Water Adhesion: From Lotus Leaf to Rose Petal, Jiangyou Long, Peixun Fan, Dingwei Gong, Dafa Jiang, Hongjun Zhang, Lin Li, and Minlin Zhong, *ACS Applied Materials & Interfaces* 2015 7 (18), 9858–9865, DOI: 10.1021/acsami.5b01870” Copyright 2015 American Chemical Society.

Nature does not only provide examples of extreme non-wettability. Surfaces which are superhydrophilic in nature include shark skin, fish scales, lizard skin or the precorneal tear film spreading on the human eye among others [110].

This chapter provides an overview of different techniques applied to achieve extreme wetting behavior. Following the thesis of Wenzel [66], roughness enhances the existing wetting behavior, thus making hydrophobic surfaces even more hydrophobic and increasing the hydrophilicity of inherent hydrophilic surfaces with increasing roughness. Therefore, usually chemical and topographical alteration of technical surfaces are combined to achieve significant changes in wetting behavior. The following chapters give detailed insight into chemical surface alteration, topographical alteration and a combination of both by laser treatments.

Quick summary

- Nature delivers fascinating examples of extreme wetting phenomena which inspire researchers all over the world. Both chemistry and topography are adapted through various techniques to mimic the naturally observed structures and their wetting behavior.

3.5.1 Chemical surface alteration

As the wetting response is directly connected to the surface chemistry, chemical surface treatments are a popular method to push the wetting behavior into extremes, e.g., superhydrophobicity or superhydrophilicity. As Vazirinasab et al. [111] point out in their review on superhydrophobic surface coatings for corrosion protection applications, in order to achieve superhydrophobic wetting properties high energetic substrates like metals should first be altered topographically to increase roughness and be coated with low energetic compounds in a second step. These could be long alkyl chains, organic silanes, fatty acids or polymeric compounds among others [112].

Application of such coatings can be realized, among other techniques, by templating, etching, hydrothermal synthesis, anodization or electrodeposition, chemical vapor deposition, sol-gel-processes, dip coating where details and exemplary works can be found in references [111–113]. Application is also possible via simple methods like spray coating of stearic acid, where the addition of nanoparticles can result in an effective combination of roughness and low energy of the surface [114]. Not only the resulting contact angle between liquid medium and surface but also adhesion and mechanical stability as well as cost effectiveness need to be taken into account when assessing the usability of superhydrophobic surface coatings [115].

Pronounced hydrophilicity can be necessary especially in the medical sector, e.g., in order to stimulate protein adsorption or platelet adhesion and can be achieved by electropolymerization of poly(ethylene glycol) dimethacrylate on metallic substrates for example [116]. Also, biocompatibility as well as antibacterial properties can increase with increasing hydrophilicity e.g., of titanium surfaces which is a common implant material [117]. Hydrophilic polymer coatings moreover act as anti-biofouling barriers and can be applied in various ways. In their review, Huang et Ghasemi [118] discuss 3D-grafting of polymeric coatings like hydrolysis-based coatings or layer-by-layer assembly. On metallic substrates like Mg, hydrothermal treatment showed promising results in the formation of a $\text{Mg}(\text{OH})_2$ -coating combined with Si-O compounds in order to tune the corrosion resistance of Mg alloys applied as implant materials [119,120]. Though usually with application of a coating, the chemical modification of surfaces in order to alter their wetting response is focused, often coatings also influence the surface roughness especially if nanoparticles are applied during the coating process which again can influence the wetting response as shown in the models of Wenzel [66] and Cassie and Baxter [68]. While traditionally, properties like the achieved wetting state, coating durability, adhesion properties and many more technical factors are discussed, especially environmental aspects continuously are gaining more attention. PFAS (Per- and Polyfluoroalkyl Substances) for example are well known for their effective wetting transformation of surfaces, e.g., by rendering them superhydrophobic with excellent self-cleaning properties, anti-fouling as well as anti-icing behavior [121], but show highly concerning environmental impacts. Therefore, researchers are increasingly concentrating on developing targeted wetting conditions without the use of harmful chemical coatings by mimicking naturally occurring structures combined with environmental-friendly coatings if necessary [122,123]. Moreover, usually

high-energetic technical surfaces undergo a wetting transformation without any additional coating as discussed in chapter 3.4, a mechanism which needs further investigation accompanied by strict control of sample preparation, storage and packaging. In order to create certain topographical features which often are inspired by nature, different techniques can be applied which will be summarized in the following chapter.

Quick summary

- *The surface energy of substrates can be altered by application of polar or nonpolar coatings where various application techniques exist.*
- *Often, the chemical coating of surfaces is accompanied by topographic changes which again influence the wetting behavior.*

Besides coating functionality and durability, environmental aspects need to be taken into account, especially if potentially harmful substances are used in order to tune the wetting behavior. Therefore, investigation of naturally occurring wetting transitions as well as control of wetting behavior by topographical alteration is of special importance.

3.5.2 Topographical surface alteration

When it comes to manipulating the wetting behavior of solids by adaptation of topography, patterns in the micro- and nanoscale are of great interest to the research community. Usually, the characterization of the wettability is conducted by measuring the static contact angle of a liquid (typically water) droplet in the μl -range, where the ratio between droplet size and surface heterogeneity must be considered when assessing the influence of surface topography. Therewith, droplet distortion by single topography features should be avoided on the one hand and it needs to be assured, that the droplet captures an average roughness on the surface on the other hand [67].

Depending on the desired adaptation of wetting properties, different methods could be applied. Random roughness features can usually be achieved by rather simple preparation methods. Chemical etching with a subsequent chemical coating of metallic substrates shows promising wetting properties with high contact angles, low water adhesion and many connected effects like ant-icing or anti-fouling properties [105,124]. Similarly, sandblasting in combination with low energetic chemical coatings can be applied to achieve random roughness on metallic surfaces leading to comparable wetting properties as the previous described etching-based preparation route [125]. It needs to be taken into account that as soon as chemical coatings are applied after roughening the surface, the coatings not only alter the surface energy but also potentially surface topography [126] leading to very complex interpretations of such wetting results. The amount of different available roughening technologies offers nearly unlimited possibilities to create random roughness patterns where also the combination of different methods finds application. Shot peening for example was successfully applied to copper to create dislocation forests which were attacked by a following chemical etching in order to create hierarchical surface patterns depicting superhydrophobicity after a chemical treatment with stearic acid [127].

Besides randomly spread topographic features, techniques resulting in surface structures with a preferred orientation also find application in the wetting community. Techniques as simple as grinding [56] also combined with acid etching [128] are popular in order to tune the wettability. While grinding grooves spread directionally over sample surfaces, they do not portray a strict periodicity. Periodic surface patterns are especially of interest when it comes to the mimicking of naturally occurring surface structures exhibiting outstanding wetting properties. Anisotropic periodic line patterns can result in non-axisymmetric droplets, especially on hydrophilic surfaces due to capillary forces pulling the droplet along pattern grooves if they are smaller than the capillary size of water, which is given as 2 mm by Kubiak et al. [129]. Pinning of the droplet perpendicular to surface grooves also greatly influences the wetting behavior and might as well depend on the initial hydrophilicity of the smooth reference surface. Droplet spreading is expected to decrease with increasing hydrophobicity and a transition to the Cassie-Baxter wetting state [129].

Of course, such anisotropic droplets could also be formed on directional structures not following a strict periodicity, but they cannot allow for the same reproducibility as periodically patterned surfaces. Periodic patterns can be achieved e.g., by nanoimprint lithography combined with wet etching, where

additionally applied chemical coatings can tune the wettability to superhydrophobicity as portrayed in reference [130] for line patterns. In general, lithography is a common technique to tune the topography of different substrates in order to influence the wetting behavior, e.g., UV nanoimprint lithography [131], electron-beam lithography [132] or laser interference lithography [133] just to name a few. Zhang et al. [134] equipped an epoxy coating on steel with a sandpaper roughness transferred by soft lithography.

In their review, Shen et al. [135] provide details and a summary of exemplary studies on different less traditional techniques for surface texturing for example electrical discharge machining relying on the melting of the material in order to create the desired surface pattern or electrochemical machining which could be performed with or without templates and also heavily influences chemical surface termination just to name two. They also include laser beam machining, where in recent decades, laser processing of solid substrates to alter the surface topography has become increasingly popular among scientists all over the world. It is especially attractive due to the vast possibility of parameter variations e.g., laser pulse duration, laser energy, beam overlap, scanning speed and laser frequency among others [135]. Complex interaction processes between the laser beam and the surface result in material removal and either allow for the fabrication of statistic roughness or periodic patterns. The fabrication of strictly periodic patterns in the micrometer range on metallic substrates to tune the wetting behavior into extreme wetting states often is realized by a rather new laser pattern method called direct laser interference patterning (DLIP). More details on laser-based techniques to alter the wetting behavior are given in the following chapters as they also found application in this work.

Quick summary

- *Roughness of substrates can be altered by different techniques to create either random, ordered or even strict periodic roughness features.*
- *Anisotropic topographic features show the potential for anisotropic wetting in dependence of surface chemistry.*
- *As increasing roughness leaves polar substrates in a more hydrophilic state, often roughening is combined with chemical surface alteration especially if high hydrophobicity and / or low water adhesion are desired.*

3.5.3 Traditional laser-based surface treatments

Laser treatments of technical surfaces especially with short (SP)- and ultra-short-pulsed (USP) lasers have become popular in the research community due to their versatility in the creation of isotropic or anisotropic, random or periodic, simple or hierarchical patterns on different substrates where femtosecond and picosecond pulsed laser treatments appear to be the most common [136] and also found application in this thesis.

Short laser pulses typically refer to pulse durations in the ms and ns time range where the laser-material-interaction is driven by thermal effects, e.g. “heat conduction, melting, evaporation and plasma formation” [137]. In order to reduce the formation of melt structures, laser pulses shorter in duration and high in intensity are favorable. The classification of laser pulses as ultra-short might depend on the material where pulse durations < 1 ps are usually classified as ultra-short for metals and < 10 ps for ceramics [138]. When the pulse duration falls below the time needed to transfer energy between free electrons and the lattice, usually described by the two-temperature-model, fast heating occurs and no equilibrium state can develop between lattice and electrons. This leads to an overheated liquid where the material reaches the vapor phase at high kinetic energies resulting in ablation and prevention of heat affected zones [137,139,140]. For ultrashort laser pulses, highly complex ablation mechanisms occur depending on the energy density (fluence) and penetration depth of the laser [137,140] where ablation was found to be dominated by spallation at small energy densities and transfer into phase explosion, fragmentation and vaporization for higher beam energy densities. For longer ps-pulses, trivial fragmentation dominates the ablation process [141]. Reference [142] provides a lucid summary of the relations between the laser pulse duration τ_p , the lattice heating time τ_L and the cooling time of the electrons τ_e :

- $\tau_p \gg 1 \text{ ns} \gg \tau_L \gg \tau_e$: ms laser ablation; ablation is dominated by melting; thermal equilibrium between lattice and electron $\rightarrow$ heat transfer laws
- $\tau_p > 1 \text{ ns} \gg \tau_L \gg \tau_e$: ns laser ablation; ablation is dominated by melting and vaporization, heat conduction causes energy loss; thermal equilibrium between lattice and electron $\rightarrow$ heat transfer laws
- $\tau_L > \tau_p \gg \tau_e$: ps laser ablation; ablation dominated by direct transitions between solid and vapor/plasma; melted zone can form; lattice temperature below electron temperature (transitional state between ns and fs ablation)
- $\tau_L \gg \tau_e \gg \tau_p$: fs laser ablation; ablation dominated by direct transitions between solid and vapor/plasma; heated electrons transfer energy to lattice ions within a few ps, ions break lattice bonding before energy transfer to neighbors $\rightarrow$ negligible heat conduction

While laser beam properties therefore directly determine the resulting surface morphology, the material's state also influences the ablation mechanism, where the amount of removed material directly depends on intrinsic material properties like the ablation threshold and surface properties like roughness

or oxide content. Roughness as well as surface oxidation were found to increase laser absorption which is especially important in multi-pulse agglomeration [76,143].

Continuous scanning of a pulsed laser beam over the surface allows for patterning of large sample areas. Pulse overlap is determined by the laser frequency and the scanning speed as well as the hatching distance and is of great importance due to heat accumulation in the material, especially if a single spot is irradiated multiple times. Heat accumulation and a resulting increase in the temperature is generally unfavorable for the creation of defined surface patterns [137,144,145]. With increasing pulse numbers, plastic deformation and defect accumulation in the substrate become more severe and the ablation threshold decreases. This phenomenon is known as incubation. Incubation effects can facilitate material removal especially at lower pulse energies, while temperature management poses a challenge due to possible heat accumulation [146,147].

By adjusting the hatching distance and scanning direction, primary patterns can be created on a surface in a direct laser writing process (DLW), where for example periodic lines or cross patterns can be created which also found application in the experimental pre-work of this thesis. Due to the scanning of the laser beam over the surface in order to create the primary pattern, the achievable pattern size highly depends on the focus diameter of the laser on the surface and is usually limited to 5-15 μm [148]. Laser parameters proved to not only influence the resulting pattern but also the wetting state and transitions between Cassie-Baxter and Wenzel wetting [43,149]. Freshly laser-treated metallic surfaces show (super)hydrophilic behavior, which only converts into (super)hydrophobicity by minimization of the high surface energy, e.g., by storage in atmospheres rich in organic compounds or chemical coating as discussed before [33,98].

Besides the pattern formation due to material ablation and re-solidification, the formation of periodic substructures called LIPSS (laser induced periodic substructures) is often observed during USP patterning. These substructures typically show periodicities in the range of the wavelength of the laser beam and occur as a result of the irradiation with linearly polarized ultra short laser pulses on various materials, where a distinction is made between low-spatial frequency LIPSS (LSFL) and high-spatial frequency LIPSS (HSFL) depending on their periodicity [150]. Different theories evolve around the complex formation of LIPSS, e.g., plasmonic theory postulating the interference of surface plasmon polaritons with the primary laser beam, Sipe theory relying on surface electromagnetic waves interfering with the incident laser beam or a theory considering the self-organization of the laser irradiated material [150–152]. The formation of HSFL is not understood by these theories highlighting the complexity of the mechanisms underlying LIPSS formation [150]. LIPSS, as well as random bumpy features in a similar size range, show promising results for the hydrophobization of surfaces after nonpolar termination though water adhesion might be highly dependent on the morphology of the created nanostructures [80,153]. The combination of parallel laser grooves with LIPSS and/or resolidified nanoparticles created in a laser writing process showed promising results for the design of highly hydrophobic surfaces where especially the height of the primary pattern seems to strongly

influence the resulting wetting behavior [154].

In this thesis, a single ps-laser beam was scanned over the sample surface where the hatching distance was optimized to suppress the formation of a periodic primary structure and favor the formation of random surface roughness.

Quick summary

- *Laser-based surface treatments show high potential in the alteration of wetting behavior. The adaptation of different laser parameters allows for careful adjustment of the desired topographic features.*
- *The formation of LIPSS is highly complex – the periodic ripple structure can also influence the wetting behavior.*
- *Right after laser treatment, metallic surfaces usually depict high surface energy which can either be reduced by chemical post-processing or natural aging via adsorption of volatile organic compounds inducing a wetting transition.*
- *Laser-based surface treatments can be used to create random roughness features but also to engrave primary patterns, e.g., in a direct laser writing process. Feature size of the primary pattern is limited by the laser focus diameter, which is why more elevated laser-based techniques are needed for the effective and fast production of periodic surface patterns in the lower μm -range.*

3.5.4 Direct laser interference patterning and its applications in wetting

To create smaller patterns which still offer strict periodicity and reproducibility, an interference-based technique can be applied, the so-called direct laser interference patterning (DLIP). In the DLIP setup, a laser beam is split into two or more sub-beams which are brought to interfere on the sample surface and transfer the interference pattern to the surface by laser ablation. Thereby the number of interfered laser beams directly determines the pattern on the surface where two beams form periodic line patterns, and three or four beams create point patterns as shown in Figure 6. The periodicity of the created line pattern p is determined by the applied laser wavelength λ and the angle between the beams 2α by equation (7) [148,155].

$$p = \frac{\lambda}{2 \sin(\alpha)} \quad (7)$$

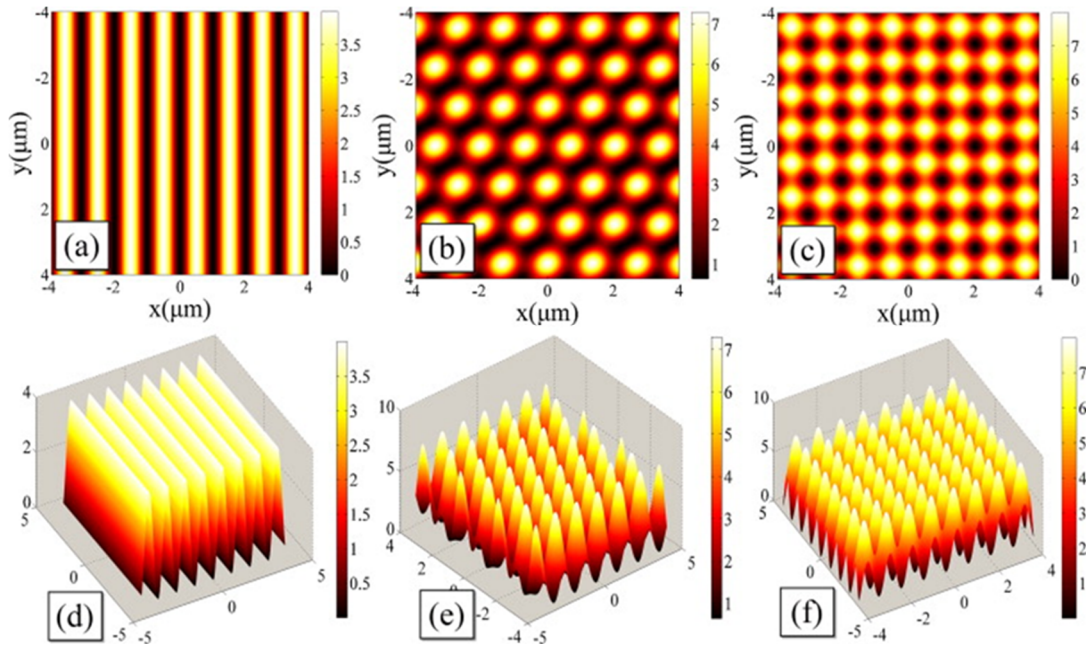


Figure 6: Images of simulation results of 2D intensity distributions for a two-beam (a), three beam (b) and four (c) beam setup with the corresponding 3D distributions underneath in (d) - (f) [156].

Used with permission of Elsevier Science & Technology Journals, from Direct modification of silicon surface by nanosecond laser interference lithography by Dapeng Wang, Zuobin Wang, Ziang Zhang, Yong Yue, Dayou Li, Carsten Maple, Applied Surface Science, Volume 282, year of copyright: 2013; permission conveyed through Copyright Clearance Center, Inc.

In order to cover the entire surface area with the desired pattern, the single laser spots need a careful alignment and adjustment of the pulse overlap both in scanning direction and for the hatching distance where the exact mathematical determination of the pulse overlap and the accumulated fluence follows complex mathematical considerations [157]. Also incubation effects need a detailed assessment in the DLIP set up which can be found for copper in reference [76] with detailed analyses of the impact of oxide formation, deformation state, defect formation, LIPSS formation, topography development (primary and sub-pattern) as well as beam polarization. On copper, DLIP-processing in the fs-regime causes spallation and, with increasing laser fluence, phase explosion which is accompanied by a stronger expulsion of melt which also influences the sub-pattern formation of the hierarchical surface

features [158]. Fs-DLIP processing of copper also likely leads to a strong decoration of the surface with oxidic nanoparticles which are referred to as “flakes” in literature and which can be removed by post-processing e.g., etching in citric acid [52]. Due to the broad variety of surface patterns which can be created by DLIP processing of metallic substrates in the μm -range with a strict control of pattern geometry and periodicity, DLIP has become very popular in the wetting community in order to tune the wetting behavior to extremes. While this thesis focuses on metallic substrates, i.e., copper, DLIP is applicable to a wide range of materials including polymers and ceramics [159].

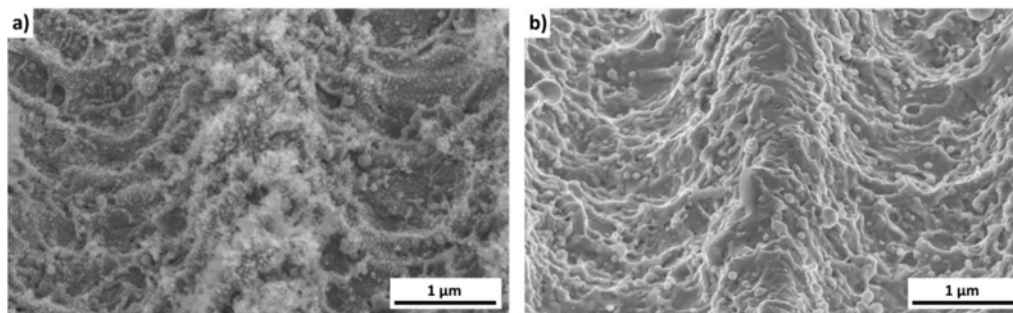


Figure 7: (a) Fs-DLIP processed copper surface with line pattern showing the oxidic flake decoration mainly on the topographic maximum. (b) Surface (a) after chemical post-processing by citric acid etching to remove the oxidic structures [52].

Reprinted with permission from “In-Depth Investigation of Copper Surface Chemistry Modification by Ultrashort Pulsed Direct Laser Interference Patterning, Daniel W. Müller, Anne Holtsch, Sarah Löblein, Christoph Pauly, Christian Spengler, Samuel Grandhyll, Karin Jacobs, Frank Mücklich, and Frank Müller, Langmuir 2020 36 (45), 13415-13425, DOI: 10.1021/acs.langmuir.0c01625”. Copyright 2020 American Chemical Society.

Transitions from hydrophilic to (super)hydrophobic properties were achieved by ns-, as well as fs- and ps-DLIP on metallic substrates with varying geometries [25,49–51]. Again, especially the decoration with nanoparticles / flakes seems to strongly influence resulting contact angles [160]. In reference [49], 4-beam-DLIP was applied on aluminum in both the fs- and ps-regime where number of pulses and periodicity were kept the same for both. Due to the differences in pulse duration, significant differences in the resulting patterns were observed with constantly deeper structures after the ps treatment which again induced higher and more stable hydrophobicity over time. DLIP is not limited to the fabrication of one uniform surface pattern but can create gradient patterns with gradually varying spatial periods leading to spontaneous droplet motion towards more hydrophilic sample areas [161]. DLIP structuring also goes beyond the adaption of contact angles and droplet adhesion towards other wetting based applications like self-cleaning [162] or anti-icing for aerodynamic applications [163]. The application of DLIP line patterns on copper proved to not only significantly increase contact angles over time but to also improve antibacterial efficiency [25,164].

Apparently, many different studies show the power of DLIP when it comes to the alteration of wetting properties, especially for the development of high hydrophobicity. Still, fundamental investigations are required considering topographical and chemical surface alterations induced by DLIP to allow for a clear interpretation of the observed wetting states and therewith for a targeted design of surfaces. DLIP - as laser processing in general - induces complex changes to the surface due to the formation of hierarchical patterns on the one hand but also due to induced changes in surface chemistry on the other hand. The

latter can be caused by oxidation, possible subsequent deoxidation and agglomeration of adventitious carbon groups if in contact with the ambient atmosphere. Oxidation accompanies the topographic changes and is drawn responsible for observed wetting transitions on laser treated copper surfaces from (super)-hydrophilicity to (super)-hydrophobicity by some researchers due to an observed deoxidation from CuO to Cu₂O upon aging [97,165,166], which contradicts the accepted effect of hydrocarbon adsorption upon atmospheric storage on surface hydrophobicity [104]. At the same time, due to the laser induced deformation, microstructure also undergoes changes. All these aspects combined with the previously discussed challenges on wetting characterization in general raise the need for systematic multi-scale investigations to distinguish between chemical and topographical influences on wetting behavior. They should take into account sample preparation, sample storage, sample packaging, SCA measurement techniques, microstructure, laser parameters, oxidic reaction products and finally the effect of hierarchical structures. Especially for the evaluation of the influence of laser topography a systematic approach that goes beyond empirical variation of laser parameters is required to capture the impact of primary as well as secondary topographic features. Only such fundamental investigations will allow the design of surface patterns with a desired wettability without extensive parameter studies.

Quick summary

- *DLIP is a complex technique which allows for a highly reproducible patterning of surfaces with strictly periodic patterns. Properties of the resulting pattern can be precisely controlled by adapting the laser setup.*
- *DLIP demonstrates promising results for the adaptation of the wetting behavior.*
- *While many studies portray a variation of patterning parameters to vary laser patterns and assess the impact on the wetting properties of the surfaces, there is still a lack in systematic investigations.*
- *As adaptation of surface topography by DLIP is accompanied by chemical surface changes of the base material as well as adsorption of carbonaceous layers, changes in the microstructure and finally the formation of not only a primary periodic pattern but complex hierarchical structures, strictly systematic investigations are needed to allow for a correct interpretation of DLIP wetting results.*

4 Overview of this work

The above chapters provide an introduction into the topic of this thesis and a profound insight into the state of the art of the analysis of the wetting behavior of technical surfaces. In order to answer the research questions introduced in chapter 2, a multi-scale study was set up, which is summarized in Figure 8. Paper 0 [167] captures the experimental pre-work and provided the motivation for the detailed study of the wetting behavior of copper surfaces and the evaluation of topographical and chemical influences in the following investigations. A series of fundamental research questions focusing on the metallographic preparation of copper and the reproducibility of static contact angle measurements needed to be answered in publication 1 [168] and 2 [169]. To assess the influence of measurement and sample induced influences in publication 2 including sample packaging and storage, polished copper samples were used to avoid overlaying effects of topographical and/or chemical surface modification e.g. by laser patterning. These fundamental investigations laid the foundation stone for the investigation of the influence of intrinsic material properties like microstructure and surface defect density on the aging and wetting behavior of copper (publication 3 [170]). A detailed assessment of the influence of surface chemistry was conducted in part A and B of publication 4 [171] with an in-depth evaluation of the adsorption of volatile organic species on flat copper reference samples on the one hand. On the other hand, the role of copper oxides by reactive magnetron sputtering was observed. The results of these analysis were of the utmost importance for the investigations of the influence of surface topography within the fourth research objective (publication 4, part C+D [171]). Before the analysis of the effect of complex hierarchical topographies, the effect of simple isotropic roughness applied by ps laser-roughening was investigated. In the last step, ps- and fs-DLIP was applied to produce two patterns with similar primary topography but different secondary roughness. Additionally, a structure with a deeper primary pattern prepared by ps laser pulses of higher intensity was produced to also allow for the assessment of the influence of variation in primary topography.

This chapter provides a brief outline of the papers included and offers a more detailed summary of each publication (conducted experiments, applied methodology and main results) and how it contributes to the research objectives on the following pages.

Details on applied parameters as well as discussions of the results can be found in the publications themselves which are inserted in chapter 5 of this thesis.

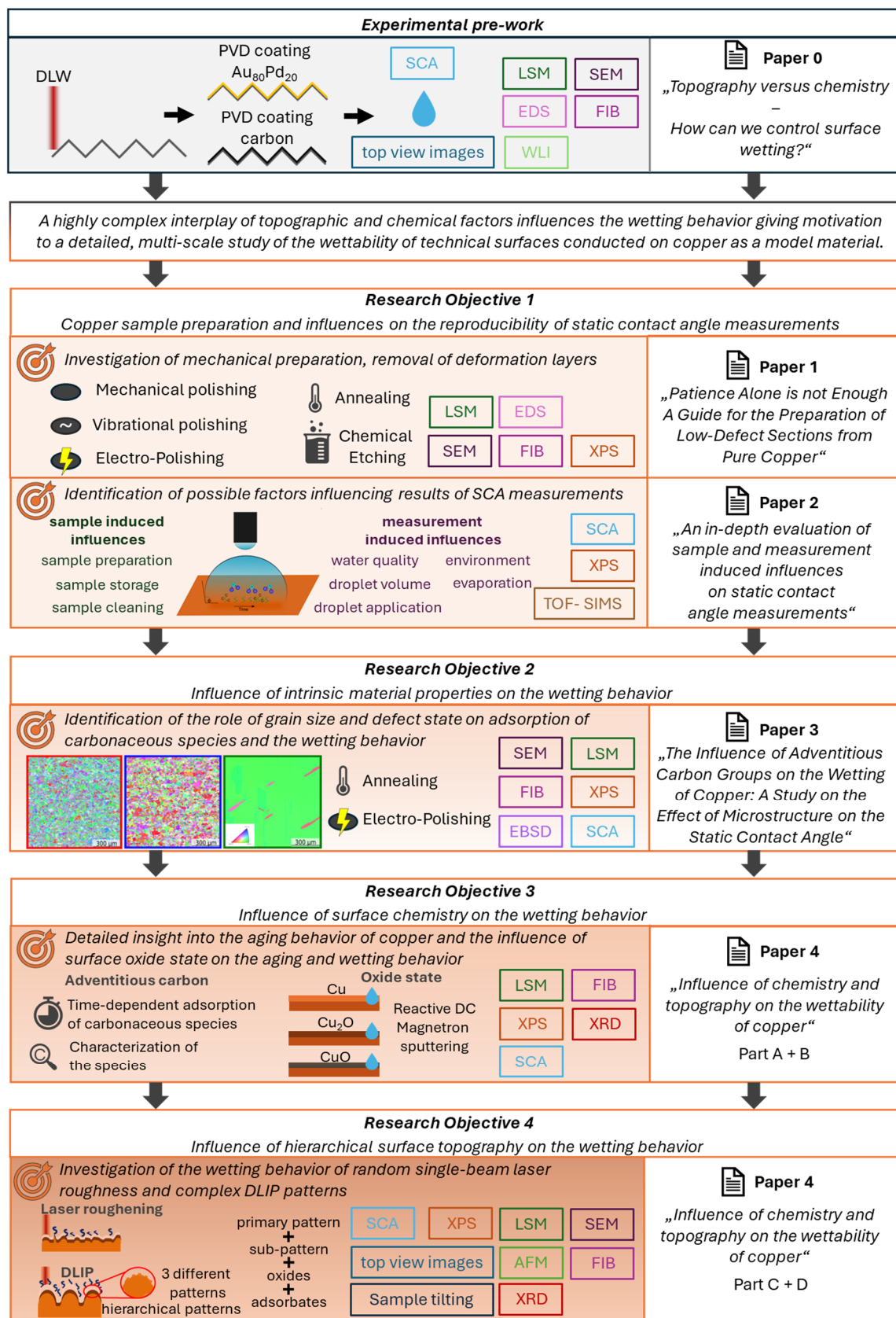


Figure 8: Overview of the content structure of this thesis.

Paper 0 refers to reference [167], paper 1 to reference [168], paper 2 to reference [169], paper 3 to reference [170] and paper 4 to reference [171]. (Abbreviations: PVD – Physical vapor deposition, LSM – Laser scanning microscopy, SEM – Scanning electron microscopy, EDS – Energy-dispersive x-ray spectroscopy, FIB – Focused ion beam, WLI – wight light interferometry, TOF SIMS – Time of flight secondary-ion mass spectrometry, EBSD – Electron backscatter diffraction, XPS – X-ray photoelectron spectroscopy, AFM – Atomic force microscopy, XRD – X-ray diffraction)

Outline

- Paper 0** [167] Laser writing on steel was combined with physical vapor deposition to create varying chemical surface termination while maintaining the primary topography. It was found that both surface topography and surface chemistry greatly influence the resulting wetting behavior. A complex interplay of both factors was found and motivated a strictly systematic investigation of the development of the wetting behavior of technical metallic surfaces using copper as an example material in the following publications.
- Paper 1** [168] Before detailed wetting analyses were conducted, basic investigations of the chosen material and its preparation with chemical analyses via XPS were conducted in order to ensure high quality surface finishes not only for wetting tests but also for subsequent sample preparation e.g., laser patterning. Metallographic preparation of copper proved to be delicate due to its high ductility. Besides a guideline for the metallographic preparation of high purity copper, the electro-chemical removal of preparation induced deformation layers was investigated in different setups allowing for the preparation of multiple samples at once.
- Paper 2** [169] Paper 2 focuses on the methodology of wetting analysis by taking sample as well as measurement induced influences into account of SCA analysis. Various factors were found to affect SCA results of polished copper surfaces where sample storage and packaging especially show a heavy influence on the SCA due to the adsorption of volatile organic species analyzed in detail by XPS and TOF-SIMS. Paper 2 proved that the apparent simplicity of SCA measurements can lead to great variations in the results if they are not prepared and conducted in a highly controlled manner.
- Paper 3** [170] As laser processing not only alters surface topography but also surface chemistry and intrinsic material properties like microstructure, a stepwise approach was chosen to correctly determine the role of each individual factor. Paper 3 focusses on the role of copper microstructure in the SCA development by creating different microstructures via preparation (see Paper 1) and heat treatment. Microstructure was found to influence the adsorption of hydrocarbons, especially the adsorption rate but to not majorly alter the SCA once a sufficient amount of adventitious carbon is accumulated.
- Paper 4** [171] After Paper 3 observed the impact of microstructure on wetting behavior and again found a complex adsorption dynamic of volatile organic species, part A of Paper 4 deals with a detailed investigation of these organic adsorbates. Control of sample storage is of the utmost importance in order to ensure reproducible SCA measurements. No stagnation of the adsorption could be found after a few weeks of controlled storage, which is why storage conditions and times should be kept identical for samples under direct comparison to each other. Non-polar hydrocarbons were found to terminate the adsorption layer and overrule oxidic surface termination in part B of Paper 4. Topography can show its full potential for hydrophobization after the formation of layers of adventitious carbon. Isotropic topography already showed to increase SCA by 25 %. DLIP demonstrated the complex impact of primary and secondary topography where the slightest change can induce distinct differences in the wetting behavior including SCA, wetting state and droplet adhesion.

Experimental pre-work – Summary of publication 0 [167]

In order to investigate the influence of surface chemistry widely separated from the influence of surface topography, line patterns created by fs direct laser writing on steel were coated with Au₈₀Pd₂₀ or with amorphous carbon in a PVD-process. The samples were kept under ambient conditions and cleaning was performed in ethanol before the wetting analysis; adsorption of organic carbon was not monitored. Sample characterization included roughness measurements by LSM, evaluation of primary topography as well as sub-pattern morphology by SEM and analysis of coating homogeneity by EDS and by FIB-cross sections. The PVD coating maintained the primary topography but induced changes to the secondary roughness: The amorphous carbon coating enhances LIPSS observed in the pattern valleys while the Au₈₀Pd₂₀ coating reduces the LIPSS characteristic.

SCA measurements showed a pronounced anisotropy on the non-coated patterned steel sample which was greatly reduced by the Au₈₀Pd₂₀-coating. Top-view images showed air-inclusions under the droplet for the latter which disappeared over time. Such air-inclusions indicating a Cassie-Baxter wetting could not be observed for the uncoated steel sample. Furthermore, the amorphous carbon coating appeared to reduce the SCA significantly, where top-view images showed a pronounced spreading of water in the pattern grooves. SCA measurements of flat reference surfaces complemented the wetting analysis to apply theoretical wetting models according to Wenzel and Cassie-Baxter where image processing methods were employed to determine the wetted area fraction.

Summary of the main results

- *Varying surface chemistry in combination with anisotropic line patterns shows a strong influence on wetting behavior, e.g., static contact angle, wetting state and wetting anisotropy.*
- *Especially for the assessment of wetting anisotropy, top view images of the droplet are a meaningful complement to SCA measurements.*
- *Topography alone does not determine the wetting behavior which highly depends on surface chemistry: Depending on surface chemistry, line pattern can show different degrees of anisotropic wetting in the Wenzel state. But also, isotropic hydrophobic behavior with suppressed droplet spreading and a transition from CB-wetting to Wenzel wetting over time can be induced by an adequate chemical termination.*
- *The study highlights the complexity of the interaction between topography and chemistry in the wetting of technical surfaces. More detailed studies are necessary to evaluate the extent of each parameter, especially under consideration of volatile organic species and adventitious carbon. For the investigation of the influence of surface topography, hierarchical structures need to be considered in order to determine the role of the primary pattern as well as secondary sub-patterns forming due to laser material interactions.*

Research Objective 1: Copper sample preparation and influences on the reproducibility of static contact angle measurements

Summary of publication 1 [168] and its implications on the research objective

Metallographic sample preparation is the basis for most material analysis and characterization as well as further processing steps, e.g., laser patterning. Polished surfaces also typically serve as reference samples in wetting analysis of topographically and / or chemically altered surfaces. The artefact free preparation of copper, especially of pure copper grades like CW008A ($\geq 99,95$ % Cu) used in this study, poses a great challenge for metallographic preparation due to its high ductility. Therefore, publication 1 aimed at providing an orientation for metallographic copper preparation including optional further steps to remove induced fine crystalline deformation layers. Grinding on silicon-carbide-paper proved to be problematic due to embedding of SiC particles into the copper which break out in later polishing states leaving strong artefacts and scratches on the surface. Fine grinding with a 15 μm polishing suspension showed promising results instead, followed by a sequence of diamond polishing where usually at first higher force levels were applied which are then reduced to 10 N. The presented routine delivered smooth surfaces with an average roughness of 4 ± 1 nm. Though this routine showed very promising results, it should be highlighted that it needs to be understood as an orientation guide, which needs repeated checks of the sample surface under the microscope after each polishing step. Depending on sample state and on polishing supplies e.g., age and hardness of the disks, adaptations like repetition of existing or inclusion of additional steps might be needed. If particles are imprinted besides low forces, it was found during ongoing sample preparation within this thesis that repeating the final 1 μm polishing step with higher amounts of suspension can be beneficial to achieve mirror like finishes. Also, the inclusion of an additional 3 μm polishing step at higher forces (15 N) might be useful depending on the sample state. However, as presented in the routine in publication 1, a reduction of the force to 10 N in the final polishing steps is necessary to suppress imprinting of abrasive particles into the sample surface. Publication 1 moreover provides recommendations for preparation of especially soft samples, e.g., high-temperature annealed copper samples which are prone to heavy deformation if not handled correctly. As the metallographic routine induces a fine-crystalline deformation layer, publication 1 discusses different setups for a removal to reveal the bulk microstructure. While vibrational polishing did not show promising results, a horizontal setup for electro-polishing of multiple samples in phosphoric acid at once is presented relying on a holder entirely fabricated of copper to reduce the risk of cross-contamination. It was shown that the shape of the counter electrode greatly influences the material removal rates as well as the surface finish. XPS analysis was employed to control the successful removal of the high viscose phosphoric acid.

Summary of the main results

- *Mechanical metallographic preparation of copper is a major challenge due to its high ductility and the resulting artefacts.*
- *Grinding of the surfaces should be avoided whenever possible, reduction of polishing forces in the final steps showed promising results.*
- *Electro-polishing in ortho-phosphoric acid is beneficial for the removal of fine-crystalline deformation layers where the simultaneous polishing of several samples under identical conditions becomes possible by applying the introduced setup of horizontal electro-polishing.*
- *XPS proved the cleanliness of the samples after the preparation.*

Summary of publication 2 [169] and its implications on the research objective

Publication 2 focuses on sample as well as measurement induced influences on static contact angle measurements in order to gain a deeper understanding of the measurement technique and its reproducibility as it was applied in all further publications for wetting analyses. For the sample induced influences, sample preparation was discussed; sample storage/packaging and sample cleaning were analyzed experimentally. Sample packaging/storage showed strong influences on static contact angles due to restriction or provision of adventitious carbon groups. Packaging of freshly prepared copper samples in polystyrene sample boxes showed reduced SCAs compared to ambient storage without a sample box. Wrapping freshly prepared copper samples in woodfree paper before placing them in polystyrene boxes greatly enhanced SCAs especially in combination with prolonged storage times. For prolonged storage times, humidity was kept low by adding silica beads to airtight containers the wrapped samples were stored in. Detailed analysis of the samples stored in the wrapping paper and of the paper itself by XPS and TOF-SIMS suggest that no material is directly transferred from the paper to the sample. Instead, the paper appears to increase the concentration of carbonaceous species in vicinity of the sample and thereby acts as a donor of adventitious carbon which was most likely adsorbed by the paper itself from the atmosphere before. It thereby was shown that the dynamic changes of the wetting response due to the adsorption of volatile organic compounds are not limited to reactive freshly prepared laser patterned samples or substrates with pronounced roughness but that also polished flat surfaces undergo these changes after preparation. All further effects were analyzed on hydrophilic and on hydrophobic flat copper samples to understand the extent of the effects in dependence of the initial wetting behavior induced by different sample storage. Cleaning of the samples in ethanol before SCA measurements showed similar effects of SCA reduction on initial hydrophilic as well as hydrophobic samples due to the removal of nonpolar carbonaceous groups. In general, measurement induced influences like water grade, droplet volume, application method and humidity during the measurement showed much smaller impact on the SCA. Still experiments were run on both hydrophilic as well as hydrophobic samples in order to quantify the impact as also small effects might sum up to strong

disturbance if the conduction of the measurement is not controlled. Droplet evaporation showed stronger effect on hydrophilic than on hydrophobic surfaces due to a faster volume reduction of the droplets with lower SCAs. An existing approach for a self-built climate chamber/measurement cell (see reference [81]) was found to not effect SCAs on initially hydrophobic surfaces but to possibly influence SCAs on hydrophilic surfaces stored in the water saturated climate chamber before measurement. Therefore, a new setup was introduced aiming at droplet application under ambient conditions and a subsequent quick saturation of the atmosphere with water vapor. By that, the droplet and its SCA can be observed for several minutes with minimized reductions in droplet volume by evaporation. Such increased observation times might be especially important for patterned surfaces to determine if the droplet settles over time. In general, it was observed that the aged hydrophobic surfaces are less prone to scattering of the SCA via measurement induced influences.

Summary of the main results

- *SCA measurements are an alleged facile and fast method for wetting analysis. Publication 2 showed that a variety of sample as well as measurement induced influences can affect SCA results. It is the responsibility of the researcher to assure reproducible measurement conditions as well as sample conditions.*
- *Sample packaging and storage showed the greatest impact on the resulting SCA as they affect the adsorption of volatile organic species. Wrapping the samples in woodfree paper proved to create a storage atmosphere enriched in volatile organic compounds and therewith accelerate wetting transitions.*
- *An experimental setup which enables droplet application under atmospheric conditions with a subsequent quick saturation of the atmosphere with water was introduced and applied throughout the following wetting analysis to allow for prolonged droplet observation.*

Take-away message for the next research objectives

While addressing the first research objective within publication 1 and 2, the challenges around the metallographic preparation of copper were highlighted and an orientation for a preparation guide was developed which formed the basis for sample preparation in the following experimental works. The introduced setup for electro-polishing found application in publication 3 to reveal the bulk microstructure. Publication 2 revealed that despite the common assumption of SCA measurements being facile and straight forward, a broad variety of sample and measurement induced influences need to be considered to achieve reproducible measurement results. Especially sample state (packaging and storage) proved to strongly affect the outcome of SCA measurements. It was controlled in all following measurement series – details can be found in the respective publications.

Research Objective 2: Influence of intrinsic material properties on the wetting behavior

Summary of publication 3 [170] and its implications on the research objective

Publication 3 [170] focuses on the influence of copper microstructure on the static contact angle under consideration of dynamic adsorption processes of adventitious carbon. Three different microstructures were created: first a surface finish with a fine-crystalline deformation layer induced by mechanical polishing, second the bulk microstructure of the cold-rolled copper sheet revealed via electro-polishing after mechanical preparation and third the high-temperature annealed microstructure with reduced surface defects and grain boundaries revealed by mechanical- and electro-polishing. The samples were stored wrapped in cellulose containing tissues under controlled conditions and SCA were measured after 0, 5, 10, 20 and 30 days of storage. LSM, SEM and FIB analyses were applied for characterization of the sample surface and EBSD was conducted for analysis of the microstructure. XPS measurements were synchronized with SCA analyses on day 5, 20 and 30 after sample preparation on an additional sample set to avoid contamination. Sample packaging and storage was not only controlled for samples which underwent wetting analysis but for the XPS samples as well. Another experimental run was performed on two types of freshly prepared samples (mechanically polished with and without subsequent electro-polishing) to capture the effects of adsorption of carbonaceous species in early-stage aging. Directly after preparation, different SCAs were detected on the microstructure types with higher SCAs on the mechanically polished surface. Already after storage for 5 days, most of the differences vanish and the SCAs keep on converging. Apparently, long-term wetting behavior does not majorly depend on microstructure. In contrast, XPS revealed continuously higher amounts of adsorbed hydrocarbons on the mechanically prepared samples rich in defects and grain boundaries which are known to increase surface energy [105] and therewith cause higher chemical activity of these samples and higher adsorption rates [104]. The other two sample types showed comparable adsorption behavior suggesting a minor effect of grain size and bulk deformation compared to fine-crystalline surface layers packed with preparation induced defects. Also, the affinity to oxygen was investigated by XPS. The composition of the adsorption layers was comparable with slightly increased polar components on the mechanically polished surfaces which also was prone to stronger native oxidation. Analyses of the SCA development over time in dependence of the C/Cu ratio and the relative amount of polar adsorbates allowed for a systematic assessment of the wetting transition process. Possibly, a threshold concentration of adsorbed volatile organic species is responsible for the primary wetting transition to the hydrophobic regime, where additional adsorption causes further gradual growth of the SCA. This threshold concentration might depend on the sample type and microstructure.

Summary of the main results

- *Long-term wetting behavior does not seem to significantly depend on the microstructure, e.g., grain size and defect density.*
- *Transition rates from hydrophilic to hydrophobic appear to be influenced by the microstructure where fine-crystalline layers rich in surface defects proved to accelerate hydrocarbon adsorption. In contrast, grain boundaries and bulk deformation seem to play a subordinate rule.*
- *No saturation of adsorbed hydrocarbons was observed throughout 30 days suggesting continuously ongoing adsorption. Still, for the wetting transition a threshold concentration which might depend on sample type and microstructure appears to exist. Once this threshold is exceeded, only gradual changes in SCA are observed with ongoing aging.*

Take-away message for the next research objectives

The experimental work evolving around research objective 2 was of great importance for the upcoming research objectives. Laser processing is always accompanied by microstructural changes, especially near the substrate surface. Publication 3 showed that for the analysis of long-term wetting behavior, microstructural differences can be neglected if samples are stored for a sufficiently long period of time under conditions which provide volatile organic compounds as the adsorption of adventitious carbon due to surface energy minimization overrules the energetic effects of microstructural differences on the SCA.

Research Objective 3: Influence of surface chemistry on the wetting behavior

Summary of publication 4 A+B [171] and its implications on the research objective

The experimental work from previous papers already showed a strong impact of the adsorption of volatile organic compounds on the wetting behavior during aging of the samples. To gain a deeper understanding of the dynamics of the adsorption processes as well as the nature of adsorbed species, detailed studies were conducted in part A of publication 4 [171]. It was found that samples stored at ambient conditions showed a return to more hydrophilic behavior with time once humidity rose instead of surface hydrophobization which can be achieved by controlled storage conditions. In a further experimental run, polished copper samples were wrapped for storage under controlled conditions (humidity was kept low), and their wetting behavior was monitored throughout 43 weeks accompanied by XPS measurements of analogous stored samples. While SCA showed stable results, a continuously growing adsorbate layer was observed. Additionally, an XPS tilting experiment proved the termination of the surface with nonpolar hydrocarbon groups. These results not only support the findings from the previous publication [170] but indicate that both chemisorption as well as subsequent ongoing physisorption might be responsible for the growing accumulation of hydrocarbons while SCA stabilizes once the interaction is dominated by a sufficiently thick adsorption layer.

Next, the influence of oxidic termination of copper on the SCA was investigated (see part B of publication [171]). Magnetron sputtering was employed on polished copper samples to create even layers of Cu, CuO and Cu₂O. LSM measurements, FIB cross-sections and XRD-analysis were conducted for characterization of the layers. No significant influence of surface oxide on the SCA of aged samples was found. XPS analyses revealed the dominance of adsorption films with comparable ratios of polar to nonpolar species. A Cu-termination showed stronger adsorption which was traced back to a higher chemical activity due to a lack of surface passivation once the samples came in contact with the atmosphere.

Summary of the main results

- *It was found that the adsorption of adventitious carbon shows a significant influence on wetting behavior and that the adsorption dynamics in atmospheric conditions are highly sensitive towards any changes e.g., in humidity. Therefore, it is recommended to avoid storage in uncontrolled ambient conditions.*
- *Adsorption appears to go despite stabilized SCAs, e.g. due to physisorption.*
- *Oxidic termination plays a minor role for the long-term SCA due to subsequent adsorption of volatile organic species where the total amount of adsorbates might depend on the oxide state due to related differences in chemical activity.*

Take-away message for the next research objectives

Research objective 3 delivers a deep insight into the influence of surface chemistry on the wetting behavior and its time-dependency. The adsorption of volatile organic species was found to dominate the sample-water-interaction and to mask different oxidic states of the surfaces. While effects of topography were kept as small as possible due to thorough mechanical preparation, hydrophobic SCAs above 100° were achieved only due to controlled aging of the samples. Measured SCAs under controlled storage conditions also only showed small standard deviations and a high reproducibility highlighting the impact of the strict control of sample as well as measurement induced influences on SCA analysis as observed in publication 2.

The results of the previous research objectives build the foundation to analyze research objective 4 with a focus on the influence of surface topography altered by laser roughening and DLIP. Especially DLIP is accompanied by a multitude of changes to the metallic sample including microstructure, whose effect on the wetting behavior was analyzed in research objective 2, surface chemistry, whose effect on the wetting behavior was analyzed in research objective 3 and finally topography, whose effect on the wetting behavior was the focus of the final research objective 4.

Research Objective 4: Influence of hierarchical surface topography on the wetting behavior

Summary of publication 4 C+D [171] and its implications on the research objective

As DLIP creates hierarchical complex multi-scale patterns, section C of publication 4 [171] first analyzed the influence of a random isotropic roughness introduced by ps laser roughening on polished copper samples. With topographic features in the nm-range, LSM analysis was complemented by AFM measurements, SEM analysis and FIB cross-sections. Chemical analysis was done by XRD and XPS measurements revealing an oxidic surface and a strong adsorption of hydrocarbons after aging under controlled storage conditions. SCA increased by approximately 25 % in relation to the polished and aged reference due to the minor topographic changes. In section D of the paper, complex DLIP patterns were created with a periodicity of 6 μm and again they were packed and stored under controlled conditions for aging for multiple weeks. Similar primary patterns with a depth of approximately 500 nm were produced by fs- and ps-DLIP introducing a variation of the secondary roughness due to the different pulse durations. Additionally, a deeper ps-pattern (approximately 1 μm in depth) was created to determine the influence of the primary pattern. For topographic and chemical characterization, LSM, AFM, SEM, FIB, XRD and XPS with sputter profile detection were employed. The fs-pattern is characterized by an increased roughness of the network structure inside the pattern valleys with a decreased roughness on the pattern peaks while the analogue ps-pattern has stronger nanoparticle decoration on the pattern peaks which becomes even more pronounced for the ps-pattern with doubled depths. Roughness in the valleys is reduced for ps-patterns compared to the fs-structure. Chemical analyses showed the oxidic character of the surfaces with a strong termination of hydrocarbons after aging and comparable compositions of the adsorption films of the DLIP patterns. Wetting analysis revealed a strong influence of the secondary roughness as different wetting behavior was observed for the two fs / ps twin structures. The fs-pattern was dominated by high isotropic SCAs, air inclusions and rolling of the droplet if tilted, while the ps-twin-pattern showed anisotropic wetting with lowered SCAs parallel to the primary pattern, no signs of CB wetting and a high water adhesion with sticking droplets even after turning the sample upside down. The deeper ps-pattern showed wetting behavior closer to the fs-pattern, despite strongly increased particle decoration on the topographic maxima. Tilting of the samples left droplet residues on the fs- and the deeper ps-pattern after rolling of the droplet – further agglomeration of adventitious carbon is expected to reduce the water residues and further enhance droplet rolling / lower water adhesion. Subsequent studies will have to clarify if more pronounced adsorption of adventitious carbon / stronger nonpolar surface termination also might at one point counteract topography-induced pronounced wetting anisotropy and adhesion as observed on the flatter ps-twin-structures.

These investigations show the strong effect of topography where even the secondary roughness can induce major wetting differences for the same primary patterns after aging: Increased roughness of the crater networks in pattern valleys with minor roughness on the pattern peaks appears to stabilize air inclusions with suppressed wetting anisotropy, highly hydrophobic SCAs and reduced water adhesion.

Due to the limited image resolution, the degree of CB wetting cannot be assessed – e.g. if water penetrates secondary roughness on peaks. If roughness is greater on the pattern peaks and reduced in the valleys, it appears that Wenzel or related states like rose petal wetting / Cassie impregnating wetting (wetting of primary but not of the secondary roughness, see references [77,79]) is favored. This is accompanied by wetting anisotropy and high water adhesion. Still, these effects can be overruled by an increased depth of the primary pattern pushing the wetting behavior towards CB, very high SCAs, reduced anisotropy and water adhesion though air inclusions appeared less stable than with the fs-pattern.

The results obtained within this measurement series including chemical and topographical analysis combined with elevated wetting characterization show that even slight changes in topography can induce significant differences in the wetting behavior. Not only variations in aspect ratio but also line patterns of the same periodicity can produce varying wetting responses due to fine differences in the secondary roughness. These observations are not only meaningful for the tailored design of surfaces with distinct wetting behavior but also need to be considered as soon as coatings are applied which may preserve the dominating primary pattern but easily impact secondary roughness features.

Summary of the main results

- *Topography shows a great impact on wetting behavior if combined with supporting surface chemistry e.g., adsorption layers of adventitious carbon induced by controlled sample storage.*
- *With adsorbed hydrocarbons even simple and homogeneous roughening of the substrate can induce significant increase of the SCA.*
- *Complex surface patterns offer the chance for the creation of more extremely wetting states. DLIP line patterns can both induce anisotropic wetting in the hydrophobic regime with high water adhesion as observed on rose petals but also push the behavior towards lotus-like wetting with SCAs around 170° , air inclusions, suppressed wetting anisotropy and droplet rolling.*
- *The interpretation of the influence of surface topography asks for a determined analysis of both the primary and the secondary topography features. Especially DLIP offers the chance for a tailored design of the wetting behavior if the role of both structural layers is considered.*

5 Included Papers

Paper 0

Topography versus chemistry – How can we control surface wetting?

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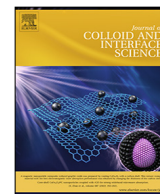
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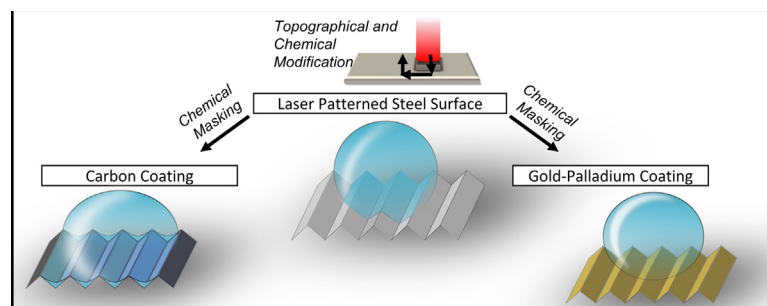
Topography versus chemistry – How can we control surface wetting?

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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Wetting characterization and the production of engineered surfaces showing distinct contact angles or spreading behavior is of major importance for many industrial and scientific applications. As chemical composition plays a major role in the wetting behavior of flat samples, wettability, capillary forces and resulting droplet spreading on anisotropic surface patterns are expected to be highly dependent on surface chemistry as well.

Experiments: To gain understanding of the fundamental principles of the interplay between surface topography and surface chemistry regarding water wettability, anisotropic line patterns were produced on steel samples in a direct laser writing process. Homogeneous surface coatings allowed for a chemical masking of the laser patterns and therewith the identification of the influence of surface chemistry on static contact angles and wetting anisotropy.

Findings: While a carbon coating leads to pronounced wettability and spreading along the topographic anisotropy, an inert gold–palladium coating can fully suppress anisotropic droplet spreading. Model calculations show that an amorphous carbon coating leads to Wenzel wetting while the gold–palladium coating causes air inclusions between the water and the surface in the Cassie-Baxter wetting state. Only in combination with the right chemical composition of the surface, directional patterns show their potential of anisotropic wetting behavior.

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1. Introduction

The surface of a material is largely determining its properties as interactions with the environment take place at the surface. The surface is, therefore, controlling many phenomena like wetting, friction, or light interaction. In particular, wetting properties often are used as an indicator of the interaction of topographically or

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chemically altered surfaces with the environment. Wetting properties of surfaces can be characterized by analyzing the contact angle a liquid forms on the surface under investigation between the liquid-solid-interface and the liquid-gas-interface. In case of water as the wetting liquid, the wetting properties can range from hydrophilic surfaces (contact angle $< 90^\circ$) to more water repellent behavior for hydrophobic surfaces (contact angle $> 90^\circ$). In the past decades, super-hydrophilic (contact angle $\ll 90^\circ$) or super-hydrophobic (contact angle $> 150^\circ$, small contact angle hysteresis) surfaces in particular have been the subject of much research [1].

Since many surfaces occurring in living nature demonstrate remarkable wetting properties owed to their distinct surface topography, mimicking extinct wetting properties has been a challenge in science for many years: The superhydrophobicity and self-cleaning behavior of the lotus leaf could be adapted to silicon wafers by femto second laser patterning in combination with chemical coatings [2,3]. The parahydrophobic wetting properties of rose petals with high contact angles and high water adhesion [4] on the other hand could be replicated through soft lithography [5] or femtosecond laser patterning [3]. Producing surface patterns with distinct wetting behavior as for example long lasting hydrophobicity is relevant for many different applications: Antimicrobial efficiency is strongly influenced by the wetting behavior [6,7]. Especially laser treatments often lead to anisotropic contact angles [8–12] which can be favored for implant cell interactions [13]. Moreover, wetting has a great impact on tribology, as friction and lubrication both are influenced by contact angles [14–16] or on other phenomena like bonding between different materials [17,18].

On an ideally smooth surface the contact angle θ is defined by Young's equation, considering the surface tensions of the three involved interfaces liquid (l), solid (s) and gas (g) [19]:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \times \cos(\theta) \quad (1)$$

For this definition of the contact angle, all three phases involved are assumed to at least form a mechanical equilibrium state [20]. The contact energy between the liquid and the surface depends on the type of interaction between them. Materials like glass can form hydrogen bonds between water and the substrate and wetting is therefore dominated by short-ranged chemical forces. In contrast, for materials like gold, long-ranged van der Waals forces dominate the liquid-substrate interaction [20,21].

As in reality, ideally smooth surfaces do not exist and especially technical surfaces are often characterized by major roughness, more advanced approaches are necessary to describe wetting states on real surfaces. Wenzel stipulated a new wetting theory considering surface roughness filled with water altering the wettability. Roughness is introduced by the roughness factor R as the ratio of the real surface area enlarged by roughness and the projected sample area [22].

$$\cos(\theta_w) = R \times \cos(\theta) \quad (2)$$

In opposite to the Wenzel state where water is completely wetting the entire surface, in the Cassie-Baxter (CB) state, air is trapped between the droplet and the surface as the water does not penetrate the roughness resulting in an enlarged contact angle θ_{CB} compared to the contact angle on a smooth surface [23]. The wetted area fraction is introduced as the factor f .

$$\cos(\theta_{CB}) = f - 1 + f \times \cos(\theta) \quad (3)$$

While in theoretical investigations clear distinctions between the Wenzel and the CB wetting state are possible, this is not easily the case for the wetting behavior of real technical surfaces. Often, metastable transition states are observed [24,25].

In many cases laser patterning is used to alter the wetting behavior of metals [26–31] or polymers [32–34] as it portrays an

easy yet fast way to structure large sample areas. Moreover, laser patterning does not only enable distinct topography changes by setting laser parameters but also leaves a chemically modified, highly reactive surface. Especially for wetting characterizations this reactive surface layer is of great interest as significant changes in wetting behavior from hydrophilic to hydrophobic and from Wenzel to Cassie-Baxter (CB) state occur simply during storage in ambient air conditions [35–39]. The simultaneous modification of topography and chemical composition during laser processing, poses a challenging task for understanding the wetting behavior of such generated surfaces as both factors significantly influence wetting.

Therefore, the characterization of different wetting states and phenomena is a challenging task as chemical, physical, and engineering aspects have to be taken into account [20]. All the more, important it is, to break down different influences to gain better understanding of the fundamental wetting aspects of engineered surfaces. In this context, in particular a separate investigation of the influence of surface topography and surface chemistry is crucial since these are the main factors influencing wetting.

Decoupling of chemical and topographic influence was studied by Hasan et al. [40] who optimized thermoplastic embossing of metallic glass so that chemical composition was not affected. They were able to show that the specific adjustment of the topography alone is sufficient to produce a transition from the Wenzel to the CB state. Schnell et al. [41] used a femtosecond laser to pattern a titanium alloy with varying strut widths and showed that the wetting anisotropy is influenced by the pattern expression, surface chemistry, and aging state of the samples. They recommended to perform further investigations with different surface coatings. Akkan et al. [42] modified the surface topography by laser and plasma treatment, leading to a fibrous nanostructure combined with microcraters and coated the surfaces afterwards to equal out chemical differences. They were able to show that only topographical differences already can lead to different wetting states of the substrate. Interestingly, no major changes during exposure to ambient air were reported.

However, the interdependencies of chemistry and topography of anisotropic structures in regard of their wetting behavior in terms of contact angle, droplet distortion and water spreading have not been investigated in detail.

In this work we want to take a closer look into the influence of surface topography and chemistry on the wetting behavior of periodically patterned steel surfaces manufactured by direct laser writing. To take the chemical modification resulting from laser processing out of the equation, the substrates are coated after laser processing with carbon and gold-palladium to mask the inhomogeneous surface chemistry and create chemically homogeneous surfaces. Both direct laser writing as well as PVD-coating enable a quick sample production and are also applicable in industry. As for flat samples the wetting behavior is determined by their chemical composition, major influence of the different coatings on the wetting properties of the patterned steel samples are expected.

2. Materials and methods

2.1. Materials

Steel coupons (AISI 304, BRIO Kontrollspiegel GmbH) with a mirror-polished finish and dimensions of $20 \times 20 \times 1 \text{ mm}^3$ were used for the experiments. The specimens were subjected to an established three-stage cleaning method consisting of ten-minute ultrasonic baths in cyclohexane, acetone, and ethanol [43]. This thorough cleaning in the above order removes polar and apolar impurities, leaving the samples well prepared for further processing.

2.2. Direct laser writing

Directional surface structures were produced by direct laser writing (DLW) to investigate possibly induced anisotropic wetting behavior. In order to generate a precise laser pattern, a focused laser beam emitting femtosecond pulses is scanned over the prepared steel samples creating periodic lines.

A Ti:Sapphire source emits the ultrashort laser pulses with a wavelength of 800 nm and a pulse duration of 100 fs at Full Width Half Maximum (FWHM). The beam diameter is defined by an aperture to 3 mm and the beam is focused on the sample by a lens resulting in a spot diameter of 55 μm at 50 mW beam power. As shown in Fig. 1 the sample is moved in x and y direction to obtain a homogeneous line pattern with a periodicity of 50 μm .

As laser processing parameters can strongly alter the surface topography, chemical composition and therewith the wetting behavior [29,44], parameters were kept constant for structuring the different samples to ensure the same topographical features on all samples.

2.3. PVD-coating

Laser processing leaves the surfaces with an inhomogeneous oxide layer [45]. To better understand the influence of surface topography and its interplay with the chemical composition of the surface regarding wetting behavior, the patterned samples were coated in a PVD process using the EMITECH K950X, leaving a control group of samples uncoated, which therefore exhibit a surface chemistry typical for the here used laser process.

Two different coating materials were used. As wetting properties are strongly influenced by adhesive carbon groups [37], the first set of samples is coated with an amorphous carbon layer. As a second coating material, a layer containing a high amount of gold ($\text{Au}_{80}\text{Pd}_{20}$) is selected to create an inert surface chemistry avoiding native oxidation. The coating duration is set to 10 minutes to create a homogeneous but at the same time thin enough layer to preserve the laser topography. The amorphous carbon can be deposited independent of time in a single arc ignition.

Simultaneously with the laser patterned samples, merely polished specimens are also coated and served as reference samples for the wetting characterization. Fig. 2 gives a schematic overview of the patterned and coated samples.

2.4. Surface characterization

White light interferometry (Zygo NewView 7300 Optical Profiler) was applied for adjusting the laser writing setup to assure the desired homogeneous pattern parameters. Roughness analysis of the periodic structures was carried out with the Olympus LEXT OLS4100, as confocal laser scanning microscopy is characterized by a higher lateral resolution than white light interferometry. Structure dependent parameters like the periodicity P , the structure depth R_c and the rms -roughness were chosen to characterize surface topography.

Optical analysis was further carried out by scanning electron microscopy (SEM) using a FEI Helios NanoLab600 FIB. Secondary electrons were detected at an acceleration voltage of 5 kV, 1.4 nA beam current and a sample tilt of 52° to achieve a better depth resolved impression of the topographical features. The FIB also allowed cross-sectioning of the sputtered samples for an analysis of the interface between the substrate and the coating, as well as the thickness of the carbon and $\text{Au}_{80}\text{Pd}_{20}$ layers. To protect the surface from degradation induced by the 30 kV ion beam, a platinum protective layer was applied first.

Chemical characterization by means of energy-dispersive X-ray spectroscopy (EDS) was carried out to demonstrate a homoge-

neous distribution of the PVD-coatings over the surface using 15 kV beam voltage for the $\text{Au}_{80}\text{Pd}_{20}$ layer and 12 kV for the coating containing the lighter carbon atoms.

2.5. Contact angle measurements

The samples were stored in ambient air after the PVD-sputtering and cleaned with ethanol before the wetting tests, to remove impurities like dust and to ensure comparable sample conditions. Static contact angle measurements were performed on a Krüss DSA 100 by applying 3 μl of double distilled water on the surface. To allow the droplet to reach a stable wetting state and at the same time minimize the influence of water evaporation during the measurement at room temperature, measurements were taken 5 s after the droplet came in contact with the surface. Each measurement was repeated at least 3 times on different areas of the sample. On top of that, for the patterned samples, contact angles were measured parallelly and perpendicularly to the direction of the primary periodic pattern. To capture not only the pattern dependence on the static contact angle but also on the droplet distortion, time-dependent top views of the applied droplets were taken using a digital optical microscope (VHX-7000, Keyence). Therefore, an additional set of experiments was conducted by applying 3 μl droplets of double distilled water with an Eppendorf pipette. With droplet dimensions in the mm range being significantly bigger than the applied pattern period and depth, a general description of the influence of the pattern on the water wettability in terms of static contact angles and droplet distortion is valid. For visualization purposes the droplet size is highly underestimated in the graphical abstract. For exact droplet sizes please refer to Fig. 8.

3. Results and discussion

3.1. Surface characterization

First, the morphology of the patterned and coated samples was observed via SEM. Fig. 3 shows SEM-images of the primary line pattern under a tilting angle of 52° and high-resolution images of the secondary nano-structures in the peripheral areas of the primary lines, where they are best visible. The secondary structure consists of laser-induced periodic surface structures (LIPSS). A distinction is made between high spatial frequency LIPSS and low spatial frequency LIPSS, the latter being characterized by a period in the order of the magnitude of the laser wavelength and an orientation perpendicular to the polarization (in this setup up in line with the primary line structure) as shown in Fig. 3 [46–48].

The SEM-analysis suggests that the topography of the laser pattern is preserved after the coating process: the primary line pattern is clearly visible after the PVD-sputtering process. The nano roughness consisting of LIPSS undergoes minor changes as a result of applying the coating, whereby the carbon-coating enhances the structural features while the $\text{Au}_{80}\text{Pd}_{20}$ coating settles into the valleys of the periodic LIPSS blurring them to some degree. To further analyze the influence of the coating on the topography, roughness parameters were measured and compared for the three patterned samples.

The polished steel surfaces demonstrate a S_a -roughness of 4 nm $\pm$ 1 nm. The sputtered gold-layer on a flat sample does not affect the roughness (4 nm $\pm$ 1 nm), while the carbon coating decreases the S_a -roughness slightly to 3 nm. However, when considering the standard deviation, it can be stated that the coatings do not affect the roughness of the flat samples.

Next, the roughness parameters of the laser patterned samples are investigated.

Table 1 summarizes the roughness analysis on patterned surfaces.

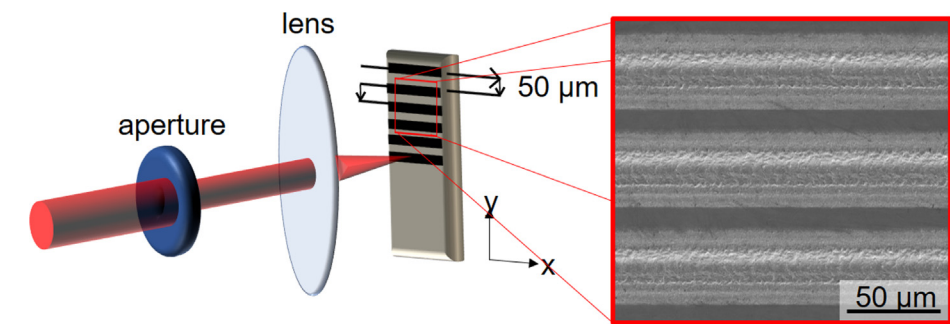


Fig. 1. Direct Laser Writing Setup and resulting periodic line pattern.

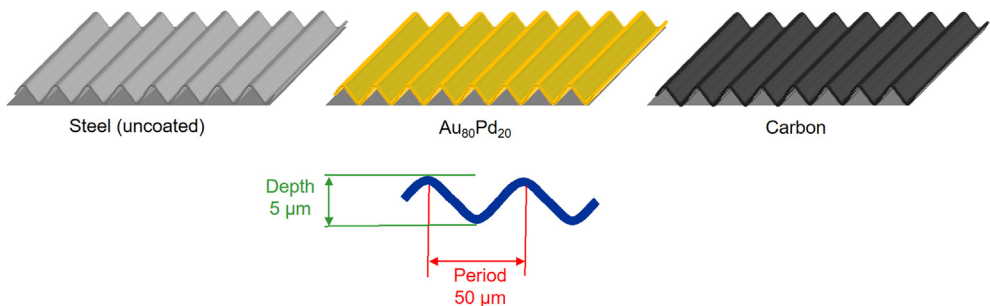


Fig. 2. Schematic overview of the laser patterned samples investigated in this study. The laser patterned samples demonstrate a line pattern with a periodicity of 50 µm. The uncoated samples exhibit a surface chemistry typical for the direct laser writing process used here and are compared to PVD-coated samples with either an amorphous carbon layer or a layer containing a high amount of gold (Au₈₀Pd₂₀).

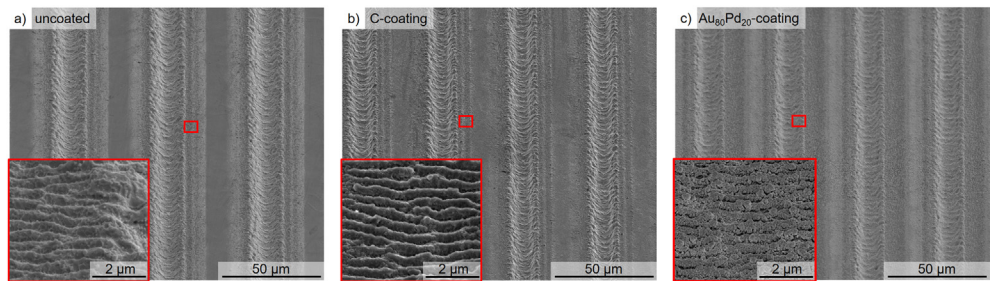


Fig. 3. Analysis of the pattern morphology by secondary electron microscopy under 52° of the uncoated (a), the C-coated (b) and the Au₈₀Pd₂₀-coated (c) laser patterned surfaces. The red rectangles mark the positions where the high-resolution images of the secondary nano-structures were taken, which are shown in the insets.

It is assumed that the conducted roughness analysis mainly depicts the micro roughness caused by the periodic line patterns while nano roughness (LIPSS) cannot be detected because of the limited lateral resolution of the laser scanning microscope of 120 nm (height resolution 10 nm). Since it is reported in literature [9,49] that micro roughness is the relevant influencing factor for static contact angle measurements as conducted in this work, while nano roughness strongly affects the contact angle hysteresis, it can be assumed that the values reported in Table 1 are the most critical for this study.

The roughness parameters measured for the laser patterned samples are in accordance with the visual observations by SEM (Fig. 3), demonstrating the highest roughness for the carbon-coated samples. Nevertheless, the PVD-sputtering process alters the roughness of the steel-surface and the pattern depths only slightly indicating a coating thin enough to preserve the topographical features. Thus, PVD-sputtering fulfills the goal of changing the chemical composition of the surface without critically affecting its topography, which makes it possible to study the effect of a variation of surface chemistry on the wetting properties of laser patterned samples.

In order to analyze the quality of the PVD-coatings in more detail, the coating homogeneity was investigated by EDS analyses. Element maps in Fig. 4 provide information about the distribution of the deposited elements.

Table 1
Roughness analysis of patterned surfaces. The structural depth of the line-like pattern is characterized by R_c , the overall roughness by rms perpendicular to the structure and S_a for the surface roughness.

	Steel	Au ₈₀ Pd ₂₀	C
rms [µm]	1.478 ± 0.067	1.496 ± 0.085	1.629 ± 0.126
S_a [µm]	1.155 ± 0.076	1.226 ± 0.075	1.3 ± 0.087
R_c [µm]	4.886 ± 0.274	4.311 ± 0.466	5.095 ± 0.655

The entire surface is covered with the main coating elements Au and C, demonstrating a homogeneous and continuous coating. Contrasts visible in the element maps can be attributed to topographical shielding due to the orientation angle between the EDS detector and the electron beam.

The iron and chromium signal originate from the steel substrate, while the oxygen is part of a native oxide layer on the steel surface, but can also occur as a result of the laser patterning as an oxidic reaction layer between the steel substrate and the gold/carbon coating [50]. It must be mentioned here that EDS has a reduced sensitivity for light elements (atomic number lower than sodium), which is why the intensity of the carbon map is reduced in comparison with the Au signal [51]. In addition, the primary electron beam undergoes only a slight attenuation by electron excitations due to interaction with the light carbon atoms and can, therefore, penetrate deeper into the material [52]. Consequently, the elemental mappings of the carbon-coated samples demonstrate stronger Fe and Cr signals stemming from the underlying steel substrate. Additionally, an increased oxygen-concentration can be observed for the carbon-coated samples. It is assumed that more oxygen from the underlying steel surface can be detected. But it also must be considered that the Au₈₀Pd₂₀-coating is expected to show mainly inert behavior due to the high amount of gold, and therefore no native oxidation should take place, whereas the adsorption of oxygen rich molecules cannot be excluded for the carbon coating. The EDS analyses could show a homogeneous distribution of both coating materials, Au₈₀Pd₂₀ and amorphous carbon.

In the PVD process, the thickness of the sputtered layers is determined primarily by the sputtering time and procedure. Depending on the sputtered element, differences in the coating thickness can occur. Therefore, the patterned and coated samples were investigated via FIB-cross-sectioning (Fig. 5).

The gold coating includes distinct pores, and an accumulation of particles is visible. FIB-cross-sections were taken at an untextured area of the sample, but the accumulation is believed to be the reason for blurring the LIPSS as shown in Fig. 3. The optically determined thickness of the Au₈₀Pd₂₀-coating is $39.5 \text{ nm} \pm 12.5$. As was also suspected in the visualization of the LIPSS in Fig. 3, the carbon layer covers the patterned surface more uniformly and leads to significantly fewer pores between the coating and the surface. The thickness of this layer can therefore be determined more precisely to $55.1 \text{ nm} \pm 8.5$. In summary, the characterization of the surfaces showed that direct laser writing created a homogeneous linear pattern with a secondary nano-roughness (LIPSS) on steel substrates. The coatings were used to vary the chemical composition of the surface while maintaining the topographic features. A thickness of several tenths of nm has proven useful here.

3.2. Wetting behavior

Contact angle measurements were performed to investigate the influence of the laser patterns and the PVD coatings on the wetting properties of the samples, thus demonstrating the effect of a distinct surface topography in combination with a known surface chemistry. As shown in Fig. 6, the contact angle was measured parallelly and perpendicularly to the primary line-like pattern to capture a possible anisotropy in the wetting behavior.

Regarding the flat and polished samples, the steel sample shows typical values of 75° [29,53]. The fact that the contact angle on the flat Au₈₀Pd₂₀ coating is increased is somewhat surprising since it is reported that contamination-free flat gold surfaces are hydrophilic, while even minimal contamination of less than one monolayer increases the contact angle with water to about 50° [54]. The fact that higher contact angles were recorded in the present measurements of the Au₈₀Pd₂₀ coating may indicate a more pronounced carbon contamination on the one hand and be a consequence of

the addition of Pd on the other. It is reported in literature that the adsorption of carbon groups from the atmosphere can strongly influence the wetting properties [26,27]. Long et al. [37] have shown that the adsorption of polar carbon compounds leads to hydrophobization of a copper substrate after laser patterning. In particular, the ratio of polar to non-polar carbon compounds seems to be of crucial importance [55]. The amorphous carbon coating meets the range of contact angles reported in literature for tetrahedral amorphous carbon on steel at room temperature [56].

For the patterned surfaces, a clear influence of the patterning process on the wettability of the surfaces is visible. The steel surface demonstrates an increase of the perpendicular contact angle to nearly 120° , whereas the parallel contact angle stays nearly unchanged, thus, demonstrating a clear anisotropy of the contact angle with respect to the orientation. According to [57], the degree of wetting anisotropy is determined by the difference $\Delta\theta$ of the contact angles perpendicular and parallel to the primary pattern. In case of the here investigated pattern this anisotropy is generated by an elongation of the droplet in direction of the pattern due to capillary forces induced by the line-like pattern acting as open microchannels [58–61]. Additionally, perpendicularly to the line-like pattern the triple line is pinned at the edges of the pattern and needs to overcome great energy barriers to move [62]. Obviously, according to the results from the static contact angle measurement, the steel structure shows with 45.6° the strongest wetting anisotropy, followed by the coated samples with 6.9° for the Au₈₀Pd₂₀ coating and 6.1° for the carbon coating. It should be noted that no wetting anisotropy could be verified for the Au₈₀Pd₂₀ coating when taking the standard deviation into consideration. When considering the influence of the coatings on the orientation-dependent contact angles on the patterned samples, it becomes obvious that they follow the same trend as the equilibrium contact angles on the smooth reference specimens: The carbon coating on the patterned surface leads to further hydrophilization, while the Au₈₀Pd₂₀ coating further hydrophobizes the patterned steel samples. Nevertheless, as the contact angle on the flat surface coated with Au₈₀Pd₂₀ is still slightly below 90° , according to Wenzel [22] a decrease in the contact angle with higher roughness is expected.

The static contact angle measurements already prove the hypothesis of a strong influence of surface chemistry on the wetting behavior of patterned surfaces. To gain a better understanding of the fundamental interactions caused by the coatings, model calculations based on the static contact angle results for the unpatterned reference samples were conducted to verify whether the wetting states of the patterned surfaces corresponded more to the Wenzel behavior or the CB-state. In literature, the Wenzel wetting state also is compared to a noncomposite material as the water penetrates the roughness entirely while the CB state is referred to as a composite with encapsulated air pockets between the droplet and the material [62,63].

The Wenzel factor R was determined to be 1.292 ± 0.02 by measuring the average surface enlargement due to laser patterning on the three surface types by means of confocal laser scanning microscopy. In contrast, the CB factor σ of the wetting surface portion was determined optically by image processing methods. Thereby, light microscopic images of high brightness of the patterned surfaces allow overexposure of the structural plateaus in contact with the water in the case of CB wetting. A subsequent threshold binarization using *Amira* Version 5.3.1 allows the calculation of the surface fraction of the plateaus to 35.7 %. Fig. 7 shows the comparison of the two calculated models with the values determined in the static contact angle measurements for the laser patterned surfaces.

The diagram in Fig. 7 shows that the hydrophilic carbon coating fits the Wenzel model, while the hydrophobic Au₈₀Pd₂₀ coating

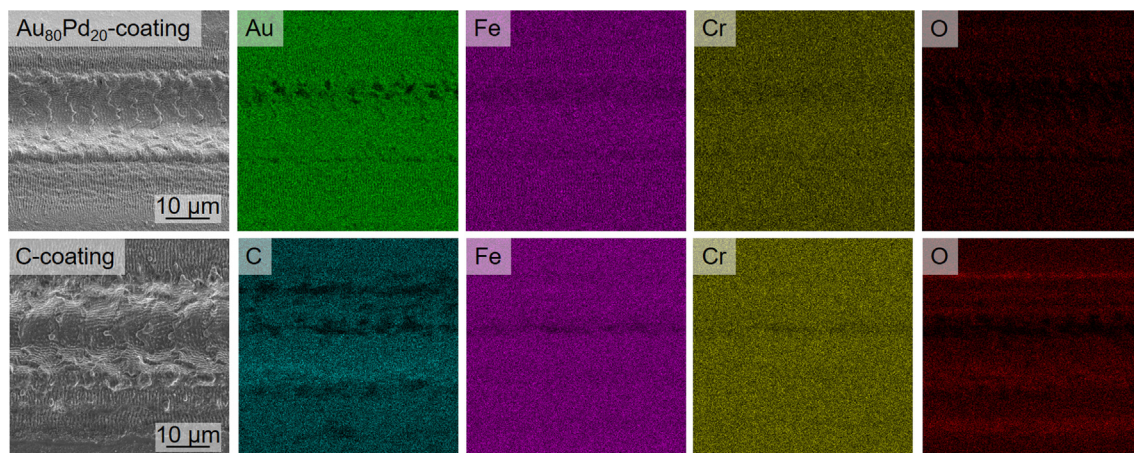


Fig. 4. Analysis via energy-dispersive X-ray spectroscopy of the laser patterned and coated surfaces. Both carbon and $\text{Au}_{80}\text{Pd}_{20}$ show a homogeneous and continuous distribution over the sample surface.

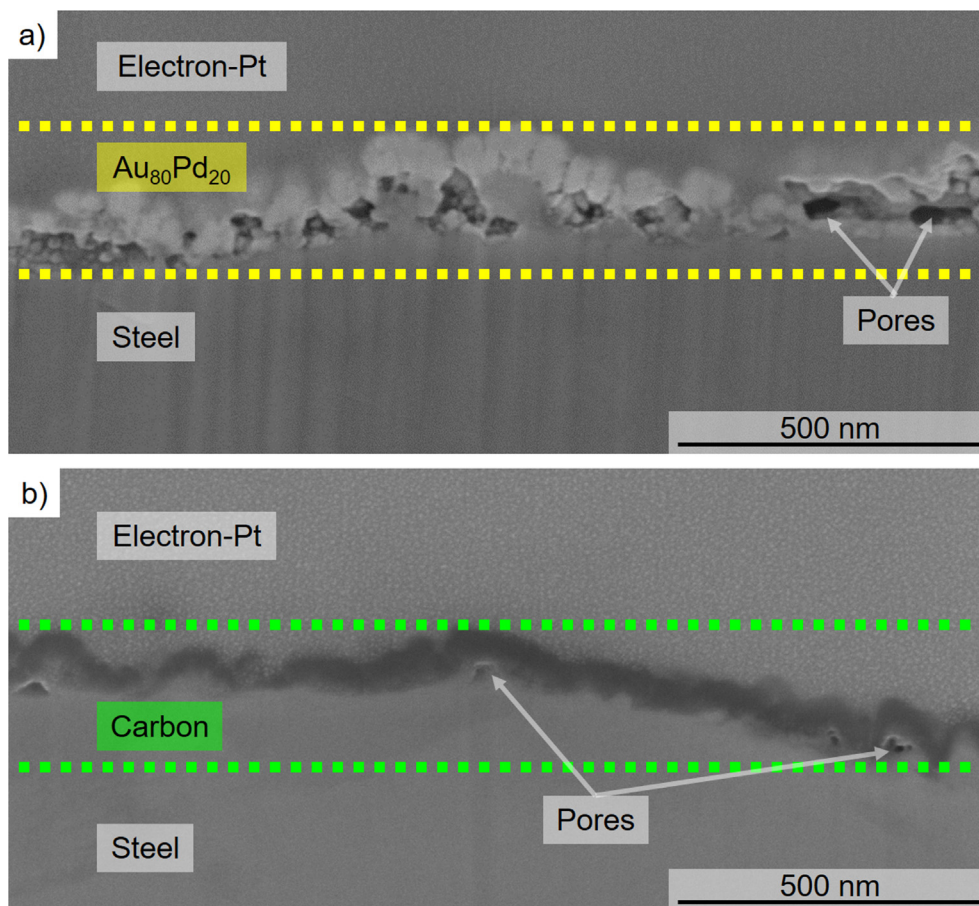


Fig. 5. FIB-cross-sections of the patterned and sputtered samples. (a) $\text{Au}_{80}\text{Pd}_{20}$ layer on the steel substrate. Pores between the layer and the substrate are visible. (b) Amorphous carbon layer on the steel substrate. Pores only exist in the laser patterned surface while the carbon layer smoothly covers the steel substrate.

shows good agreement with the CB model. The values for the uncoated steel sample, on the other hand, range exactly between the two wetting models with its parallel contact angle being close to the CB-Model and its perpendicular contact angle to Wenzel wetting behavior. Surprisingly, according to Fig. 6 both coatings cause similar wetting anisotropy, while the model calculations suggest opposite wetting states on the coated samples and therefore, different degrees of wetting anisotropy would be expected.

To closer investigate the surface patterns' effect on a possibly induced anisotropic wetting, the droplets were additionally examined in top view over a period of 30 s as shown in Fig. 8. This allows not only the observation of the liquid–solid interface, but also the length and width measurement of the applied droplets. For line-like patterns, elliptical shapes are expected [57,64,65]. In addition to the contact angle difference, the droplet distortion can be used to characterize the wetting anisotropy. It is defined as the quotient

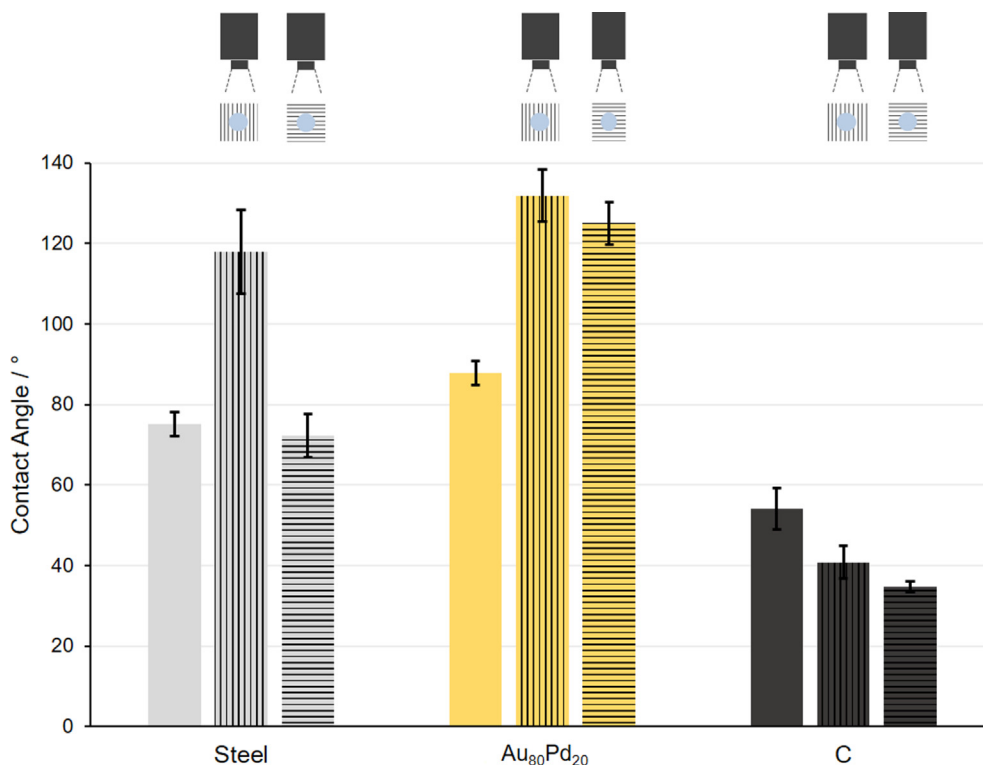


Fig. 6. Results of the static contact angle measurement on the uncoated, Au₈₀Pd₂₀-coated and the C-coated polished and patterned samples. On the laser structures the contact angle was measured parallelly and perpendicularly to the primary laser pattern, whereby an orientation of the camera in direction of the line-like pattern denotes the perpendicular case and an orientation of the camera in normal direction with respect to the line-like pattern the parallel case. It should be noted that the visuals above the diagram highly underestimate the droplet size.

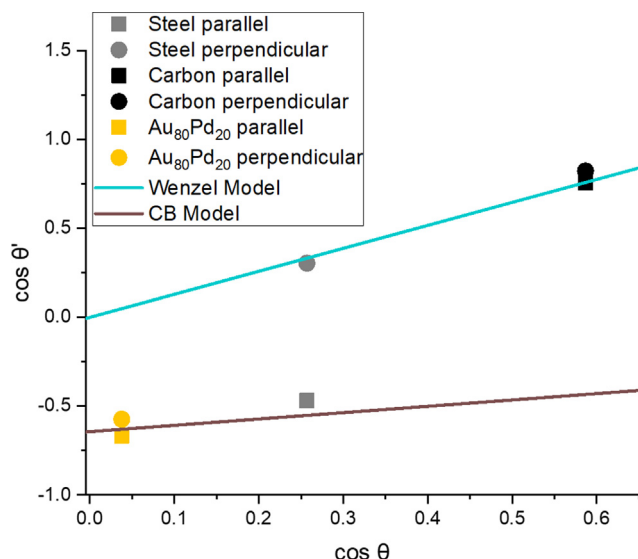


Fig. 7. Comparison of the Wenzel Model (blue) and the Cassie-Baxter Model (brown) with the experimental results from Fig. 6. θ displays the contact angle on the flat surfaces while θ' is the contact angle on the patterned surfaces.

of the length of the droplet (typically in direction of the primary pattern) and the droplet width [57,62].

The Au₈₀Pd₂₀ coating exhibits a stable wetting front over the period studied and no wetting anisotropy could be observed. Furthermore, there are clearly visible air inclusions in the structural valleys, which thus confirms the CB condition calculated in the model. The CB state and the associated air inclusions inside the

pattern do not allow for a significant wetting of the microchannels (i.e., the line-like pattern) with the droplet sitting on top of the surface asperities, which explains the nonexistence of wetting anisotropy as the effect of the microchannels on the contact line in terms of capillary forces and contact line pinning is minimal [66]. This also demonstrates that a pattern depth of 4 to 5 μm (Table 1) is sufficient to produce CB-wetting with clearly visible air inclusions and a pinning of the baseline of the droplet.

The detailed images in Fig. 8 show that after 30 s some of the air inclusions have disappeared, so the structural valleys are - at least partially - wetted after all. This observation corresponds to the two-step transition from the CB to the Wenzel state described by Murakami et al. [25]. Starting from the contact line, structural valleys are wetted and then progressively spread out. In reference [25], it is described that this transition is comparatively slow for water, and complete Wenzel de-wetting does not occur before evaporation of the water. This behavior thus explains the high contact angles and the nonexistence of wetting anisotropy over the time period studied here. It must be noted, however, that atomistic simulations have already shown that metastable states exist between the clearly separated CB and Wenzel wettings [24], but their occurrence has not been investigated in detail in the present work.

The behavior in terms of the liquid's distribution over the surface for the uncoated sample, is as expected from literature, showing an elliptical shape. It is also in accordance with the contact angle measurements, showing a pronounced wetting anisotropy. The elliptical shape of the droplet can be observed already 1 s after drop deposition. 5 s after drop deposition, a change in the wetting front's appearance is visible suggesting that a stable wetting stage is reached. The darkened edges of the drop indicate an accumulation of water in the peripheral areas, slowly pushing the wetting

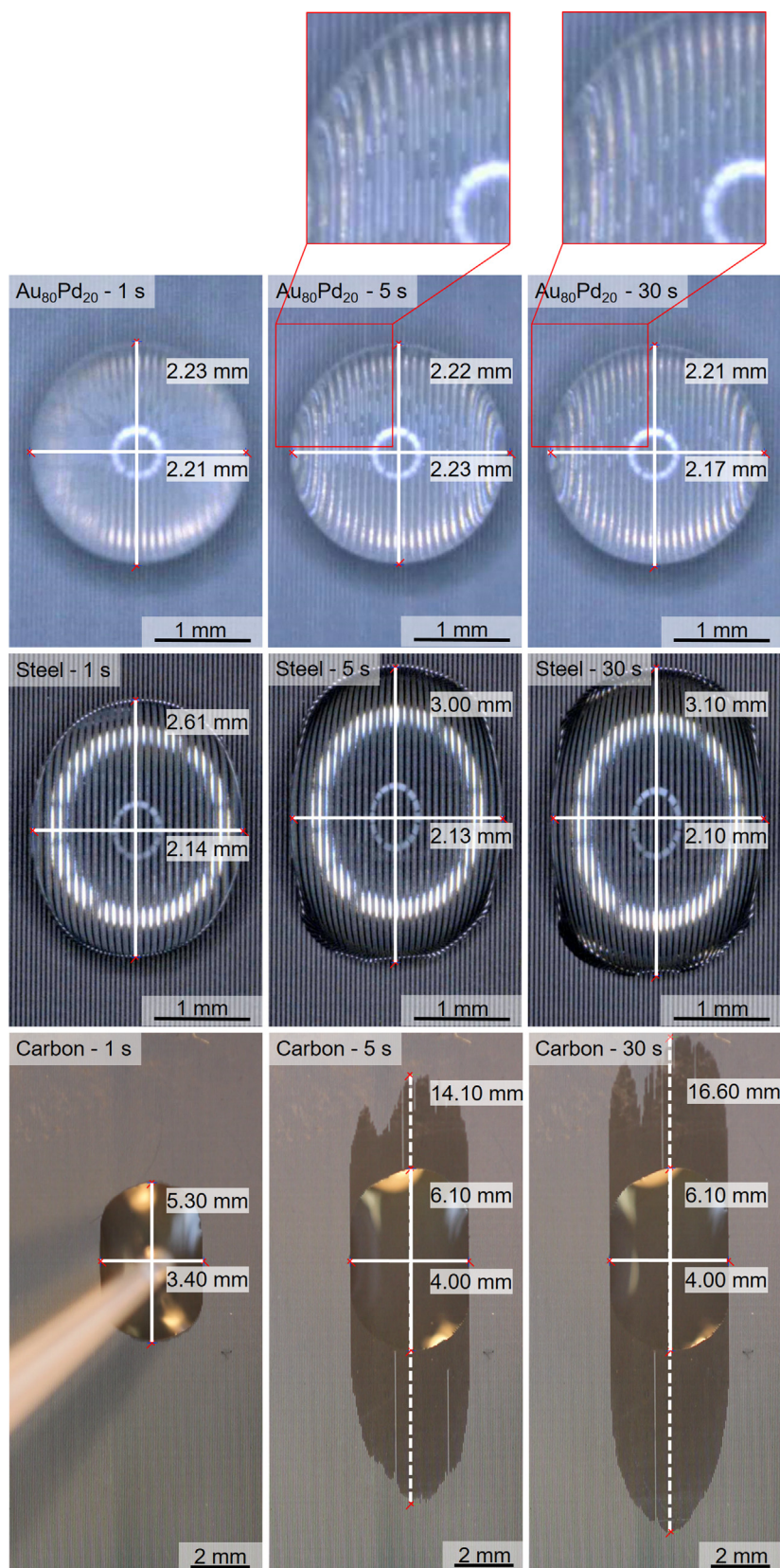


Fig. 8. Top views of 3 µl of bidist water on the three surface types 1, 5, and 30 s after drop deposition.

front further out along the primary structure. On the left and right sides of the droplet the contact line is not visible anymore, which is likely a result of bulging of the droplet induced by a pinning of the

droplet on the pattern's edges. Air pockets beneath the droplet, which would indicate CB wetting, were not observed. Still, it is noticeable that according to the model calculations the two direc-

tional components of the contact angle are split between the wetting models. This behavior cannot be conclusively explained at this point and further investigations will be necessary.

In strong contrast to these two clearly defined drop shapes, the sample with the carbon coating shows a steady advance of water especially along the pattern (i.e., inside the structural channels) also referred to as liquid filaments in literature [67,68]. Resulting from the reduced contact angles on the carbon coating, the structural channels can be fully wetted. The increased roughness inside the channels due to pronounced LIPSS further enhances the Wenzel wetting [22]. The capillary forces inside the line-like pattern acting as open microchannels increase, thus favoring a liquid propagation inside the channels in direction of the primary pattern [66]. Wetting according to Wenzel is clearly present here, which increases droplet spreading in all directions and thus also corresponds to the model calculations. Interestingly, despite the water still slightly advancing inside the microchannels after 5 s, the size of the actual droplet sitting on the pattern stayed constant after 5 s, which might indicate that no further liquid from the droplet is flowing into the channels but the liquid already in the channels is distributed along the channels. This highly pronounced anisotropy could not be detected in the static contact angle measurements, since the strong spreading leads to relatively small contact angles and, therefore, does not allow for a detection of the outer droplet contour. Moreover, the water inside the channels cannot be detected by contact angle measurements, and therefore, not contribute to the wetting anisotropy measured in this fashion. This highlights the importance of analyzing the droplet distortion.

Topographic patterns with a depth in the μm -range and a rather small aspect ratio of about 0.1 apparently can produce both CB- and Wenzel-wetting depending on the chemical composition of the uppermost surface.

It is reported in literature that not only the wetting behavior according to Wenzel or CB but mostly capillary forces and interactions of the contact triple line with topographic surface features influences the droplet distortion [9]. Next to topographic features like the aspect ratio, slope of the sidewall, structure depth, and many more, also chemical inhomogeneities can cause a pinning of the triple line [57,64]. Following the Gibbs inequality effect, a droplet can be pinned on a structural tip in a specific wetting region [64,69].

According to reference [66] anisotropic wetting on unidirectional surfaces by capillary forces is mostly dominant on hydrophilic surfaces showing Wenzel wetting, while the effect decreases with increasing hydrophobicity and a transition to the CB state. Thereby, it is clear that the effect of surface patterns on wetting anisotropy correlates with the portion of the created microchannels (here by direct laser writing), which are wetted. In case of a CB type wetting, this portion is very small leading to negligible effects. These observations are in good agreement with the presented results.

The strong anisotropic wetting behavior of the patterned and carbon coated samples is believed to be caused by capillary forces pulling the droplet in the direction of the primary structure. Water can enter the microchannels formed by the laser process easily due to the hydrophilic nature of the carbon coating [66]. Liang et al. [62] state, that roughness has a higher impact on the wetting anisotropy on hydrophilic surfaces which could be an additional reason for the hydrophilic carbon-coating displaying a strong wetting anisotropy as it also is characterized by the most pronounced LIPSS and therewith highest roughness values (compare Table 1).

In case of the steel sample capillary forces are reduced compared to the carbon coating due to less wettability. The hydrophobic CB state on the gold coating does not allow the water to wet the pattern valleys significantly and, therefore, capillary forces cannot pull the water into the microchannels. Thus, indicating that wet-

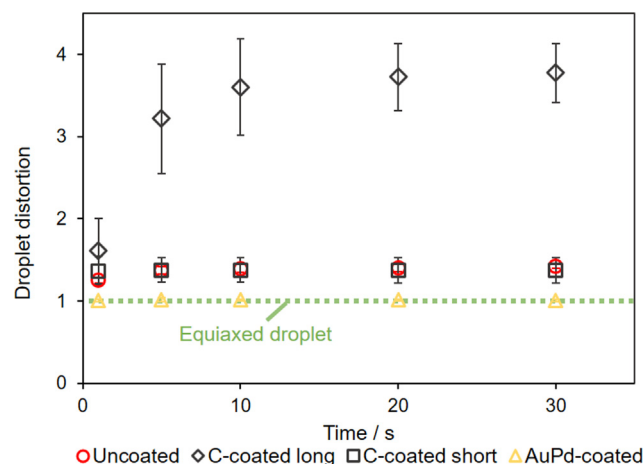


Fig. 9. Droplet distortion and its development over time. The carbon-coating shows under consideration of its liquid filaments the strongest droplet distortion.

ting transitions from CB to Wenzel state do not influence anisotropic wetting of a hydrophobic material.

It should be noted that influences of gravity can be neglected in droplet spreading, since the structures are in the sub-millimeter range and thus the forces at the interfaces are decisive [68].

To get a better impression of the detected droplet distortion and its changes over time, distortions for all samples are summarized in Fig. 9. Surprisingly, the distortion on the steel sample is the same as on the carbon sample if the liquid filaments inside the microchannels are not taken into consideration. As expected from Fig. 8, the $\text{Au}_{80}\text{Pd}_{20}$ coating eliminates droplet distortion, while the carbon coating strongly enhances droplet distortion when considering the liquid filaments. After ten seconds, all samples reach a stable condition.

The application of a line-like pattern by laser processing to a steel sample causes, as suspected, wetting anisotropy. Surprisingly, chemical modifications without influencing the topographic characteristics are sufficient to cancel the wetting anisotropy as in the case of the $\text{Au}_{80}\text{Pd}_{20}$ coating or to significantly enhance it as for the carbon coating which even allows for advancing liquid filaments on the patterned surface. At the same time the effect of the surface patterns on the contact angle and wetting state also depends on surface chemistry, where a greater wettability is observed on the patterned surfaces coated with carbon (Wenzel wetting) and a decreased wettability on the patterned surfaces coated with $\text{Au}_{80}\text{Pd}_{20}$ (CB wetting). Hence, this study shows that when investigating the influence of surface patterns (i.e., topography) on surfaces' wetting properties both topography and chemistry of the surfaces have to be considered as their effects are mutually dependent on each other.

4. Conclusions

Unlike earlier wettability studies which focused on the influence of different topographies of the same chemical composition [40], this study describes in detail the strong effect of different surface chemical compositions on a known topography. Thereby different approaches from literature are combined by applying anisotropic surface patterns in a laser process [41] and a subsequent PVD-coating [42].

Precise anisotropic line-like patterns were produced on steel surfaces by femtosecond direct laser writing, which were subsequently sputtered in a PVD process to mask the generated patterns with uniform and chemically homogeneous $\text{Au}_{80}\text{Pd}_{20}$ or carbon coatings.

Wetting experiments with water droplets showed the expected wetting anisotropy on the patterned, uncoated steel sample with drop elongation in direction of the primary pattern. Static contact angle measurements parallel and perpendicular to the pattern indicate that a modification of the surface chemistry in form of uniform coatings can reduce this wetting anisotropy significantly.

A complete analysis of the wetting anisotropy was only possible by looking at the drop shape in top view, which, in particular for the hydrophilic carbon coating, leads to a strong deviation of the results observed in static contact angle measurements in terms of the degree of anisotropy. Due to Wenzel wetting it shows the strongest wetting anisotropy with advancing liquid filaments. The most hydrophobic coating ($\text{Au}_{80}\text{Pd}_{20}$) shows no wetting anisotropy even after 30 s, although air bubbles underneath the water droplet characterizing the wetting state clearly as CB start to dissolve leaving the droplet in an assumed metastable wetting state.

It was shown that topographic features such as directional patterns alone do not characterize wetting behavior, but that the interaction with surface chemistry is crucial. Topography can only take effect on the wetting behavior, capillary forces, and the resulting droplet distortion in combination with an adequate surface chemistry.

It is commonly accepted that anisotropic surface patterns induce anisotropic wetting behavior. Usually different degrees of wetting anisotropy are explained by the influence of topographic features such as resulting capillary forces [58] and contact line pinning [70] on the surface wettability of metals [71,72] as well as polymers [70]. Many studies focus on the variation of wetting anisotropy by applying different laser parameters during the patterning process to adjust sample topography [10,28,73]. This study shows that controlled changes in the chemical surface composition of the patterned surfaces are sufficient to achieve extreme wetting behavior. The $\text{Au}_{80}\text{Pd}_{20}$ coating showed similar behavior as hydrophobized [74] or long time stored [6,75] laser patterned samples while the carbon coating showed increased wettability that usually just appears shortly after laser patterning [6,31]. If superhydrophobic surfaces are to be achieved, based on literature [76], smaller periods in combination with an $\text{Au}_{80}\text{Pd}_{20}$ -coating could be beneficial while according to Wenzel [22] for the hydrophilic carbon coating any additional roughness is believed to result in a stronger hydrophilicity. Our results show that it is crucial to take surface chemistry into account when designing surfaces for anisotropic wetting behavior, especially considering that laser patterned surfaces often show a pronounced decrease of wettability with time, thus reducing anisotropic wetting behavior [6].

The behavior of steel in laser processing and the resulting topographies are well known [77] and we showed that the following homogeneous masking of the surface chemistry by PVD-sputtering is sufficient to produce extreme wetting behavior of the applied coatings, ranging from hydrophilic behavior with high droplet distortion to hydrophobic behavior with no droplet distortion.

This study therefore does not only give new insight into the fundamentals of the influence of surface chemistry on wetting but also relevant findings for application processes. Instead of adjusting the laser patterning parameters to achieve certain topographic features, distinct changes in the wetting behavior are possible by simply changing the surface chemistry in a PVD process.

By leaving the topography unchanged and masking it with homogeneous coatings, a strong influence of surface chemistry on the wetting behavior of topographically altered surfaces was demonstrated. These findings are beneficial for the design of surfaces with distinct wetting properties and anisotropy, for example the design of antimicrobial / antiadhesive surfaces, anti-icing patterns, self-cleaning surfaces and many more.

Further investigations of the individual roles of topography and especially of surface chemistry are necessary to characterize their interplay in the wetting properties of patterned surfaces. A broader variety of coatings will help to further sharpen the knowledge of the crucial influence of surface chemistry. Especially the accumulation of carbon species on the coated samples has to be considered in further investigations and should be combined with simulations that are believed to be of great importance to gain a fundamental understanding of the interface forces between water and chemically altered surfaces. Also, studies focusing on different topographies while maintaining a homogeneous surface chemistry are believed to be of great importance. Both influences need to be investigated independently in more detail before general assumptions about the wettability of chemically and topographically altered surfaces can be made based on the known contact angle of flat reference surfaces.

CRediT authorship contribution statement

Sarah Marie Lößlein: Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Frank Mücklich:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Philipp Grützmacher:** Conceptualization, Methodology, Validation, Investigation, Writing – Review and Editing, Visualization, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Paper 1

Patience Alone is not Enough – A Guide for the Preparation of Low-Defect Sections from Pure Copper

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Patience Alone is not Enough – A Guide for the Preparation of Low-Defect Sections from Pure Copper

Geduld allein reicht nicht! – Ein Leitfaden zur Herstellung defektarmer Schliffe von Reinkupfer

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Abstract

The preparation of metallographic sections from soft metals such as pure copper constitutes a particular challenge: the high degree of ductility promotes the formation of preparation artifacts and complicates the preparation of homogeneous, low-deformation surfaces. A metallographic preparation routine is therefore presented which has proven effective for pure copper and which can also be applied to additionally soft annealed samples. The subsequent removal of fine crystalline deformation layers is discussed and different setups for electropolishing and its optimization are presented.

Kurzfassung

Weiche Metalle, wie Reinkupfer, stellen eine besondere Herausforderung in der metallographischen Schliffpräparation dar: Die hohe Duktilität fördert die Entstehung von Präparationsartefakten und erschwert die Anfertigung deformationsarmer homogener Oberflächen. Vorgestellt wird daher eine metallographische Präparationsroutine, die sich für Reinkupfer bewährt hat und auch auf zusätzlich weichgeglühte Proben übertragbar ist. Die anschließende Entfernung feinkristalliner Deformationsschichten wird diskutiert und verschiedene Aufbauten zur Elektropolitur und deren Optimierung werden vorgestellt.

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Keywords

Metallography, preparation of metallographic sections, deformation layers, pure copper, soft annealed copper, electropolishing

1 Introduction

Metallography allows us to visualize the inner structure of metals: following a successful metallographic preparation, the microstructure as the totality of all phases, defects, and their fractions [1], can be analyzed. But why is this information relevant? Alongside the task of assuring quality, metallography plays a crucial role in failure analysis [2]. Metallography is not only widely used in an industrial environment. Metallographic techniques are also applied in the field of research to analyze and develop the microstructure of novel alloys and the resulting properties. The preparation of metallographic samples is furthermore intended to provide artifact-free sample surfaces in preparation for further processing steps such as laser structuring metallic materials [3].

Taking into account all possible influencing factors in the context of developing suitable routines, it quickly becomes evident that metallography is not unlike detective work: it is thrilling, challenging, varied, and, above all, full of surprises. In metallography, a classical approach involves four steps: First, if samples are too large, they are sectioned, if they are too small, they are enlarged by embedding. The sample is subsequently ground on grinding disks under water cooling using increasingly fine grits. It is then polished on polishing cloths under addition of polishing suspensions, followed by final polishing to, where necessary, remove remaining artifacts and deformation layers [4]. Once the final polishing step is accomplished, etchants can be used to contrast the individual microstructural constituents.

Schlagworte

Metallographie, metallographische Schliffpräparation, Deformationsschichten, Reinkupfer, weichgeglühtes Kupfer, Elektropolitur

1 Einleitung

Die Metallographie ermöglicht es, den inneren Aufbau von Metallen sichtbar darzustellen: Das Gefüge als die Gesamtheit aller Phasen, Defekte und deren Anteile [1] kann nach einer erfolgreichen metallographischen Präparation analysiert werden. Doch warum sind diese Informationen relevant? Neben der Qualitätssicherung spielt die Metallographie in der Schadensanalyse eine entscheidende Rolle [2]. Außerdem findet die Metallographie nicht nur im industriellen Umfeld, sondern auch in der Forschung breite Anwendung bei der Analyse und Entwicklung des Gefüges neuer Legierungen und der daraus resultierenden Eigenschaften. Die metallographische Probenpräparation dient zudem auch der Erstellung artefaktfreier Probenoberflächen als Vorbereitung weiterer Bearbeitungsschritte, wie beispielsweise der Laserstrukturierung metallischer Werkstoffe [3].

Unter Berücksichtigung aller möglichen Einflussfaktoren zur Entwicklung geeigneter Routinen fällt schnell auf, dass die Metallographie einer Detektivarbeit nicht unähnlich ist: Spannend, herausfordernd, abwechslungsreich und vor allem voller Überraschungen. Die klassische Vorgehensweise der Metallographie umfasst vier Schritte: Zunächst werden zu große Proben getrennt, zu kleine werden mittels Einfassung vergrößert. Anschließend wird die Probe auf Schleifpapier unter Wasserkühlung mit aufsteigender Körnung geschliffen, danach folgt die Politur auf Poliertüchern unter Zugabe von Poliersuspensionen, gefolgt von der Endpolitur, um gegebenenfalls letzte Artefakte und Verformungsschichten abzutragen [4]. Ist die endgültige Polierstufe erreicht, können Ätzmittel zur Kontrastierung der einzelnen Gefügebestandteile genutzt werden.

2 Material and Methods

Soft materials such as copper and aluminum present us with particular metallographic preparation challenges: the materials' high ductility complicates the removal process and can easily lead to deep deformations in the sample surface [4, 5]. This manuscript presents a preparation routine for the generation of artifact-free surfaces which allows to completely remove deformation layers in a final polishing process. Oxygen-free copper (CW008A, Haecker Metall, ≥ 99.95 % Cu, cold-rolled) of 1 mm thickness serves as model material. It is delivered in mill-finished condition. The samples were cut to coupons of the size 10×20 mm². Copper is widely used in the industry for its electrical and thermal conductivity and its good corrosion resistance derived from the formation of passivation layers in the atmosphere [6, 7]. However, it is also subject of scientific research relating to antibacterial and antiviral surfaces owing to the cytotoxic effect of copper on microorganisms [8–10]. The research on copper at the institute is currently focused on the modification of functional surface properties, for instance, in order to specifically influence the wetting behavior or the elimination of bacteria. The latter is currently also subject of experiments on the ISS as part of the two projects “BIOFILMS” and “Touching Surfaces” [11].

Owing to its wide variety of applications, copper has been thoroughly researched and various preparation routines have already been developed [1, 4, 12–15]. However, the copper sheet at our disposal is extremely soft and presents an extra challenge, since it is 1 mm thin. Thus, high material removal cannot be realized by grinding. Therefore, a new method was developed on a Struers polishing machine TegraPol-21. The method is particularly designed such that it can also be applied to additionally soft annealed samples.

2 Material und Methodik

Weiche Werkstoffe, wie Kupfer und Aluminium, stellen uns vor besondere Herausforderungen bei der metallographischen Präparation: Die hohe Duktilität der Materialien erschwert den Abtrag und führt leicht zu tiefen Deformationen in der Probenoberfläche [4, 5]. Das vorliegende Manuskript zeigt eine Präparationsroutine zur Erzeugung artefaktfreier Oberflächen, die durch eine abschließende Endpolitur vollständig von Deformationsschichten befreit werden können. Als Modellwerkstoff dient sauerstofffreies Kupfer (CW008A, Haecker Metall, $\geq 99,95$ % Cu, kaltgewalzt) der Dicke 1 mm, das mit einer walzblanken Oberfläche geliefert wird. Die Proben wurden in Coupons der Größe 10×20 mm² getrennt. Kupfer findet breite Verwendung in der Industrie auf Grund seiner hohen elektrischen und thermischen Leitfähigkeit sowie seiner guten Korrosionsbeständigkeit durch die Bildung von Passivierungsschichten an der Atmosphäre [6, 7]. Aber auch wissenschaftliche Fragestellungen rund um antibakterielle und antivirale Oberflächen [8–10] beschäftigen sich mit der cytotoxischen Wirkung von Kupfer auf Mikroorganismen. Die Kupferforschung am Institut fokussiert sich aktuell auf die Modifikation der funktionalen Oberflächeneigenschaften, um z. B. die Benetzung oder Bakterientötung gezielt zu beeinflussen. Zu letzterem werden aktuell in den beiden Projekten „BIOFILMS“ und „Touching Surfaces“ auch Experimente auf der ISS durchgeführt [11].

Aufgrund seiner vielfältigen Anwendungsbereiche ist Kupfer ein gründlich erforschter Werkstoff, für den bereits verschiedene Präparationsroutinen entwickelt wurden [1, 4, 12–15]. Da das vorliegende Kupferblech aber ausgesprochen weich ist und durch die Dünne von 1 mm eine zusätzliche Herausforderung bietet, da kein starker Abtrag beim Schleifen realisierbar ist, wurde an einem Polierautomat Tegra-Pol-21 der Firma Struers eine neue Methode entwickelt. Insbesondere ist diese Methode so ausgelegt, dass sie auch auf zusätzlich weichgeglühte Proben übertragen werden kann.

Furthermore, a Buehler vibratory polisher (VibroMet 2) was used. Quality control and roughness measurements were carried out on an Olympus LEXT OLS4100 laser scanning microscope. Vickers hardness measurements were conducted fully automatically on a Struers Dura Scan. For the SEM analysis of the surfaces and the deformation layers, a FEI Helios Nanolab600 scanning electron microscope (SEM) equipped with a focused ion beam (FIB) was used. In order to generate the FIB cross-section, multi-layer protective platinum coatings were deposited to avoid ion-induced damage of the substrate surface.

Potential surface contaminations were detected using X-ray photoelectron spectroscopy (XPS) on a high-resolution spectrometer Axis Nova (Kratos Analytical Ltd., UK). The system is equipped with a mono-chromatic Al K α source (1468.6 eV). The measurements were carried out with an orientation of the detector's line of sight along the normal of the sample surface. Overview spectra and detail spectra for the identification of the states of chemical bonding were recorded with a pass energy of 160 eV and 20 eV, respectively. Owing to the good sample conductivity, a compensation of potentially occurring surface charging due to the supply of low-energy electrons could be dispensed with. Minor charge-induced shifts, nonetheless occurring, were corrected by shifting the dominant photoelectron line of the carbon (C1s) to a reference binding energy of 285 eV typical for aliphatic hydrocarbon adsorbates. From the overview spectra, the concentrations for all elements detected on the sample surface were calculated (in atomic percent) applying the equipment manufacturer's (Kratos Analytical Ltd.) standard sensitivity factors. The concentration data refers to an information volume which is limited by the lateral analysis area of $400 \times 700 \mu\text{m}^2$ on the sample surface and a typical depth of information of XPS of approx. 5–10 nm.

Außerdem kam eine Vibrationspoliermaschine von Buehler (VibroMet 2) zum Einsatz. Die Qualitätskontrolle sowie Rauigkeitsmessungen wurden an einem Olympus LEXT OLS4100 Laserscanning-Mikroskop durchgeführt. Vickers-Härtemessungen erfolgten vollautomatisch an einem Struers Dura Scan. Zur REM-Analyse der Oberflächen und der Deformationsschichten wurde ein Rasterelektronenmikroskop (REM) mit fokussiertem Ionenstrahl (focused ion beam, FIB) (FEI Helios Nanolab600) verwendet, wobei zur Erstellung des FIB-Querschnitts mehrlagige Platinschutzschichten abgeschieden wurden, um ionen-induzierte Schädigungen der Substratoberfläche zu vermeiden.

Mögliche Oberflächenkontaminationen wurden durch Photoelektronenspektroskopie (XPS) an einem hochauflösenden Spektrometer Axis Nova der Firma Kratos Analytical Ltd. (UK) detektiert. Das System ist ausgestattet mit einer monochromatischen Al K α Quelle (1468,6 eV). Die Messungen erfolgten mit Ausrichtung der Detektorblickachse längs der Oberflächennormale der Probenoberfläche. Übersichtsspektren wurden mit einer Durchlassenergie von 160 eV aufgenommen, Detailspektren zur Identifikation chemischer Bindungszustände mit einer Durchlassenergie von 20 eV. Auf eine Kompensation potentiell auftretender Oberflächenaufladungen durch das Angebot nieder-energetischer Elektronen konnte aufgrund der guten Probenleitfähigkeit verzichtet werden. Trotzdem noch auftretende geringfügige aufladungsbedingte Verschiebungen wurden durch Verschiebung der dominierenden Photoelektronenlinie des Kohlenstoffs (C1s) auf eine Referenzbindungsenergie von 285 eV, typisch für aliphatische Kohlenwasserstoff-Adsorbate, korrigiert. Aus den Übersichtsspektren wurden unter Verwendung von Standard-Empfindlichkeitsfaktoren des Geräteherstellers (Kratos Analytical Ltd.) für alle auf der Probenoberfläche detektierten Elemente Konzentrationen (in Atom-Prozent) berechnet. Diese Konzentrationsangaben beziehen sich auf ein Informationsvolumen, begrenzt durch die laterale Analysefläche von $400 \times 700 \mu\text{m}^2$ auf der Probenoberfläche, und die typische XPS-Informationstiefe von ca. 5–10 nm.

It is dependent of the photoelectrons' kinetic energy which varies as a function of the element species but also of the material the photoelectrons have to cross from their site of generation to the immediate sample surface [16].

The identification of the chemical state of the copper by means of photoelectron spectroscopy is particularly challenging, as signal superpositions occur in the region of the Cu 2p doublet. Only a detailed inspection of an energy region around the Cu LMM Auger line of the copper at 918 eV measured at the same low pass energy setting (20 eV) allows for identifying the prevailing copper oxidation state [17].

21 Mechanical Preparation of Copper

The Vickers hardness of the cold-rolled copper samples is 74 ± 2 HV (test load 0.5 N) and thus already lower than the values of 91 HV [18] and 130 HV [19] for cold-rolled copper stated in the literature. Tab. 1 summarizes the developed preparation routine for this copper sheet which will be discussed extensively in the following.

In classical metallographic approaches, it is stipulated that the samples are surface ground on silicon carbide paper of different grits [20]. Working with particularly soft materials, this step goes hand in hand with the risk of SiC grains being embedded into the sample. In light microscope images, stuck SiC grains can be recognized as clearly defined dark inclusions. The EDS analysis in the SEM confirmed that they are SiC particles originating from the grinding paper (Fig. 1 a). The grains can subsequently be removed from the sample surface by applying considerably extended polishing times. However, they leave deep imprints (Fig. 1 b) and contaminate the polishing cloths resulting in a considerable formation of scratches on the surface.

Sie hängt ab von der, je nach Elementspezies unterschiedlichen kinetischen Energie der Photoelektronen aber auch von dem Material, welches die Photoelektronen zwischen ihrem Erzeugungsort und der unmittelbaren Probenoberfläche durchqueren müssen [16].

Eine besondere Herausforderung stellt die chemische Zustandsidentifikation des Kupfers mittels Photoelektronenspektroskopie dar, da es zu Signalüberlagerungen im Bereich des Cu 2p Doublets kommt. Erst eine detaillierte Inspektion eines mit gleich niedriger Durchlassenergie (20 eV) gemessenen Energiebereiches um die Cu LMM Auger Linie des Kupfers bei 918 eV erlaubt eine Identifikation des vorherrschenden Kupferoxidationszustandes [17].

21 Mechanische Präparation von Kupfer

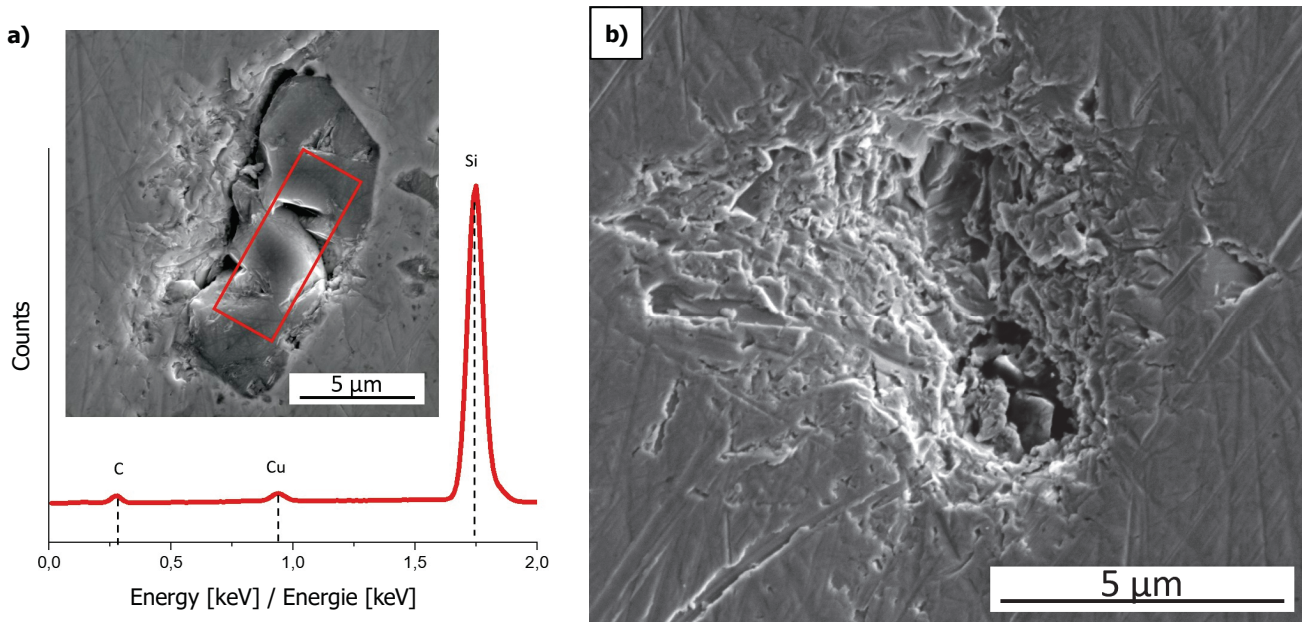
Die Vickershärte der kaltgewalzten Kupferproben beträgt 74 ± 2 HV (Prüflast 0,5 N), was bereits unter denen in der Literatur hinterlegten Werten von 91 HV [18] und 130 HV [19] für kaltgewalztes Kupfer liegt. Tab. 1 fasst die entwickelte Präparationsroutine für dieses Kupferblech zusammen, die im Folgenden ausführlich diskutiert werden soll.

Die klassische Metallographie sieht es vor, die Proben zu Beginn auf Silizium-Carbid-Papier unterschiedlicher Körnung plan zu schleifen [20]. Für besonders weiche Werkstoffe birgt dieser Schritt die Gefahr, dass sich SiC-Körner tief in die Probe drücken. Feststeckende SiC-Körner sind als klar umrissene dunkle Einschlüsse in lichtmikroskopischen Aufnahmen sichtbar. Die EDX-Analyse am REM bestätigte, dass es sich um die SiC-Partikel des Schleifpapiers handelt (Bild 1 a). Deutlich verlängerte Polierzeiten können die Körner zwar nachträglich noch aus der Probenoberfläche entfernen, allerdings hinterlassen diese dort tiefe Eindrücke (Bild 1 b) und kontaminieren die Poliertücher, was zu einer erheblichen Kratzerbildung auf der Oberfläche führt.

Step / Schritt	Suspension, diamond size / Suspension, Diamantgröße [μm]	Struers disk brand name / Scheibe Markenname Struers	Force / Kraft [N]	Time / Zeit [min]	Speed / Geschwindigkeit		Direction of rotation / Drehsinn
					Disk / Scheibe [rpm]	Holder / Halter [rpm]	
1	15	Largo	20	until flat / bis plan	150	120	contra
2	15	Largo	10	5	150	120	contra
3	6	Dac	15	4	150	150	contra
4	6	Dac	10	4	150	150	contra
5	3	Mol	10	10	150	90	contra
6	1	Nap	10	10	150	60	contra

Tab. 1: Multistage preparation routine for soft copper materials. Water-based diamond suspensions were used. If the preparation is an automated process, the force is to be applied per sample/sample holder. In the presented case, every sample holder can accommodate two samples, respectively. The wheel diameter is 25 cm.

Tab. 1: Mehrstufige Präparationsroutine für weiche Kupferwerkstoffe. Verwendet wurden Diamantsuspensionen auf Wasserbasis, die Kraft ist im Falle einer automatischen Präparation pro Probe bzw. pro Probenhalter anzuwenden. Im vorgestellten Fall konnte jeder Probenhalter zwei Proben aufnehmen. Der Scheibendurchmesser beträgt 25 cm.



Figs. 1 a and b: a) EDS spectrum (15 kV, 11 nA) of the marked particle trapped in the copper surface after grinding on SiC paper and subsequent polishing. b) SEM image of an abrasive SiC particle already broken free.

Bilder 1 a und b: a) EDX-Spektrum (15 kV, 11 nA) des markierten feststeckenden Partikels in der Kupferoberfläche nach dem Schleifen auf SiC-Papier und anschließender Politur. b) REM-Aufnahme eines bereits ausgebrochenen SiC-Abrasivpartikels.

Fine grinding with a 15 μm diamond suspension was opted for instead of the classical grinding process: The first step with increased force is necessary to generate a plane sample surface. Suspensions provide a lower removal rate than grinding paper, thus ensuring gentle processing of the materials, but simultaneously increasing the polishing time. This first preparation step is decisive for the success of all following stages as uneven sample surfaces cannot be compensated for in subsequent polishing steps. Fig. 2 a) shows the various stages of surface polishing the sample. Compared to the classical grinding process, the constant flow of abrasive particles in the diamond suspension provides a significantly reduced impression of particles. The same step is repeated applying less contact force to compensate for the severe deformation from the increased force, and, if necessary, to remove impressed diamond particles.

The subsequent 6 μm polishing step is, again, carried out applying two levels of force: The application of an increased force of 15 N per sample holder is intended to release remaining impressed diamonds from the previous step. After this step, it is thus appropriate to thoroughly clean the polishing cloth. Subsequently, 6 μm polishing is carried out with the lower force of 10 N resulting in a uniform surface, as is apparent from Fig. 2 b).

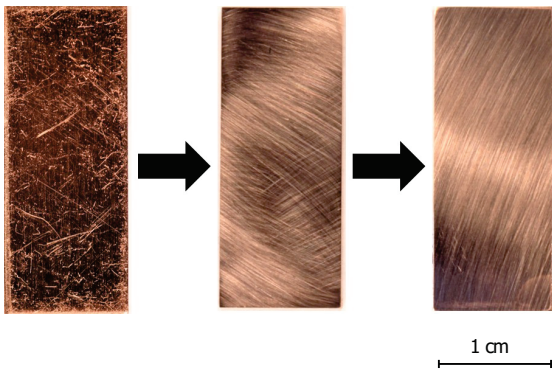
The two final polishing steps are each performed with a force of 10 N per sample holder, respectively, to prevent the diamond particles from being impressed. The times specified in Tab. 1 are merely indicative. Step 5, in particular, should be performed until an even polishing result is achieved on the whole sample surface. The holder speed in the last step was reduced to 60 rpm, as suggested by Vander Voort et al. [13]. Thus, an impression of the 1 μm diamonds could largely be prevented and, as is apparent from Fig. 2, a homogeneous surface finish could be achieved which resulted in mirror-like smooth surfaces.

Statt des klassischen Schleifens wurde ein Feinschleifprozess mit 15 μm -Diamantsuspension gewählt: Der erste Schritt mit erhöhter Kraft ist notwendig, um eine plane Probenoberfläche zu generieren. Der Abtrag mit Suspension ist geringer als auf Schleifpapier, was eine schonendere Bearbeitung des Materials zur Folge hat, aber gleichzeitig die Polierzeit erhöht. Dieser erste Präparationsschritt ist ausschlaggebend für den Erfolg aller weiteren Schritte, da die folgenden Polierschritte unebene Probenflächen nicht mehr ausgleichen können. Bild 2 a) zeigt die verschiedenen Stadien des Planpolierens der Probe. Durch die ständige Umspülung mit den Abrasivpartikeln in der Diamantsuspension wird das Eindringen im Vergleich zum klassischen Schleifprozess deutlich vermindert. Um die starke Deformation durch die erhöhte Kraft auszugleichen und um gegebenenfalls eingedrückte Diamantpartikel zu entfernen, wird derselbe Schritt mit geringerer Anpresskraft wiederholt.

Die folgende 6 μm -Politur ist ebenfalls in zwei Kraftstufen unterteilt: Die erhöhte Kraft von 15 N pro Probenhalter dient dazu, übrig gebliebene eingedrückte Diamanten vom vorherigen Schritt zu lösen. Daher ist es sinnvoll, die Polierscheibe nach diesem Schritt gründlich zu reinigen. Anschließend erfolgt die 6 μm -Politur mit der geringeren Anpresskraft von 10 N, was, wie aus Bild 2 b) hervorgeht, zu einer gleichmäßigen Oberfläche führt.

Die beiden letzten Polierschritte werden jeweils mit der Anpresskraft von 10 N pro Probenhalter ausgeführt, um ein Eindringen der Diamantpartikel zu verhindern. Die Zeitangaben in Tab. 1 dienen dabei lediglich als Orientierung, besonders Schritt Nummer 5 sollte ausgeführt werden, bis ein über die gesamte Probe ebenes Polierbild entsteht. Die Haltergeschwindigkeit in dem letzten Schritt wurde wie von Vander Voort et al. [13] vorgeschlagen, auf 60 rpm reduziert. Dadurch konnte ein Eindringen der 1 μm -Diamanten weitestgehend verhindert werden und wie aus Bild 2 hervorgeht, ein homogenes Oberflächenfinish erreicht werden, das zu spiegelglatten Oberflächen führt.

a)



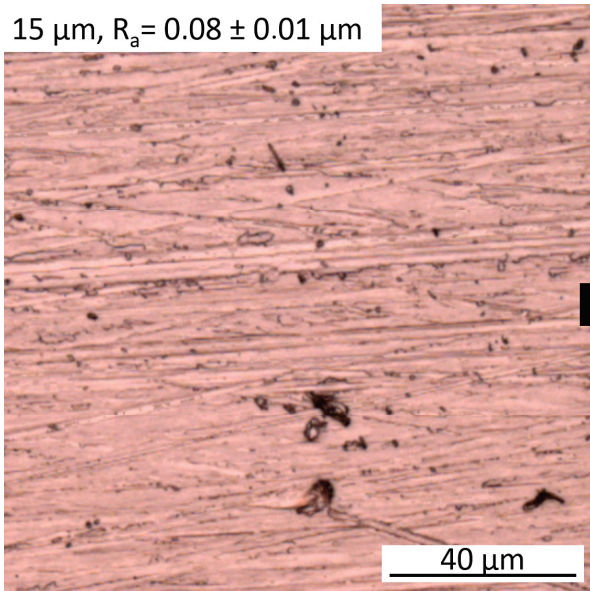
Figs. 2 a and b: a) Macroscopic image of the untreated sample surface (left), the non-flat ground surface (middle), and the flat-ground surface (right). b) Light microscope image of the surfaces after the respective polishing steps indicating average roughness values.

Bilder 2 a und b: a) Makroskopische Aufnahmen der unbehandelten Probenoberfläche (links), der nicht plan geschliffenen Oberfläche (Mitte) und der plan geschliffenen Oberfläche (rechts).

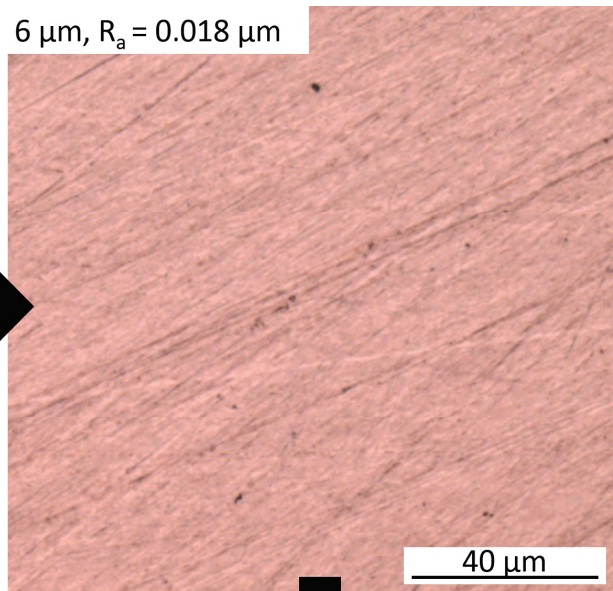
b) Lichtmikroskopische Aufnahmen der Oberflächen nach den jeweiligen Politurschritten mit Messwerten des Mittenrauheits.

b)

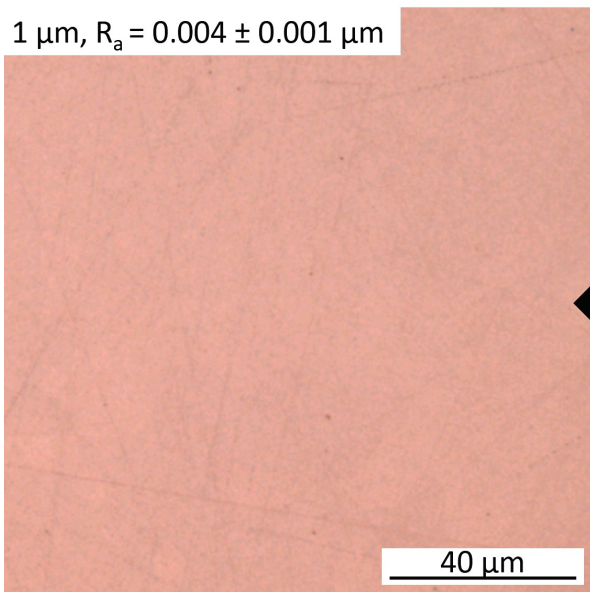
15 μm , $R_a = 0.08 \pm 0.01 \mu\text{m}$



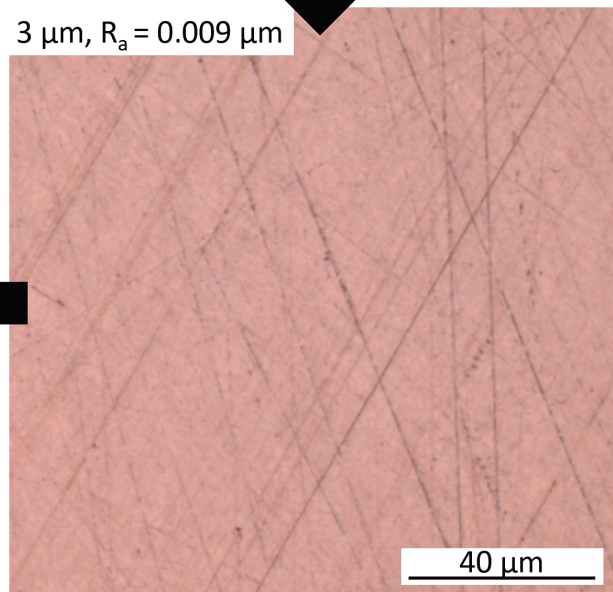
6 μm , $R_a = 0.018 \mu\text{m}$



1 μm , $R_a = 0.004 \pm 0.001 \mu\text{m}$



3 μm , $R_a = 0.009 \mu\text{m}$



If this last polishing step is carried out for too long or if the polishing disk is already worn and thus harder than initially, individual microstructural grains may topographically project, thus possibly resulting in the impression of 1 μm particles. Therefore, it is important to control this step's polishing time several times. If such artifacts occur, the preparation steps given in Tab. 1 should be repeated from step 5 on.

22 Microstructural Contrasting

The described preparation approach can serve as a basis for microstructural contrasting using etching solutions. Fig. 3 shows the polished copper sheet after five-minute etching in a solution of 100 ml distilled water and 10 g ammonium persulfate at room temperature [4].

Despite the cold rolling process, the grains in the rolling plane exhibit an equiaxed shape distribution. The intensity of the etching attack on the grain surface areas varies as a function of their crystallographic orientation. The resulting microtopography is particularly clearly revealed in the differential interference contrast.

Wird dieser letzte Politurschritt zu lange ausgeführt oder ist die Polierscheibe bereits abgenutzt und dadurch härter als ursprünglich, kann es dazu kommen, dass einzelne Körner des Gefüges topographisch hervortreten, wodurch sich gegebenenfalls 1 μm -Partikel eindrücken. Daher ist es wichtig, die Polierzeit in diesem Schritt mehrmals zu kontrollieren. Treten solche Artefakte auf, sollte die Präparation ab Schritt 5 in Tab. 1 wiederholt werden.

22 Gefügekontrastierung

Die beschriebene Vorgehensweise zur Präparation kann als Grundlage für die Gefügekontrastierung mittels Ätzlösungen dienen. Bild 3 zeigt das polierte Kupferblech nach der fünfminütigen Ätzung in einer Lösung aus 100 ml destilliertem Wasser und 10 g Ammoniumpersulfat bei Raumtemperatur [4].

Trotz Kaltwalzen zeigen die Körner in der Walzebene eine äquiaxiale Formverteilung. Die Ätzung greift die Kornflächen in Abhängigkeit von ihrer kristallographischen Orientierung verschieden stark an. Die entstehende Mikrotopographie wird im Differential-Interferenzkontrast besonders deutlich.

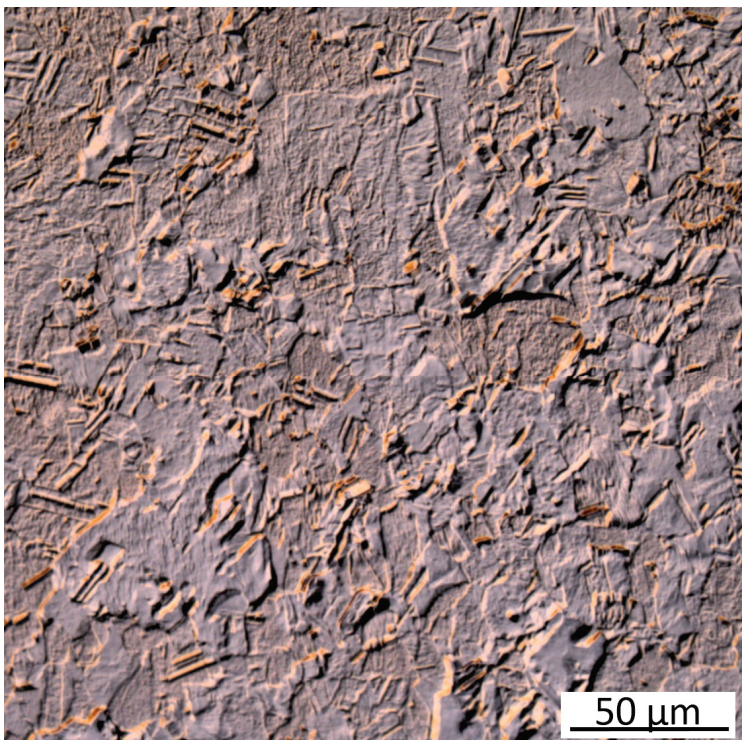


Fig. 3: Light microscope image in the differential interference contrast mode of the etched copper microstructures.

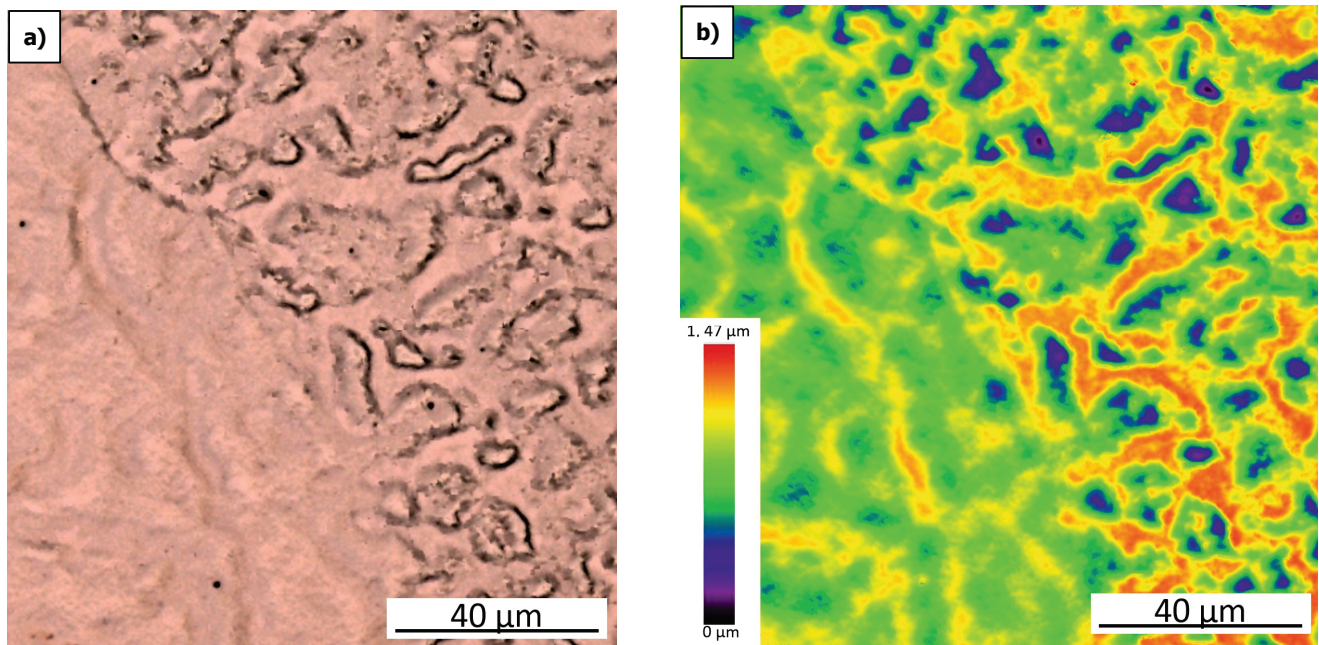
Bild 3: Lichtmikroskopische Aufnahme mit Differential-Interferenzkontrast des geätzten Kupfergefüges.

23 Preparation of Soft Annealed Samples

In the event that the microstructure revealed by, for instance, etching, is too fine-grained for a desired application, heat treatments may be specifically deployed to modify the microstructure. In order to verify whether the presented preparation routine can be applied to even softer materials, the samples were soft-annealed at 900 °C for 12 hours (1 °C heating and cooling rate) in a vacuum furnace, such that the Vickers hardness could be reduced to 40 HV (test load 0.5 N). Preparation experiments have shown that it is recommendable to already perform the steps 1 to 4 in Tab. 1 prior to the heat treatment to avoid deep surface deformations of the sample. The sustained high temperature treatment of copper leads to the evaporation of the material from the surface. A thermal etching process can furthermore modify the topography of the grains as a function of their orientation [21]. Fig. 4 shows the sample surface right after the high temperature heat treatment.

23 Präparation weichgeglühter Proben

Ist das durch z. B. eine Ätzung sichtbar gemachte Gefüge zu feinkörnig für die gewünschte Anwendung, können Wärmebehandlungen gezielt eingesetzt werden, um die Mikrostruktur zu variieren. Um die Übertragbarkeit der vorgestellten Präparationsroutine auf noch weichere Werkstoffe zu überprüfen, wurden die Proben bei 900 °C für 12 Stunden (1 °C Heiz- und Kühlrate) im Vakuumofen weichgeglüht, wodurch die Vickershärte auf 40 HV (Prüflast 0,5 N) reduziert werden konnte. Versuche zur Präparation haben gezeigt, dass es sich empfiehlt, Schritt 1–4 in Tab. 1 bereits vor der Wärmebehandlung durchzuführen, um tiefen Deformationen an der Probenoberfläche vorzubeugen. Bei der anhaltenden Hochtemperaturbehandlung von Kupfer kommt es zur Abdampfung des Materials von der Oberfläche. Außerdem kann die Topographie der Körner durch thermisches Ätzen orientierungsabhängig modifiziert werden [21]. Bild 4 zeigt die Probenoberfläche unmittelbar nach der Hochtemperaturwärmebehandlung.



Figs. 4a and b: a) Light microscope images of the copper surface after annealing in vacuum at 900 °C for 12 hours. b) Height profile of the section shown in a).

Bilder 4a und b: a) Lichtmikroskopische Aufnahme der Kupferoberfläche nach einer Glühung im Vakuum bei 900 °C für 12 Stunden. b) Höhenprofil der in a) gezeigten Probenstelle.

Before moving on to 1 μm polishing, the 3 μm suspension polishing step should be performed until the thermally modified layer is completely removed.

24 Removal of Deformation Layers

As a consequence of the abrasive removal, mechanical preparation routines give rise to deformation layers near the sample surface, regardless of heat treatments eventually performed, as is apparent from the FIB cross-section in Fig. 5 a) for a non-heat treated copper sample. Their thickness is several hundred nm and they obscure the basic structure of the sample, as is particularly evident in Fig. 5 b). The original grains can be suspected by bright/dark contrasts. However, they are superimposed by a fine crystalline layer.

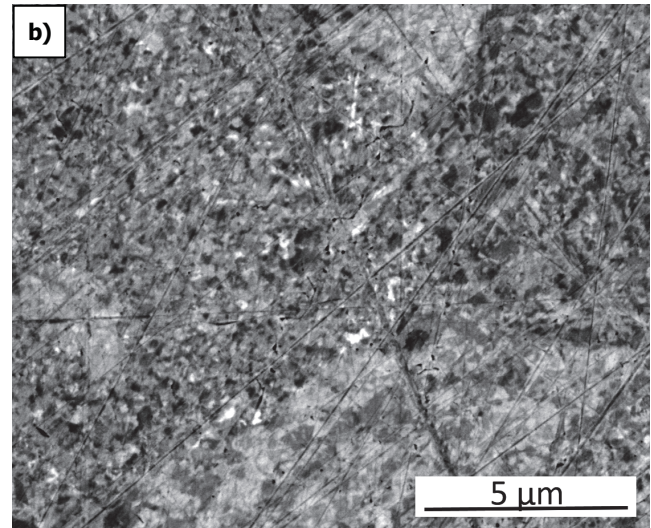
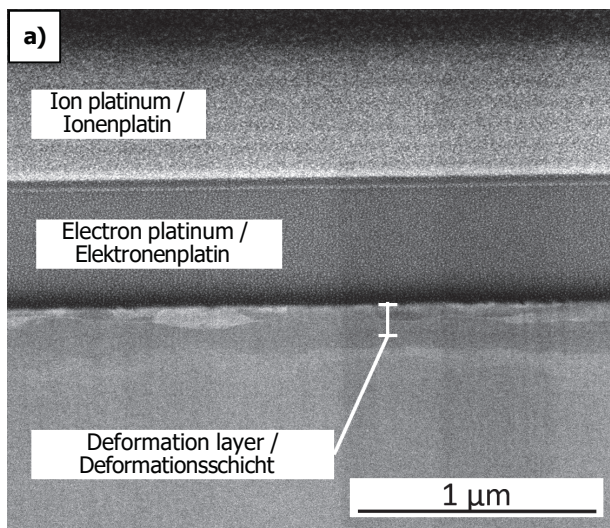
EBSD examinations, for instance, require the microstructure to be revealed. In this case, polishing using colloidal silicon dioxide has proven to be insufficient. Vibratory polishing is a well-known method for removing the deformation layers [22]. Fig. 6 a) shows that vibratory polishing resulted in suspension particles being heavily impressed, even at low

Die Politur auf der 3 μm -Suspension sollte durchgeführt werden, bis die thermisch modifizierte Schicht vollständig abgetragen ist, bevor der Übergang zur 1 μm -Politur erfolgt.

24 Entfernung von Deformationsschichten

Unabhängig von gegebenenfalls durchgeführten Wärmebehandlungen, führen mechanische Präparationsroutinen durch den abrasiven Abtrag zu Deformationsschichten nahe der Probenoberfläche, wie sie im FIB-Querschnitt in Bild 5 a) für eine nicht wärmebehandelte Kupferprobe sichtbar sind. Ihre Dicke beläuft sich auf mehrere hundert nm und sie verdecken das Grundgefüge der Probe, was in Bild 5 b) besonders deutlich wird. Die ursprünglichen Körner sind durch hell-dunkel-Kontraste zu erahnen, sind aber überlagert von einer feinkristallinen Schicht.

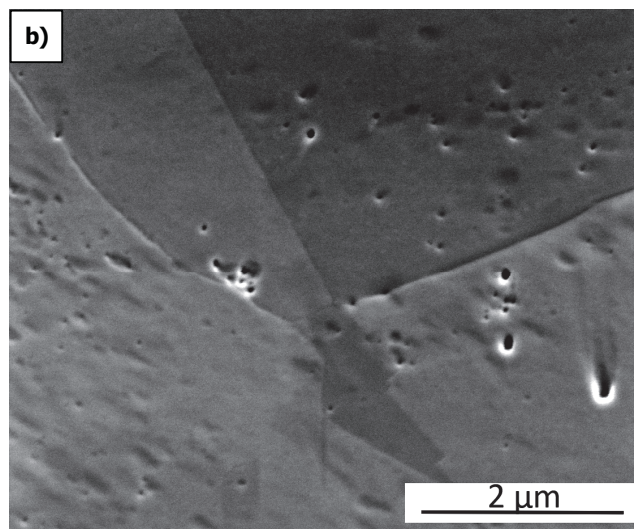
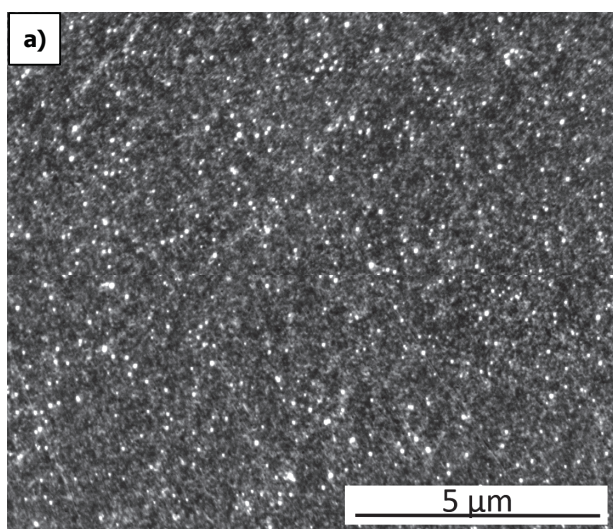
EBSD-Untersuchungen benötigen beispielsweise ein freigelegtes Gefüge, wobei sich eine oxidische Politur mit kolloidalem Siliziumoxid in diesem Fall als nicht ausreichend erwiesen hat. Ein bekanntes Verfahren zur Beseitigung der Deformationsschichten stellt die Vibrationspolitur dar [22]. Wie aus Bild 6 a) hervorgeht, hinterließ die Vibrationspolitur auch bei geringen



Figs. 5 a and b: a) FIB cross section of a copper sample after the preparation routine given in Tab. 1. A deformation layer can be recognized on the sample surface underneath the protecting platinum layers.

b) Backscattered electron image of the surface of the polished sample.

Bilder 5 a und b: a) FIB-Querschnitt einer Kupferprobe nach der Präparationsroutine aus Tab. 1. Unterhalb der schützenden Platinschichten ist eine Deformationsschicht an der Probenoberfläche zu erkennen. b) Rückstreuungsaufnahme der Oberfläche der polierten Probe.



Figs. 6a and b: a) SEM image of artifacts after vibratory polishing. b) Tilted SEM image of artifacts after electropolishing.

Bilder 6a und b: a) REM-Aufnahme von Artefakten nach der Vibrationspolitur. b) Gekippte REM-Aufnahme von Artefakten nach der Elektropolitur.

amplitudes and low sample loading. Electropolishing copper in concentrated phosphoric acid by anodically dissolution, a technique already established for more than 60 years, offers an alternative to vibratory polishing [23–25]. As can be seen in Fig. 6 b), smaller artifacts are also induced by the electropolishing process. However, they do not represent a chemical contamination. In fact, they are microscopic pitting holes which could not be avoided, not even by widely varying the parameters of voltage and time. They may possibly be attributed to the defect-rich cold-rolled sheet surface.

However, as they represent only small topographic artifacts without any impact on the surface chemistry and microstructure, electrolytic polishing proves to be suitable to remove the deformation layers from the sample. In order to examine a potential chemical contamination of the samples by the chemical polishing process, a sample mechanically polished according to the steps in Tab. 1 and two samples electropolished in ortho-phosphoric acid (85%, Grüssing) were XPS measured. After the mechanical preparation, the samples were cleaned with fully demineralized water, diluted

Amplituden und Beschwerden der Proben stark eingedrückte Suspensionspartikel. Eine Alternative zur Vibrationspolitur bietet die elektrolytische Politur, bei der das Werkstück anodisch in Lösung geht, welche sich für Kupfer in konzentrierter Phosphorsäure schon vor über 60 Jahren etabliert hat [23–25]. Wie aus Bild 6 b) hervorgeht, verursacht auch die Elektropolitur kleinere Artefakte, die allerdings keine chemische Kontamination darstellen. Es handelt sich vielmehr um mikroskopische Pittinglöcher, die auch durch eine breite Variation der Parameter Spannung und Zeit nicht verhindert werden konnten. Sie sind eventuell auf die defektreiche Oberfläche des kaltgewalzten Bleches zurückzuführen.

Da es sich aber lediglich um kleine topographische Artefakte ohne Auswirkung auf Oberflächenchemie und -gefüge handelt, zeigt sich die elektrolytische Politur als geeignet, um die Deformationsschichten von der Probe zu entfernen. Um eine mögliche chemische Verunreinigung der Proben durch die chemische Politur zu untersuchen, wurde eine nach Tab. 1 mechanisch polierte Probe mit zwei in ortho-Phosphorsäure (85%, Grüssing) elektropolierten Proben einer XPS-Messung unterzogen. Die Reinigung nach der mechanischen Präparation erfolgte mit vollentsalztem Wasser, verdünntem Spülmittel

detergent, and ethanol. The electropolished samples were cleaned with water and ethanol. As Fig. 7 shows, the copper samples are especially characterized by a contamination with oxygen from native oxidation and with carbon adsorbed on the surface due to the atmospheric sample storage [26]. According to high resolution detail spectra, the detected carbon (C1s) is predominantly aliphatically bound hydrocarbon with a small proportion of hydroxy, ether, and carboxyl groups. These organic adsorbate films are typical for samples stored under atmospheric conditions but also for merely transported ones.

Taking into account the peak shape and the position of the copper LMM Auger electron line in the energy range of 916 eV to 920 eV, it can be assumed that, apart from metallic copper from the bulk material, oxidic copper is present in the form of Cu_2O as well as proportions of CuO , corresponding to the regular native oxidation of copper in atmospheric oxygen [26].

In the context of electropolishing in phosphoric acid, it was of particular interest to know whether this procedure leads to phosphor contaminations on the sample surface. As is apparent from Fig. 7, only one of the two electropolished samples exhibits a slightly increased phosphor concentration. The phosphoric acid can thus be removed without any significant residues by thoroughly cleaning. The other minor contaminations (nitrogen, chlorine, sulfur, calcium) may occur due to handling, storage, and transportation. With regard to the chemical analysis of the electropolished samples, it must furthermore be noted that electropolishing was performed in a provisional setup in which the samples were taped together on their backsides using adhesive tape, representing an additional source of contamination when the samples are released and cleaned.

und Ethanol. Die elektropolierten Proben wurden mit Wasser und Ethanol gereinigt. Wie aus Bild 7 hervorgeht, weisen die Kupferproben vor allem eine Kontamination mit Sauerstoff durch native Oxidation und mit Kohlenstoff auf, der durch die atmosphärische Lagerung der Proben auf der Oberfläche adsorbiert wird [26]. Hochauflösende Detailspektren des Kohlenstoffs (C1s) identifizieren die chemische Bindungssituation des detektierten Kohlenstoffs als überwiegend aliphatisch gebundenen Kohlenwasserstoff mit einem geringen Anteil von Hydroxy-, Ether und Carboxylgruppen. Diese organischen Adsorbatfilme sind typisch für unter atmosphärischen Bedingungen gelagerte aber auch nur transportierte Proben.

Unter Berücksichtigung von Peakform und Lage der Kupfer LMM Auger-Elektronenlinie im Energiebereich von 916 eV bis 920 eV kann davon ausgegangen werden, dass neben metallischem Kupfer des Bulkmaterials oxidisches Kupfer in Form von Cu_2O aber auch Anteilen von CuO vorliegt, was der regulären nativen Oxidation von Kupfer an Luftsauerstoff entspricht [26].

Durch die Elektropolitur in Phosphorsäure war von besonderem Interesse, ob es bei diesem Verfahren zu Phosphorkontaminationen auf der Probenoberfläche kommt. Wie allerdings aus Bild 7 hervorgeht, zeigt lediglich eine der beiden elektropolierten Proben eine leicht erhöhte Phosphorkonzentration. Die Phosphorsäure lässt sich demnach ohne signifikante Rückstände durch gründliche Reinigung entfernen. Die anderen geringfügigen Kontaminationen (Stickstoff, Chlor, Schwefel, Calcium) können durch die Handhabung, die Lagerung und den Transport der Proben auftreten. Für die chemische Analyse der elektropolierten Proben muss zudem beachtet werden, dass die Elektropolitur in einem vorläufigen Aufbau durchgeführt wurde, der die Proben mit Klebeband auf der Rückseite miteinander verbunden hat, was beim Ablösen und Reinigen der Proben eine zusätzliche Kontaminationsquelle darstellt.

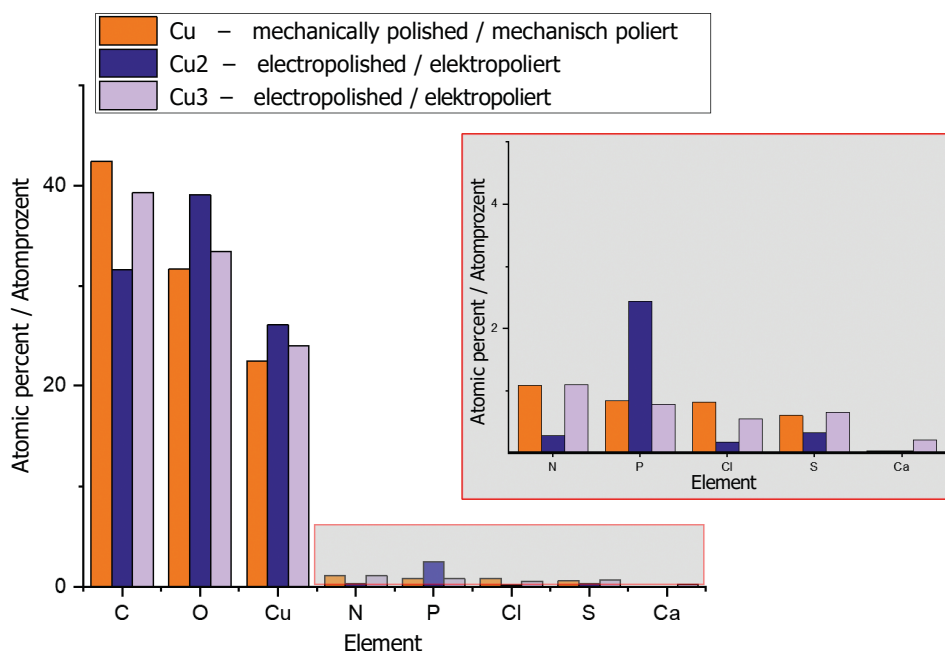


Fig. 7: XPS analysis results of a sample mechanically polished according to Tab. 1 and two electropolished samples.

Bild 7: XPS-Analyseergebnisse einer mechanisch polierten Probe nach Tab. 1 und zweier elektropolierter Proben.

To avoid these contaminations, different setups were developed for electropolishing. They will be discussed in more detail in the following section.

25 Setup for Electropolishing

The conventional setup for electropolishing stipulates that the sample to be polished is suspended in the concentrated phosphoric acid parallel to a counter electrode [27], whereby copper can also be used for the counter electrode [28]. It has the disadvantage that only one sample can be polished and that the respective sample is directly contacted, a process which may already result in severe deformations, especially working with very soft samples, and which complicates polishing the whole sample surface. To solve this issue, several samples can be taped together using copper adhesive tape such that only the uppermost protrudes from the acid and is contacted. However, as was mentioned before, samples may be contaminated with adhesive residues. Thus, this work aimed at developing a setup for electropolishing copper that allows polishing the entire surface of several samples without mechanical stresses from a direct contact and without introducing foreign material.

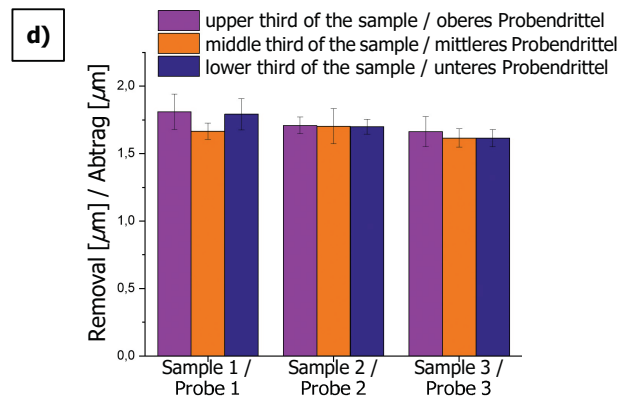
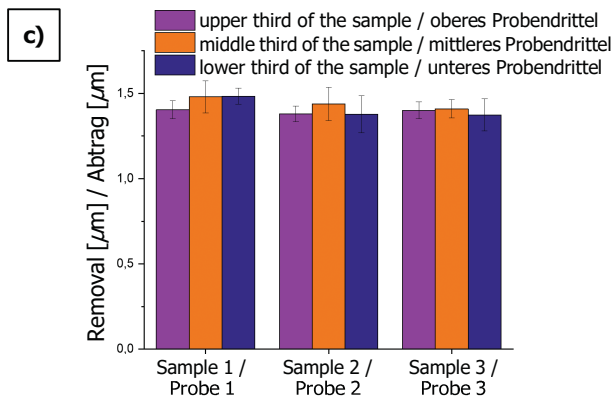
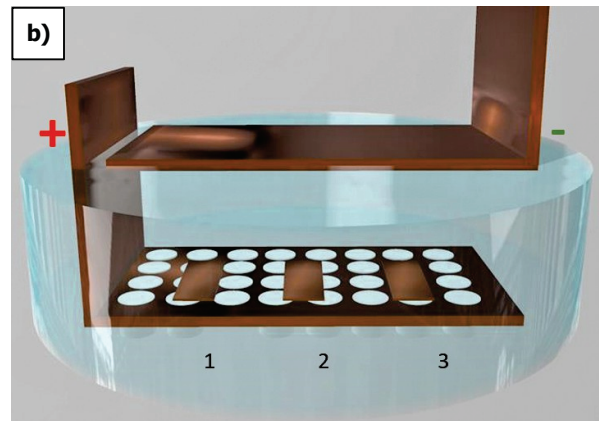
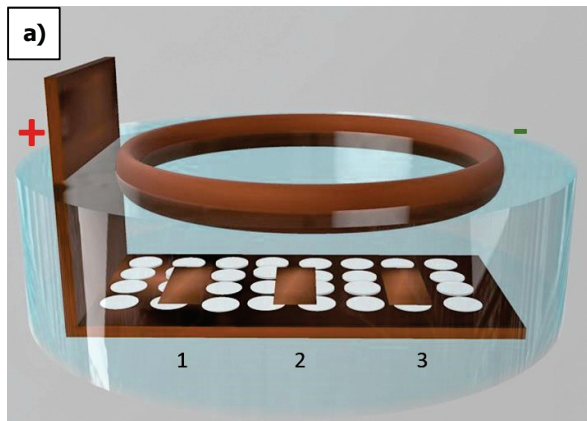
Um diese zu vermeiden, wurden unterschiedliche Aufbauten für die Elektropolitur erarbeitet, die im nächsten Abschnitt näher erläutert werden.

25 Aufbau der Elektropolitur

Der konventionelle Aufbau der Elektropolitur sieht es vor, die zu polierende Probe parallel zu einer Gegenelektrode in die konzentrierte Phosphorsäure zu hängen [27], wobei als Gegenelektrode auch Kupfer genutzt werden kann [28]. Nachteilig ist dabei, dass lediglich eine Probe poliert werden kann, die direkt kontaktiert wird, was gerade im Fall von sehr weichen Proben bereits zu starken mechanischen Deformationen führen kann und die Politur der gesamten Probenoberfläche erschwert. Um diese Problematik zu lösen, können mehrere Proben durch Kupferklebeband miteinander verbunden werden, so dass nur die oberste aus der Säure herausragt und kontaktiert wird. Da es aber wie bereits erwähnt zur Kontamination der Proben mit Kleberesten kommen kann, war es Ziel der Arbeit, einen Aufbau für die Elektropolitur von Kupfer zu entwickeln, der eine ganzflächige Politur mehrerer Proben ohne mechanische Beanspruchung durch direkte Kontaktierung und ohne Einbringung von Fremdmaterial erlaubt.

Figs. 8 a) and b) illustrate two alternative setups. In both setups, a copper sheet provided with drilled holes is used. For the sake of clarity, neither wires nor connections are shown in this figure. The holes offer the advantage of allowing spent copper ion-saturated phosphoric acid, characterized by a blue stain, to sink down such that a concentration gradient is still maintained. Two different geometric designs of the counter electrode were examined more closely: A ring-shaped counter electrode not covering the samples, aiming at preventing a contamination by particles sprinkling down from the counter electrode. And, on the other hand, a plate electrode arranged parallel to the workpiece.

In Bild 8 a) und b) sind zwei Aufbauten einander gegenübergestellt, die beide ein mit Lochbohrungen versehenes Kupferblech als Probenablage nutzen - Kabel und Anschlüsse sind in der Abbildung zur besseren Übersichtlichkeit nicht dargestellt. Die Bohrungen bieten den Vorteil, dass verbrauchte, mit Kupferionen gesättigte Phosphorsäure, die sich durch eine Blaufärbung auszeichnet, nach unten absinken kann und so ein Konzentrationsgradient weiter aufrechterhalten wird. Zwei verschiedene geometrische Ausprägungen der Gegenelektrode wurden näher untersucht: Eine ringförmige Gegenelektrode, die die Proben nicht abdeckt und damit Kontamination durch herabrieselnde Partikel der Gegenelektrode verhindern sollte. Dem gegenübergestellt wurde eine Platten-elektrode, die parallel zum Werkstück liegt.



Figs. 8 a to d: Schematic representations of the setup for electropolishing in phosphoric acid using a ring-shaped a) or plate-shaped b) counter electrode. Removal as a function of the sample position after 10 min of electropolishing at 1.5 V in setup a (c) and in setup b (d).

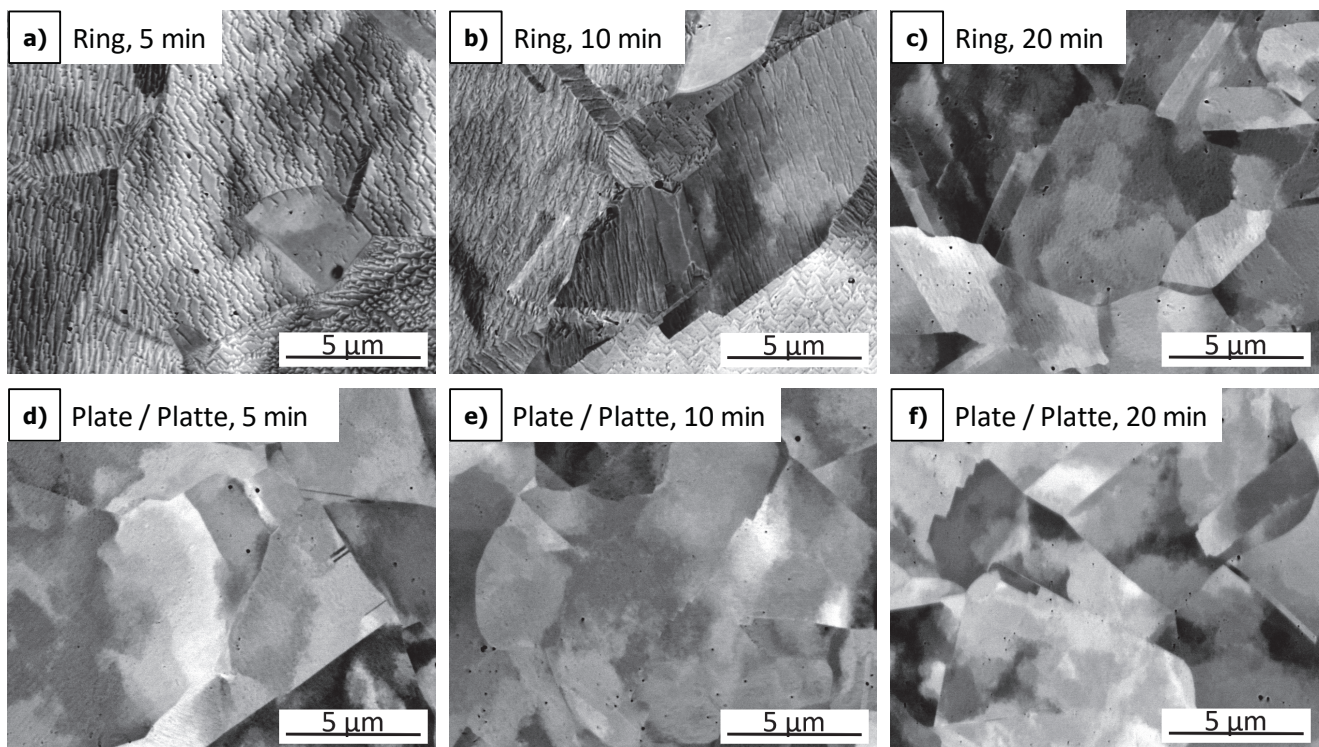
Bilder 8 a bis d: Schematischer Aufbau der Elektropolitur in Phosphorsäure mit ringförmiger a) oder plattenförmiger b) Gegenelektrode. Abtrag in Abhängigkeit der Probenposition nach zehnminütiger Elektropolitur bei 1,5 V in Aufbau a (c) und in Aufbau b (d).

Due to the different geometric design of the counter electrodes, it was of particular interest to know whether the electrolytic removal varies as a function of the sample position. For this purpose, the samples were taped lengthwise on one side using commercial adhesive tape and electropolished at 1.5 V for ten minutes in the shown setups. The removal was measured nine times in the upper, middle, and lower section of each sample, respectively. The averaged results are presented in Figs. 8 c) and d) as a function of the measurement position.

Taking into account the standard deviation of the measurements, no significant differences can be detected as a function of the sample and measurement position. The overall removal is approx. 20 % higher for the parallel setup. SEM examinations in the backscattered electron contrast were to provide information on whether the different setups lead to different surface expressions (Fig. 9).

Aufgrund der unterschiedlichen geometrischen Ausführung der Gegenelektroden, war es von besonderem Interesse, ob der elektrolytische Abtrag in Abhängigkeit der Probenposition variiert. Dafür wurden die Proben halbseitig längs mit handelsüblichem Klebeband abgeklebt und zehn Minuten lang in den gezeigten Aufbauten mit 1,5 V elektropoliert. Der Abtrag wurde im oberen, mittleren und unteren Bereich jeder Probe jeweils neun Mal gemessen. Die gemittelten Ergebnisse sind in Abhängigkeit von der Messposition in Bild 8 c) und d) dargestellt.

Im Rahmen der angegebenen Standardabweichung der Messungen können keine signifikanten Unterschiede in Abhängigkeit von der Proben- und Messposition festgestellt werden, wobei insgesamt im parallelen Aufbau ein um circa 20 % erhöhter Abtrag stattfindet. REM-Untersuchungen im Rückstreuелектроненконтраст sollten Aufschluss darüber geben, ob die unterschiedlichen Aufbauten zu verschiedenen Ausprägungen der Oberfläche führen (Bild 9).



Figs. 9 a to f: Backscattered electron image after time-staggered electropolishing using the ring-shaped counter electrode a)–c) and the parallel plate counter electrode d)–f), voltage: 1.5 V.

Bilder 9 a bis f: Rückstreuелектронenaufnahmen der Kupferproben nach einer zeitgestaffelten Elektropolitur mit der ringförmigen Gegenelektrode a)–c) und mit der parallelen Plattengegelektrode d)–f), Spannung: 1,5 V.

Significant differences in the surface expression can especially be observed for shorter electropolishing times of five and ten minutes: while in the ring-setup, the grains are, similar to an etching process, covered with facets as a function of their orientation, the parallel setup produces a smooth surface with the exposed grains of the copper sample.

After only five minutes, the parallel plate setup brings about a high quality electropolished surface: the average roughness for the ring setup after 5 minutes is 41 ± 4 nm, while it is only 16 ± 2 nm for the parallel plate setup. This marked difference with regard to the electropolished surface expression could be related to the ring setup's reduced removal or to the distribution of the field lines running perpendicular from the anode to the cathode in the parallel setup, whereas an inhomogeneous distribution of field lines cannot be excluded in the ring setup. No contamination by particles from the parallel counter electrode could be found on the samples to be polished, not even in detailed SEM analyses.

Thus, in a direct comparison and aiming at quickly obtaining surfaces as smooth as possible by electropolishing, the parallel plate setup was found to be more suitable. Both setups offer the advantage of not contaminating the samples with introduced foreign materials and, once manufactured, they can both be re-used again and again. Furthermore, consumed phosphoric acid is allowed to drain down and the overall consumption of acid is slower as, owing to the holes, less anode material is electropolished. Thus, several sets of samples can be polished in the setup before the acid must be replaced.

3 Conclusion

The herein presented preparation routine allows to obtain high quality preparations of soft copper materials. Adapting the polishing time and the contact pressure prevents an impression of abrasive particles into the sample surfaces

Vor allem die kürzeren Elektropoliturzeiten von fünf und zehn Minuten zeigen deutliche Unterschiede in der Oberflächenausprägung: Während der Ring-Aufbau die Körner ähnlich einer Ätzung orientierungsabhängig mit Facetten überzieht, zeigt der parallele Aufbau eine glatte Oberfläche mit den freigelegten Körnern der Kupferprobe.

Im parallelen Plattenaufbau liegt bereits nach fünf Minuten eine qualitativ hochwertige electropolierte Oberfläche vor: Der Mittenrauwert für den Ringaufbau liegt nach 5 Minuten bei 41 ± 4 nm, für den parallelen Plattenaufbau bei lediglich 16 ± 2 nm. Dieser starke Unterschied in der Ausprägung der electropolierten Oberfläche könnte mit dem verringerten Abtrag im Ringaufbau zusammenhängen oder mit der Verteilung der Feldlinien, die im parallelen Aufbau senkrecht von Anode zu Kathode verlaufen, während im Ringaufbau eine inhomogene Feldlinienverteilung nicht auszuschließen ist. Kontamination durch Partikel der parallelen Gegenelektrode auf den zu polierenden Proben konnten auch bei detaillierten REM-Analysen nicht festgestellt werden.

Im direkten Vergleich zeigt sich demnach der parallele Plattenaufbau für die Elektropolitur als geeigneter, um in kurzer Zeit möglichst glatte Oberflächen zu erhalten. Beide Aufbauten bieten den Vorteil, die Proben nicht durch eingebrachte Fremdmaterialien zu kontaminieren und können nach einmaliger Fertigung immer wieder verwendet werden. Außerdem kann verbrauchte Phosphorsäure nach unten abfließen und insgesamt verbraucht sich die Säure langsamer, da aufgrund der Löcher weniger Material der Anode electropoliert wird. So können mehrere Probensätze in dem Setup poliert werden, bevor ein Austausch der Säure notwendig ist.

3 Fazit

Durch die hier vorgestellte Präparationsroutine können qualitativ hochwertige Präparationen von weichen Kupferwerkstoffen erreicht werden. Die Anpassung der Polierzeiten sowie des Anpressdrucks verhindert ein Eindringen von

and particles carried over to finer polishing cloths.

Electropolishing was found to be suitable to remove mechanical deformation layers. A newly developed setup allows polishing the whole surface area of several samples without any direct contact. The geometric manifestation of the counter electrode has proved to be decisive for the resulting surfaces and their roughness. A ring-shaped electrode provided a removal with a strongly faceted grain surface similar to that after an etching process, while a parallel plate electrode completely smoothes the surface and increases the removal by approx. 20 %.

Metallographic preparation and etching recipes are subject of continuous adaptation and improvement. The PM forum ([https:// www.pm-forum.info](https://www.pm-forum.info)) offers the possibility to pursue and discuss the development of recipes and to also jointly work out even better routines in the metallography community. We would like to invite you to register for it and to participate in the discussion on the most diverse preparation recipes.

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Abrasivpartikeln in die Probenoberflächen und eine Verschleppung der Partikel auf feinere Poliertücher.

Die Elektropolitur erwies sich als geeignet zur Entfernung der mechanischen Deformationsschichten. Ein neu entwickelter Aufbau ermöglicht die ganzflächige Politur mehrerer Proben ohne direkte Kontaktierung. Die geometrische Ausprägung der Gegenelektrode hat sich als entscheidend für die entstehenden Oberflächen und deren Rauigkeit erwiesen. Eine ringförmige Elektrode führte zu einem ätzähnlichen Abtrag mit stark facettierter Kornoberfläche, während eine parallele Plattenelektrode die Oberfläche vollständig glättet und den Abtrag um ca. 20 % erhöht.

Metallographische Präparations- und Ätzrezepte sind stetiger Anpassung und Verbesserung unterworfen. Eine Möglichkeit, die Entwicklung von Rezepturen zu verfolgen, sie zu diskutieren und auch gemeinsam in der Metallographie-Community noch bessere Routinen zu erarbeiten, bietet das PM-Forum ([https:// www.pm-forum.info](https://www.pm-forum.info)). Wir möchten Sie herzlich einladen, sich dort zu registrieren und an der Diskussion rund um die verschiedensten Präparationsrezepte teilzunehmen.

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Paper 2

An in-depth evaluation of sample and measurement induced influences on static contact angle measurements

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OPEN

An in-depth evaluation of sample and measurement induced influences on static contact angle measurements

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Static contact angle measurements are one of the most popular methods to analyze the wetting behavior of materials of any kind. Although this method is readily applicable without the need of sophisticated machinery, the results obtained for the very same material may vary strongly. The sensitivity of the measurement against environmental conditions, sample preparation and measurement conduction is a main factor for inconsistent results. Since often no detailed measurement protocols exist alongside published data, contact angle values as well as elaborated wetting studies do not allow for any comparison. This paper therefore aims to discuss possible influences on static contact angle measurements and to experimentally demonstrate the extent of these effects. Sample storage conditions, cleaning procedures, droplet volume, water grade and droplet application as well as the influence of evaporation on the static contact angle are investigated in detail. Especially sample storage led to differences in the contact angle up to 60%. Depending on the wetting state, evaporation can reduce the contact angle by 30–50% within 10 min in dry atmospheres. Therefore, this paper reviews an existing approach for a climate chamber and introduces a new measuring setup based on these results. It allows for the observation of the wetting behavior for several minutes by successfully suppressing evaporation without negatively affecting the surface prior to measurement by exposure to high humidity environments.

Currently, literature research for “contact angle measurements” delivers more than four million publications. Hereunder, static contact angle (SCA) measurements are the most popular method to analyze a surface's wettability - on solid metals^{1,2} or sputtered thin films³, polymeric surfaces^{4,5}, graphene^{6,7} or even biological samples⁸. SCAs can range from hydrophilic ($< 90^\circ$) to a hydrophobic behavior with a SCA above 90° . Also extreme wetting cases like superhydrophilicity with a strong droplet spreading or superhydrophobicity with SCAs around 150° can be observed by SCA measurements⁹. Their implementation is not limited to smooth surfaces, as they are also used to analyze topographically modified structures, where recently the wettability of laser treated surfaces is focused in particular^{10–13}. Here, this method also allows for analyzing anisotropic wetting behavior, which is especially important for directionally patterned surfaces^{11,14}. For ideally smooth surfaces, the SCA can be described by the Young's equation and is considered as a thermodynamic contact angle reached by energy minimization in the three-phase wetting system consisting of liquid, solid and vapor^{9,15}. Real surfaces are characterized by roughness either fully wetted in the Wenzel wetting state¹⁶ or by partial wetting with air inclusions between the droplet and topographic features (Cassie–Baxter state¹⁷), resulting in a chemically heterogeneous surface.

Already in the 1980's researchers were aware of the strong scattering of contact angles on metallic surfaces like copper due to sample contamination, cleaning agents and cleaning procedure¹⁸. More recent studies could proof that especially a contamination with hydrocarbons plays a major role in the wetting behavior of solid materials¹⁹, as their adsorption can increase SCAs on flat copper samples from 45° to 100° . Cleaning agents can influence the composition of this airborne contamination layer and therewith alter the SCA results¹⁹. In 2015 Long et al.²⁰ showed that the adsorption layer also is highly dependent on sample storage conditions. Apparently, different studies have shown reasons for the broad scattering of contact angles in literature for the same

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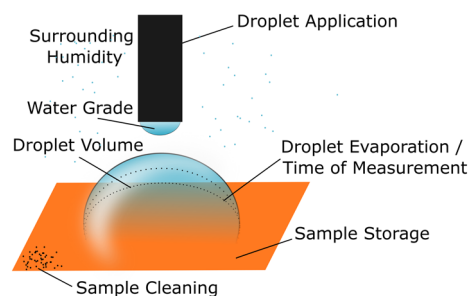


Figure 1. Overview of influences on static contact angle measurements covered in this paper.

material and various factors independent of the sample surface as droplet volume, temperature or humidity are well known²¹. However, no fixed measurement protocols exist including all possible sample or measurement induced influences and focusing on the dependence between sample contamination and resulting contact angle, which seems to be a key factor in any wetting analysis. For the dynamic measurement of receding and advancing contact angles Huhtamäki et al.²² as well as Drelich²³ provide a protocol of the measurement steps by gradually increasing and afterwards decreasing droplet volume including indications of potential measurement influences. They claim that the SCA measurement using the sessile drop method might only depict metastable results as the drop could be in any local instead of the global minimum. But different studies showed, that also dynamic contact angle measurements are often subjected to droplet disturbing effects, e.g. baseline pinning or vibrations transferred from the needle to the droplet in the sessile droplet setup²⁴ keeping the droplet from reaching the global thermodynamic minimum. Often natural vibrations in the laboratory prevent the contact angle from reaching theoretical values²⁵. Moreover, there is a lack of theoretical understanding of the resulting contact angle hysteresis²⁴ while there are well defined models for SCA measurements based on the Young's equation for ideal surfaces and on the Wenzel- and Cassie–Baxter models for real surfaces depicting roughness^{15–17}.

On top of that, especially the measurement of the receding contact angle poses a challenge if the wetting behavior is yet unknown. The starting volume needs to be estimated and can reach values up to 150 μl ²² resulting in excessively large droplet diameters strongly limiting the number of measurement replicates per sample.

In contrast, SCAs are attractive due to the simplicity of the method and so they are the established values in literature to describe the wettability of a surface, which is why they cannot be substituted by other approaches but rather supplemented to improve data interpretation²⁶. For SCA measurements a detailed discussion about potential sample or measurement induced influences also showing the extent of their impact on hydrophilic as well as hydrophobic surfaces could not be found in literature.

Because of the popularity of the SCA measurement, its simplicity and broad applicability on different materials and sample sizes, this paper aims to provide a detailed analysis of different measurement parameters and how an uncontrolled alteration of the results can be avoided. Sample induced influences as sample preparation, storage and cleaning are investigated and compared to measurement induced influences such as droplet volume, application method and many more (compare Fig. 1). Time of measurement and its connection to droplet evaporation is discussed in detail with a review of a climate chamber as suggested by Drelich²³. A new method that allows for an observation of the droplet throughout several minutes by successfully suppressing evaporation without distorting the contact angle results is presented. Based on the provided analyses, a basic framework for SCA measurements can be set allowing for a better comparability of different wettability studies in the future.

Materials and methods

Copper was chosen as a model material due to its broad application in research and industry^{13,27–29} and its common use in wetting analyses as discussed earlier^{2,18,20,30}. Copper coupons ($10 \times 25 \text{ mm}^2$) were mirror polished to an averaged roughness of $3.3 \pm 0.6 \text{ nm}$ measured by confocal laser scanning microscopy (*Olympus LEXT OLS4100*), where the preparation routine was published in an earlier work³¹. After preparation, the samples were cleaned in ethanol in an ultrasonic bath for three minutes and dried with an ambient air stream. Right before contact angle measurement, dust and particles were removed via an ambient air stream from a fan. Pressured air was avoided due to possible oil contamination²². Wetting tests were performed on a *Krüss DSA 100* equipped with a 100 μl Hamilton syringe at room temperature ($22^\circ\text{C}/\sim 20\%$ relative humidity). If not mentioned otherwise, measurements were taken 5 s after droplet application with a droplet volume of 3 μl . Images of the experimental setup for sessile drop measurements as conducted in this work together with an image of a droplet applied on a copper substrate can be found in the Supplementary Material (Supplementary Fig. S1a). The 3 μl droplet is dosed automatically with 2.5 $\mu\text{l}/\text{s}$. A fully automated program was written in the *Advance software Version 1.13* defining positions for droplet dosing and application to allow for comparable measurement conditions for all experiments keeping the influence of experimental errors as small as possible. Five seconds after droplet application a high-resolution camera takes three images of the droplet within 1 s. The *Advance software* allows for a fully automated fit of the droplet and calculation of the resulting contact angle on both sides of the droplet as well as the volume using the elliptical fit method of the software. According to the software manual the ellipse fit method is recommended for a contact angle range between 10° and 120° and therefore applicable for the analyses conducted. The fit method adapts the optically detected contour of the droplet to a conic section equation. Tangents

are placed through the three-phase point. The contact angle is calculated from the average angles on both sides of the droplet³². This was performed on three images per droplet and results were averaged to determine the SCA of the droplet (labelled as “SCA” in figures). It should be noted that in this study the measurement of copper surface wettability is primarily used to monitor the effect of the different conditions. Therefore, results are normalized to solely show the effect under investigation. Data normalization was based on a reference sample state that was defined for each experiment. The individual SCAs measured on the reference state were averaged to *Mean SCA_{Reference}*. Whenever possible all parameter variations were carried out on the same sample as the reference measurements, but in different sample areas. All experiments were conducted on multiple samples to ensure sufficient statistics. If not mentioned otherwise, normalization as shown in Eq. (1) was carried out sample wise to equal out differences resulting from other sources than the parameter under investigation. A detailed example of normalization calculations is given in the supplementary material (compare Supplementary Table S1).

$$\text{Normalized SCA} = \frac{\text{SCA}/^\circ}{\text{Mean SCA}_{\text{Reference}}/^\circ} \quad (1)$$

The reference sample is specified for each experiment. Results are displayed in box plots calculated by *OriginPro 2019* with half boxes on the left and randomly scattered data points on the right. For each experiment, a new set of samples was used to make sure that no sample area came in contact with water twice and that no experimental parameters under investigation overlap. All experiments were conducted on initially hydrophilic and hydrophobic samples adjusted by different storage conditions. Sample storage conditions were defined based on the experimental results in the chapter “Sample Storage”. The sample preparation and storage as well as pretreatments specified in this section were kept identical for all experiments.

The analysis of the surface chemistry was done by X-ray photoelectron spectroscopy (XPS) with an *Axis Nova surface analysis spectrometer* (Kratos Analytical Ltd.). In this system, photoelectrons are released from the sample's surface by monochromatic Al K α radiation of 1486.6 eV at a working pressure of 10^{-8} mbar and analyzed according to their kinetic energy by an electrostatic hemispherical sector analyzer. Relative atomic percentages were calculated by the intensities of elemental photoelectron lines, measured in survey spectra at a high electron analyzer pass energy of 160 eV and standard sensitivity factors supplied by the spectrometer manufacturer. Contributing elemental binding states were identified using detail spectra, measured with a lowered pass energy of 20 eV and therefore 8 times elevated energy resolution. Here, each binding state of an element shows a significant slight chemical shift in comparison to its elemental species. The given ratios of different C, O and Cu binding states is based on a deconvolution assuming a Shirley type background for the inelastic scattered electrons and Gaussian/Lorentzian line-shapes for each contributing binding state. The XPS information volume is given by the lateral measuring zone (0.35 mm $\times$ 0.70 mm) times the maximum escape depth of the photoelectrons, which is typically about 3–5 nm, depending on their kinetic energy and the material they have to pass.

Static Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurements for surface spectroscopy and imaging were performed using an *ION-ToF IV instrument* (ION-TOF GmbH, Münster, Germany). The primary ion gun was operated with Bi³⁺ ions with an energy of 25 keV and the emitted secondary ions were detected in positive and negative polarity.

Results and discussion

Sample induced influences. *Sample preparation.* Recently many studies aim at tailoring the wetting response by applying periodic patterns with pulsed lasers^{33,34}. An earlier study proved the strong influence of surface chemistry on the wetting behavior of topographically altered samples¹¹, which is especially important for laser patterned surfaces as the modification of topography always is accompanied by distinct changes in surface chemistry through oxidation processes³⁵. Researchers are well aware of the influence of topographical changes e.g. by laser patterning^{10,33,36–40}. Nevertheless, so far no generally valid statements can be made about the influence of topography on the wetting behavior, especially as influences of topography and chemistry are often interconnected and metastable wetting states or transitions from Wenzel to Cassie–Baxter wetting can be observed⁴¹. To make sure that such an influence does not overlay the effect under investigation in this work, flat samples were chosen as a substrate material. The sample preparation usually is directly connected to the surface topography, that proved to have a great influence on the wettability of a surface⁴². If the wettability of a solid material is to be investigated, the influence of topography should therefore be kept as small as possible by following effective preparation routines. A R_a -value below 500 nm is a reference value to avoid topographical influence on the SCA²¹. With the routine presented in Ref.³¹ and applied on the samples, the average roughness R_a of a cold rolled copper sheet could be reduced to 3.3 ± 0.6 nm. Though the surface is close to an ideal surface with the small roughness, in reality also such a minor topography contradicts the theoretical wetting according to the Young's equation and rather supports a uniform Wenzel wetting of the surface without droplet pinning.

Sample storage. While sample preparation with its resulting topography and chemistry are broadly discussed in the wetting community, little attention is paid to the storage conditions after sample preparation. As the wetting response especially of topographically altered surfaces is highly dependent on adsorbed carbon groups^{20,43,44}, storage plays a major role in the development of the wettability behavior. Different gaseous environments lead to differences in the aging related contact angle development²⁰. Usually, atmospheric conditions are chosen as the atmospheric carbon leads to the time dependent hydrophobization of metallic surfaces by adsorption of aliphatic carbon groups^{20,27}. As the composition of the surrounding atmosphere already proved to have a great influence on contact angles, we investigated, if different storage conditions in the same atmosphere also alter the contact angle. Samples were prepared in one batch, cleaned via immersion in ethanol in an ultrasonic bath and

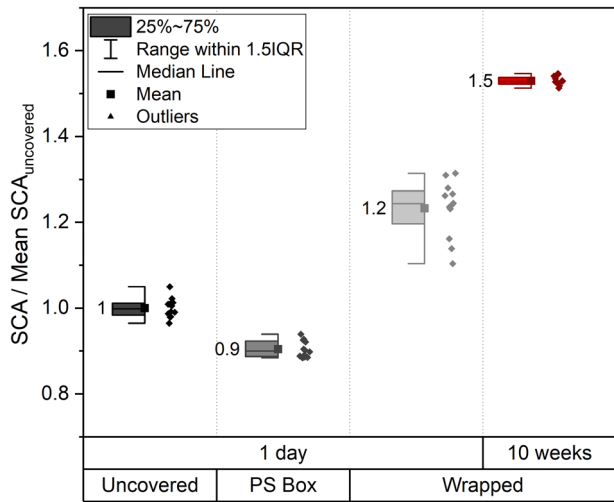


Figure 2. Contact angle of a 3 μ l droplet on polished copper samples stored without any cover (uncovered), in a common polystyrene sample box (PS Box) or wrapped in a woodfree tissue (Wrapped). For the wrapped samples a storage time of one day is compared to 10 weeks of storage. The different sample packaging methods lead to different contact angles although all were stored under the same ambient atmospheric conditions. Per storage condition two samples were investigated by applying 6 droplets each. The reference data for normalization is “uncovered/1 day”. Here data normalization was not done sample wise but with the total mean value of the two samples stored for one day uncovered as separate samples had to be used for every storage condition.

	C [at.-%]	Cu [at.-%]	N [at.-%]	O [at.-%]	S [at.-%]	C–C/C–H [at.-%]	C–O [at.-%]	O–C–O [at.-%]
						Nonpolar carbon	Polar carbon	
Copper sample	53.79 $\pm$ 0.19	22.64 $\pm$ 0.45	0.67 $\pm$ 0.08	22.46 $\pm$ 0.16	0.44 $\pm$ 0.11	44.78 $\pm$ 0.13	4.74 $\pm$ 0.04	4.27 $\pm$ 0.08
Wrapping paper	61.69 $\pm$ 0.06		0.36 $\pm$ 0.01	37.86 $\pm$ 0.09	0.08 $\pm$ 0.09	11.69 $\pm$ 0.12	39.49 $\pm$ 0.11	10.51 $\pm$ 0.05

Table 1. Averaged XPS-results of the copper surfaces wrapped in the woodfree tissue and of the wrapping paper itself.

stored either uncovered and unboxed, uncovered in a conventional sample box (polystyrene) or wrapped in a woodfree tissue (laservision A99CLSTA1302) in an identical box. The different protected samples are stored in the same atmospheric environment for one day ($\approx$ 22 h). In Fig. 2 they are compared to identical copper samples stored in the wrapping paper for ten weeks. Due to the prolonged storage time the samples were packed in air tight boxes with silica gel beads to avoid corrosive effects.

Although the samples were polished, cleaned and stored for 1 day in one batch under the same atmospheric conditions, the different additional protection measures lead to contact angle differences up to 30%. After 10 weeks in the woodfree tissue the SCA is increased even more by 50% compared to the reference sample. This experiment clearly demonstrates that also flat samples are subjected to aging induced wettability conversions, which are most likely caused by different carbon adsorption rates depending on the amount of carbon provided by the surrounding materials. We assume that the observations made by Long et al.²⁰ regarding the hydrophobization of laser patterned copper surfaces by adsorption of aliphatic carbon groups are also applicable to copper surfaces undergoing preparation without involvement of laser treatment. More recent studies underpin this assumption², and suggest that not only different atmospheres, but also different cleaning procedures lead to the incorporation of certain carbon species in the adsorbate layer¹⁹ that strongly affect the resulting wetting behavior.

For sample storage the results displayed in Fig. 2 suggest that different protection measures lead to altered micro-environments for the individual samples: The uncovered sample is exposed to a natural aging environment, while for the samples in a polystyrene box the carbon supply is restricted to the air volume inside the box. Less volatile carbon is available that can adhere on the sample, which is why they turn out more hydrophilic than the uncovered reference samples. On the other hand, the woodfree tissue seems to act as a carbon-donor increasing the amount of free carbon groups close to the sample surface and supporting their adsorption resulting in an increase of the SCA by 20% during one night of storage. Prolonged storage times seem to further increase the carbon adsorption as well as the resulting hydrophobicity.

To gain a deeper understanding of the influence of the wrapping paper, the paper itself as well as samples tightly wrapped in the paper for ten weeks (compare red data in Fig. 2) were analyzed by means of

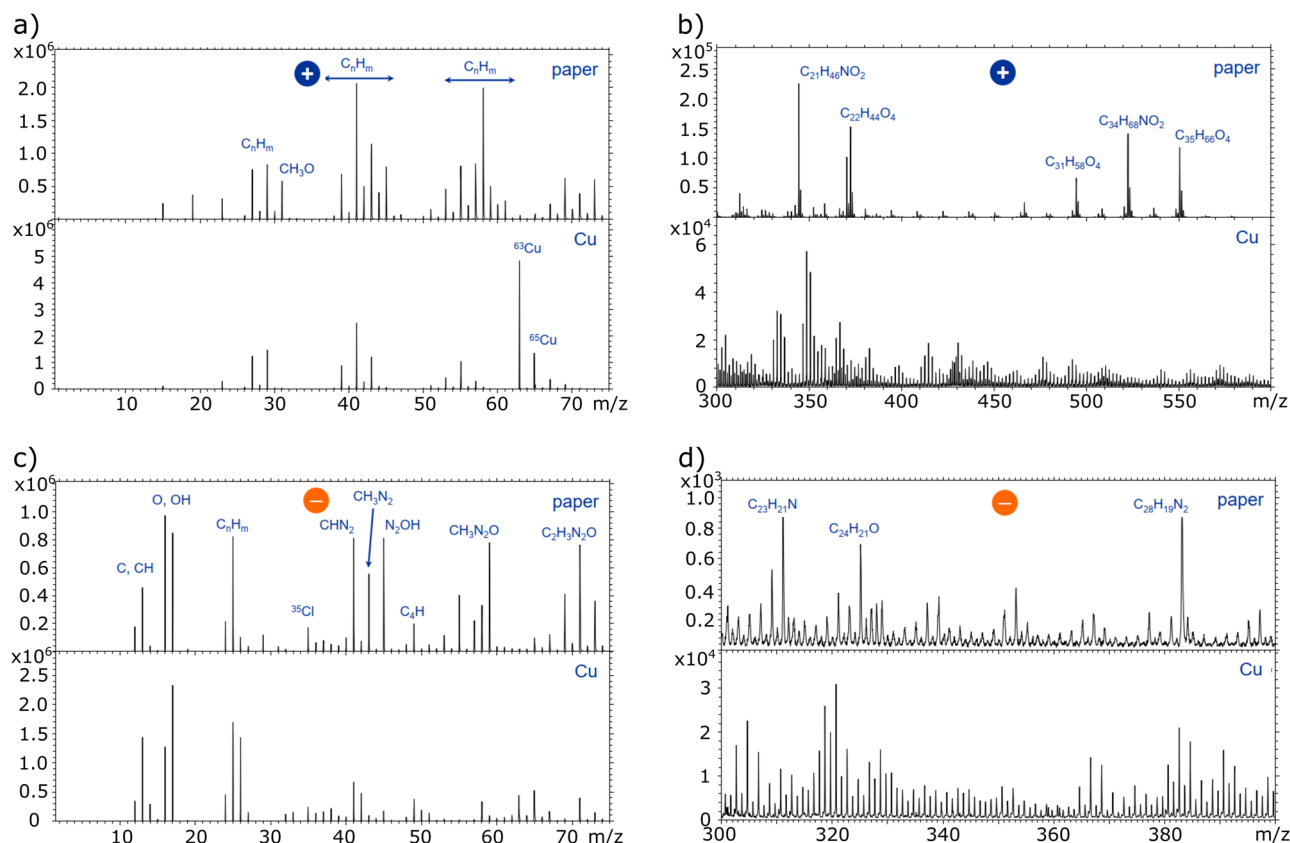


Figure 3. Positive (a,b) and negative (c,d) secondary ion spectra received on the stored sample ('Cu') and on the paper ('paper') sample are shown in a region of low masses (<75 amu) and in a region of higher masses (>300 region). The low mass secondary ion spectra of the Cu sample indicate a rather clean metallic sample with slight contaminations of typical environmental simple hydrocarbons. Some corresponding peaks are also found on the paper, but the observed peak groups differ. In the region of higher masses (>300 amu), which is significant for more complex organic molecules, the dominant peaks found on the paper at 311, 325 and 383 amu were not found on the Cu sample, which indicates that there is no complex component of the paper material like cellulose molecules transferred to the sample.

XPS-measurements. The SCAs of three samples were averaged to $108^\circ \pm 1^\circ$. Table 1 summarizes the results of the overview spectra and the C 1s detail spectrum for three measurement spots on a wrapped sample and the wrapping paper. The C 1s region contains signals from carbon-species in three different binding states: carbon bound in aliphatic and aromatic hydrocarbon at an electron binding energy of 285 eV, carbon with one oxygen as binding partner at 286.6 eV (typical for organic hydroxyl or carbonyl groups), and carbon with two oxygen atoms as binding partners at 288.4 eV (typical for carboxyl groups). In the following, carbon bound in non-polar aliphatic or aromatic hydrocarbons (signal at 285 eV) is called "nonpolar carbon", while the sum of the two others with one or two oxygen atoms as binding partners is called "polar carbon". The oxygen region of the spectrum contains always at least two signals: they stem from oxygen bound in hydroxyl and carbonyl groups at 531.2–532.3 eV and oxygen bound in carboxyl groups at 532.2–533.6 eV⁴⁵. Only the sum of the signals in the oxygen region is used here as the deconvolution of the peaks is subject to large uncertainties. Oxygen bound as water would appear also at 533.2 eV, so the presence of adsorbed water films can't be excluded.

As expected, the copper samples show a strong carbon signal as well as an oxygen signal due to native oxidation⁴⁶. Minor nitrogen and sulfur contamination could be either transmitted by the wrapping paper or be a result of the sample preparation. The detailed C 1s-spectrum reveals a dominance of nonpolar carbon being responsible for the hydrophobic wetting behavior²⁰. Interestingly, the paper itself shows a more pronounced polar carbon–oxygen content that does not seem to be transferred to the sample surface. A possible reason could be the strong bond of C–O in the cellulose fiber. The aliphatic carbon, in contrast, might only be adsorbed on the paper surface and can therefore be donated to the copper sample with its reactive surface after sample preparation. Therefore, the results in Table 1 suggest that cellulose-based paper can adsorb aliphatic carbon groups and act as a donor for these functional groups that leave the sample surface in a hydrophobic state. The small standard deviation for the nonpolar carbon on the copper samples indicates that for a tight wrapping a homogeneous transfer of the carbon groups on the sample surfaces is possible. TOF–SIMS analysis was performed to gain a better understanding of the carbon exchange between the wrapping paper and the sample.

The resulting spectra of positive and negative secondary ions with lower masses (<75 amu) in Fig. 3 indicate that there is a usual contamination of simple nonpolar hydrocarbon molecules on the Cu surface after storage

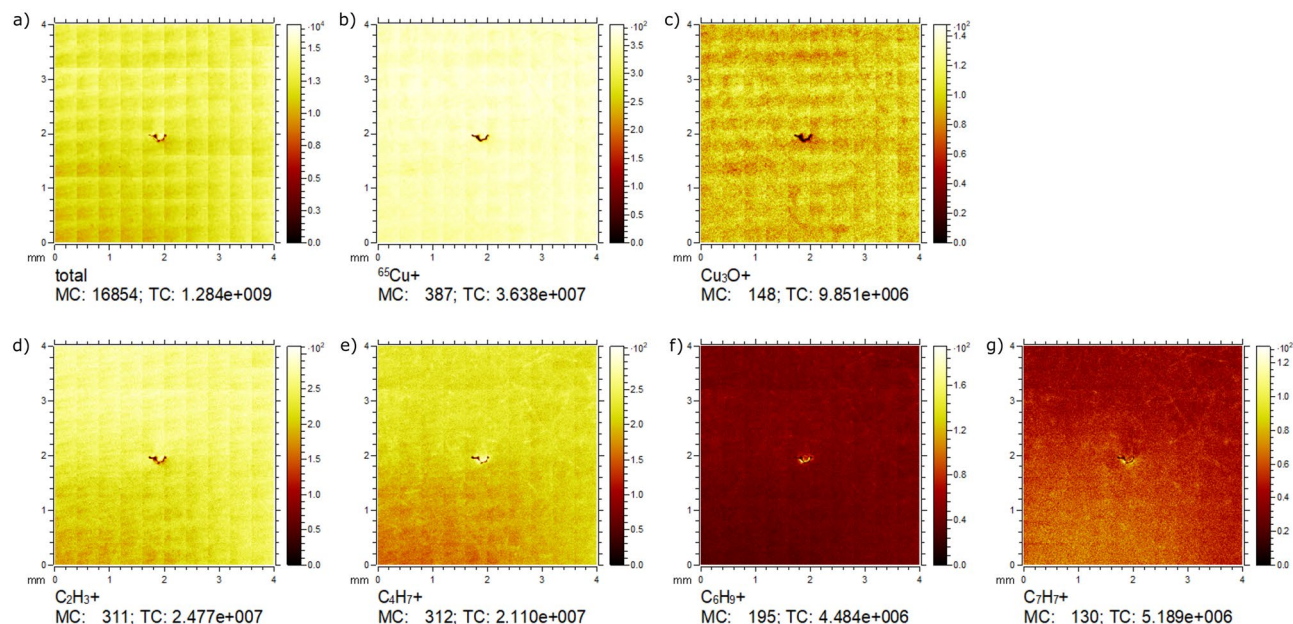


Figure 4. Lateral distribution maps of selected positive secondary ion intensities as macro raster $4 \times 4 \text{ mm}^2$ show a homogeneous allocation: (a) total positive secondary ions, (b) $^{65}\text{Cu}^+$, (c) Cu_3O^+ , (d) C_2H_3^+ , (e) C_4H_7^+ , (f) C_6H_5^+ and (g) C_7H_7^+ . An accidental particle contaminant was used for adjustment and the grid structure is an artefact of measurement in stitching mode.

and contact to the paper, which can be interpreted as caused by environmental hydrocarbon adsorptions. On the paper this contaminant may be present but overwhelmed by other small organic components. In the higher mass region, significant for more complex molecules ($> 300 \text{ amu}$), the dominant and characteristic peaks, which were found on the paper (311, 325 and 383 amu), find no correspondence on the sample surface. Side experiments, where the paper was manually pressed or even rubbed on the surface, also did not show corresponding peak groups. These measurements therefore support the thesis of the transmission of adventitious carbon initially adsorbed on the paper to the sample instead of actual paper components being transferred. The very small standard deviation of the corresponding SCA of only 1° (0.9%) indicates an even distribution of the adsorbed carbon on the sample surface. The homogeneous lateral intensity distribution of positively charged secondary ions as shown in Fig. 4 shows that the tight wrapping of the samples leads to an even transfer of carbon groups on the wrapped surfaces and therewith guarantees a stable wetting behavior in different sample areas.

Based on these results, it is possible to create both hydrophilic and hydrophobic surfaces of the same substrate simply by the control of the storage conditions. The different influences on SCA measurements investigated in this work were explored on both hydrophilic and hydrophobic surfaces. To create hydrophilic copper surfaces after preparation, one half of the sample batch was stored for one day in a polystyrene box, resulting in an average SCA of $62^\circ \pm 3^\circ$ under standard measurement conditions used as reference conditions in the following experiments. To create hydrophobic surfaces, the results presented in Fig. 2 were applied and the other half of the polished copper samples were wrapped in the woodfree tissue, placed in individual single sample boxes which are then stored in airtight boxes filled with silica gel beads to keep the humidity low in order to create a strong and homogeneous hydrophobicity. With an averaged SCA of $106^\circ \pm 1^\circ$ after 2 weeks of storage under standard measurement conditions, the desired hydrophobicity of the surfaces was achieved.

Sample cleaning. As discussed before, it is well known and accepted in literature that carbon containing adsorption layers strongly stimulate the wetting behavior of metallic substrates as the carbon adsorption reduces the surface energy^{19,20,27,47}. Still, some researchers argue that organic matter would only play a minor role in the hydrophobization of metallic surfaces⁴⁸ and rather attribute the hydrophobization process to reactions of the surface with oxygen^{33,48,49}. If oxidation was the main factor responsible, sample cleaning with solvents should not influence the contact angle significantly.

Figure 5 shows, how a 5-min ultrasonic bath in ethanol strongly lowers the contact angle of hydrophilic as well as hydrophobic samples. Before the cleaning, the SCA was measured on different areas on one half of the sample, the other half was measured after the respective ultrasonic cleaning. All results are standardized to the mean value of the measurements before the cleaning for every sample (uncleaned).

Interestingly, both samples show the same decrease in contact angle through the cleaning in ethanol of 9%. Heier et al.¹⁹ showed that cleaning agents on the one hand remove some of the carbon groups and incorporate functional groups into the adsorbate layer on the other hand. Due to the mixed polarity of ethanol it is believed to remove the nonpolar as well as polar sites on the sample surface leaving it in a more hydrophilic state - as clean copper is hydrophilic². The reduction of the contact angle by solvent cleaning is in good agreement with results from 1985¹⁸, where a contact angle dependency of the cleaning solvent and cleaning duration was observed. The

results shown in Fig. 5 indicate that the contamination layer on the sample surface indeed plays a major role in the development of hydrophobicity. The above experiment shows that while a simple cleaning in alcoholic solvents is considered as a good practice before sample imaging or analyses, for SCA measurements it has a significant influence on the measured angles. This means that no general recommendation for an “appropriate cleaning” before SCA measurements²³ should be made as often especially the composition of the adsorbed carbon layer is of great interest and might be easily disturbed by a preceding cleaning. So, if researchers decide to perform a cleaning before the measurement, they should be aware of the strong effect and perform the same cleaning for all samples to assure comparable conditions. Even hydrophilic samples only stored for one day pile up enough carbon to show a reduction of the contact angle after the ultrasonic cleaning.

Evidently, for reproducible SCA measurements many details need to be considered before the actual measurement can be conducted. Though wetting behavior of different materials has been studied extensively in the past, there is still a lack of knowledge of basic relationships between sample properties, aging behavior, and the resulting contact angles. Especially for systematic studies investigating the influence of, e.g. the microstructure, strain, micro-topography but also of surface chemistry it is of the utmost importance to create comparable sample conditions in regards of preparation, storage and sample cleaning.

Even though the general protocol of a SCA measurement seems simple and not error-prone, no standard values for the volume of the dosed liquid or the exact measurement time or the droplet application method exist. Therefore, the next section of this paper aims at investigating the influence of different parameters in the measurement protocol and setting up a universal recommendation for SCA measurements. Especially the time of the contact angle determination will be discussed to highlight the competing effects of evaporation on the one hand and the required time to reach a stable wetting condition on the other hand.

Measurement induced influences. *Probing liquid.* Similar to sample conditioning, the probing liquid used to measure the SCA should be chosen carefully. ASTM set standards for laboratory water by classifying it into four types⁵⁰. Electrical conductivity is next to the pH-value and other specifications like the total organic carbon the main criteria for water classification. The four ASTM types range from an electrical conductivity of 0.056 $\mu\text{S}/\text{cm}$ (type I) to 5 $\mu\text{S}/\text{cm}$ (type IV). Conductivity is increased by the amount of free ions in the water where a low conductivity is favorable for chemical analyses (usually type 2 or lower (conductivity < 1 $\mu\text{S}/\text{cm}$, 25 °C))⁵¹. So far, the sensitivity of SCA measurements towards the water quality used has not been discussed until now in the literature, to the best of our knowledge. Therefore, two significantly different qualities of water were compared as shown in Fig. 6. On the same samples, contact angles were measured using HPLC gradient grade analyses water with a conductivity of 0.91 $\mu\text{S}/\text{cm}$ as well as standard tap water with a conductivity of 309 $\mu\text{S}/\text{cm}$, according to the annual local water analyses report (2020). Measurements were conducted with a pipette to avoid a contamination of the microliter syringe with the tap water.

As shown in Fig. 6, no significant differences were observed for the hydrophobic samples while the tap water formed lower contact angles on the hydrophilic samples than the purified HPLC grade water. We believe that the thicker carbon rich contamination layer on the hydrophobic samples (compare section “sample storage”) shields the copper surface from the droplet and reduces the interaction forces between the substrate and the water. Noble materials like copper or gold interact via long-ranged van der Waals forces with the liquid^{7,52} that might be active for the hydrophilic samples, but interrupted by the more pronounced carbon layer for the hydrophobic samples. So, while we assume that on the hydrophobic samples the water forms interaction bonds with the carbon contamination layer, on the hydrophilic samples it rather might interact with the copper substrate leading to a different behavior of the two sample types.

Another possible factor is the altered dissolving properties of the tap water due to a higher ion concentration, and a resulting solution of the adsorbed carbon layer in the water with increased wettability of the surface.

Moreover, the tap water can be rather qualified as a molecular colloid than a pure liquid, which might also influence the surface tension of the water and therewith its wetting properties. The higher salt content of the tap water might also cause corrosion of metallic surfaces that are less capable of forming passivation layers than copper⁴⁶. Especially long-time wetting tests, where droplets might be observed for several minutes might be prone to such corrosive reactions, why we recommend opting for purified water whenever possible.

Also numerical simulations of the wetting behavior of surfaces as presented in Refs.^{2,53} usually are based on the assumption of molecular pure water. Therefore, it is seen as a good practice to use purified water for the experimental data the simulations are built on.

Droplet volume. Especially the volume of the deposited droplet is vastly varied in different studies. Volumes of water droplets range from 2 to 3 μl ^{12,54–57} to significant higher values from 7 to even 10 μl ^{34,58–60}. Sometimes, only vague information on the droplet volume or volume ranges are provided³⁷. In theory, the contact angle of ideal surfaces should not be influenced by the droplet volume. Seo et al.⁶¹ proved that superhydrophobic surfaces can fulfill the requirements for this volume independence of the SCA. For superhydrophobic samples droplet deposition can pose a challenge, especially for surfaces with low water adhesion. An increase in droplet volume can be useful here to allow the droplet to fall from the needle⁶².

To investigate the effect of droplet volume on hydrophilic and hydrophobic, but not superhydrophobic samples, droplets of three different volumes (3, 6 and 9 μl) were applied (compare Fig. 7).

The influence of higher droplet volumes on more hydrophilic samples can be traced back to the impact of gravity that is increasing with the droplet volume. Due to the improved surface wetting, the SCA decreases more for hydrophilic samples than for hydrophobic samples. Results in Fig. 7 indicate that smaller droplets deliver more accurate results with less deviation and fewer outliers. Nevertheless, droplets should also not be too small to avoid excessive disturbance through the needle during droplet application^{22,23}. For very small droplets with a

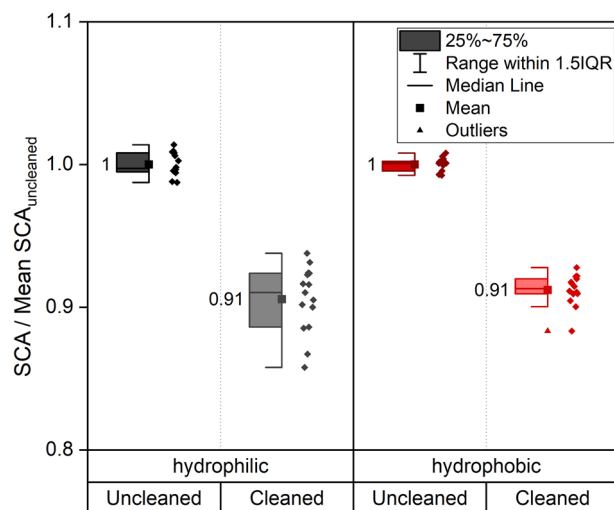


Figure 5. Influence on the SCA of ultrasonic cleaning in ethanol of hydrophilic and hydrophobic samples. For both wetting types SCAs before the cleaning (uncleaned) were compared to the SCA after cleaning (cleaned). Fifteen droplets were applied on three samples per condition. The reference data for normalization is “uncleaned”. For both wetting types a separate normalization was carried out.

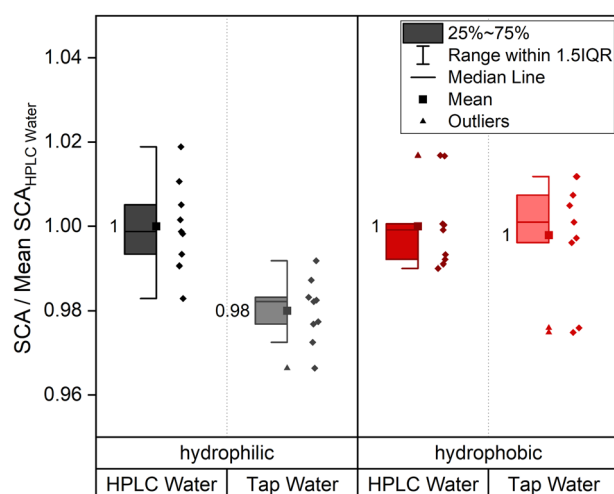


Figure 6. SCA measurements with HPLC grade water (0.91 $\mu\text{S}/\text{cm}$) compared to tap water (> 300 $\mu\text{S}/\text{cm}$). Measurements were performed on three different samples with three droplets per sample per water grade and sample condition. The reference data for normalization is “HPLC Water”. For both wetting types a separate normalization was carried out.

diameter in the μm range, line tension must be considered as it may vary with droplet diameter⁶³. For the volumes applied here with diameters in the mm range, gravity is the dominating factor. The cosine of the SCA and the reciprocal of the droplet radius show a linear relation for both wetting types (see Supporting Fig. S2) suggesting an independence of the line tension from the applied droplet volumes⁶³. A volume of 3 μl appears to be ideal to minimize the influence of gravity^{12,64} and to produce stable droplets that are not disturbed too easily by vibrations at the same time, while the droplet diameter is still small enough to allow for multiple measurements on an averaged sample size. Here, it must be highlighted that the considerations above are based on SCA measurements on topographically flat and chemically homogeneous samples. For heterogeneous sample surfaces, the droplet volume must be sufficiently high to average the surface heterogeneity. Marmur et al.²⁵ recommend a factor of 10^3 between the scale of heterogeneity and droplet size. This recommendation might not be applicable to all sample-water-systems e.g. a laser line pattern with a periodicity of 50 μm as analyzed in¹¹. Especially if anisotropic wetting behavior is to be investigated^{11,65–68} excessively large droplets might simply flood the entire sample and cover the effect of anisotropic structures. Therefore, we recommend using the smallest possible droplet volume/diameter to achieve reproducible results on different areas of the heterogeneous sample.

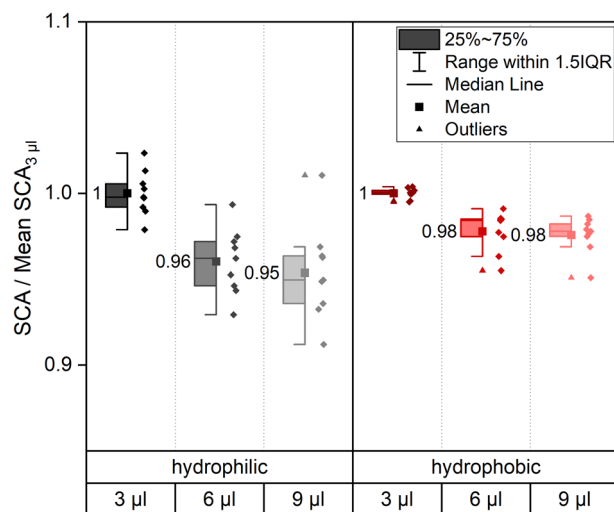


Figure 7. SCA measurements with different droplet volumes. For direct comparison of the influence of the droplet volume contact angles on the same sample were measured with 3 μl , 6 μl and 9 μl droplets. In total three samples were analyzed per wetting condition with three droplets of each volume per sample. The reference data for normalization is “3 μl ”. For both wetting types a separate normalization was carried out.

Droplet application. Once the droplet volume is set, different options for droplet application during SCA measurements are available: this can be done by dosing the droplet, leave it hanging free from the needle tip and lifting the stage until the droplet can be picked up by the sample. This procedure of droplet application (“Stage”) contrasts with the current state of the art with increasing automation of contact angle measurements where usually the needle positions are defined (“Needle”), and the stage height is kept constant. While standard devices are equipped with a microliter syringe and a needle to dose and apply the droplet, in self-built devices, pipettes (“Pipette”) can be an option to dose the exact volume. Figure 8 shows the comparison of the three different application methods. At least eight 3 μl -droplets were applied on three samples per wetting condition and application method. The reference sample for data normalization was the “Needle”-application. The results are displayed in Fig. 8 for hydrophilic and hydrophobic samples. On the hydrophilic samples, pipetting of the droplet leads to an average reduction of the SCA of 3%, whereas no deviation can be observed on the hydrophobic samples between the different application methods. We believe that the increased hydrophobicity and the associated higher energy barrier of the samples results in a decreased pressure sensitivity during droplet application. On the hydrophilic samples, in contrast, the enhanced pressure during the manual pipetting of the droplet compared to the defined gentle application by needle or stage leads to a stronger spreading of the droplet. Therefore, a reduction of the SCA is observed. On the hydrophilic samples all application methods lead to a stronger scattering of the contact angle, which might be the result of a more inhomogeneous carbon agglomeration of the samples after one day of storage (compare section “Sample Storage”). In contrast, on the hydrophobic samples only the droplet application with the pipette results in a stronger scattering of contact angles, which might be due to a less reproducible application force applied by the researcher. In general, the needle or stage method is recommended. Still, the experiment shown in Fig. 8 proofs that for extreme wetting cases (needle tip more hydrophilic than the surface under investigation) or in case of a lack of automated equipment, gentle droplet application with a pipette can be a reasonable alternative. For hydrophilic samples a pipette application is not recommendable.

Humidity. Usually, humidity and temperature can be controlled, e.g. by air conditioning. Additionally, silica gel can be used to lower the humidity and avoid corrosion of the samples during storage. Still, slight changes in both parameters often cannot be avoided for example due to sample transportation. While common laboratory air conditioning can control the temperature easily, humidity control poses a challenge as conventional air conditioners do not allow for a hygrostat-controlled humidity regulation. Moreover, slight changes in temperature are not expected to influence the resulting contact angle as fluctuations between 20 and 40 $^{\circ}\text{C}$ do not alter the surface tension of water significantly^{21,22,69}.

Humidity plays a major role in contact angle measurements when it comes to the reduction of droplet evaporation during long term measurements. To avoid evaporation, the atmosphere around the samples usually is saturated with water. Commercially available climate chambers additionally offer the possibility of changing the atmosphere to inert gases like nitrogen. Attention should be paid here because also alleged inert gases like nitrogen might be adsorbed on the sample and influence the contamination layer before the measurement. Drellich²³ showed a simple setup to suppress evaporation by putting the sample under investigation in a glass cell filled with the probe liquid and covered with parafilm. After a few minutes a saturated atmosphere should be generated inside the cell and droplets can be applied by the needle penetrating the cover of the cell²³. This approach was rebuilt (Fig. 9a) using aluminum foil instead of parafilm, as the contact between needle and parafilm could lead to contamination and as the needle showed strong bending during penetration of the elastic

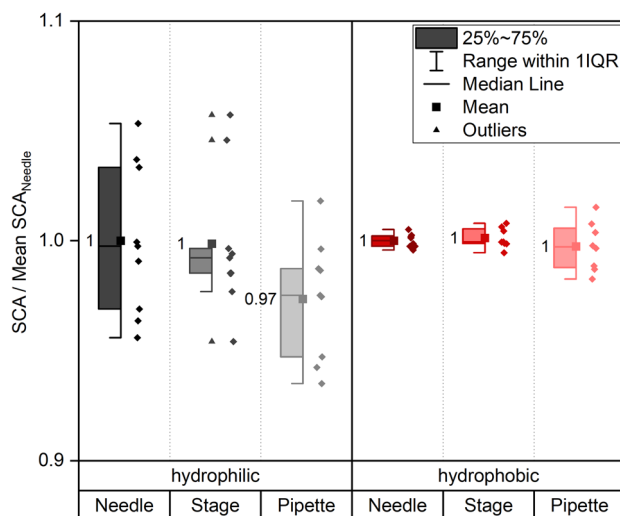


Figure 8. Comparison of different kinds of application of a 3 µl water droplet. On the same sample droplets were applied with the three methods, i.e., by moving the needle (Needle), by moving the stage (Stage) or by manual pipetting (Pipette). Measurements were repeated at least 8 times for each method on three samples. The reference data for normalization is “Needle”. For both wetting types a separate normalization was carried out.

parafilm. Photographs of the setup can be found in Supplementary Fig. S1b. It was of interest, whether exposure of hydrophilic or hydrophobic samples to the high humidity atmosphere for several minutes affects the contact angle results. This possible influence was examined by measuring the SCA on one half of the sample, removing the droplets without contamination of the remaining sample area, storing the sample for 15 min in the water filled cell set up and measuring the contact angle afterwards on the other half. The experiment was repeated three times for each wetting state and Fig. 9b shows the results before and after exposure to the high humidity atmosphere. A hygrometer included in the chamber displayed a relative humidity of 75–80% at 22 °C in an additional experimental run.

The hydrophilic samples show a reaction to the high humidity atmosphere: After 15 min of storage in the glass cell the average SCA drops by 4% and is accompanied by a pronounced scattering of the single measurements. Shchedrina et al.⁷⁰ argue that high humidity atmospheres may stop the organic carbon adsorption. Regarding the results in Fig. 9b this would not explain, why hydrophilic samples become more hydrophilic in the high humidity atmosphere. We believe that due to the hydrophilic character of the samples the surface reacts with the water molecules in the saturated atmosphere of the glass cell and a molecular water film forms on the surface. This creates a polar layer of water molecules resulting in a more hydrophilic behavior of the samples. Freund et al. showed⁷¹ that especially hydrophilic samples are prone to water film adsorption. They were only able to measure the thickness of the adsorbed film up to a relative humidity of 50% due to the meniscus forming. Extrapolation showed an expected film thickness of more than 140 nm at 80% relative humidity. The mechanism of water adsorption on metal surfaces is very complicated and influenced by different thermodynamic and kinetic parameters as the water does not form simple films consisting of water molecules on the surface, but might rather be prone to dissociation influenced by pre-absorbed oxygen^{72–74}. On oxidized copper surfaces a molecular water adsorption could only be observed after a monolayered OH-film had formed⁷⁵. In contrast, the hydrophobic samples do not seem to show any reaction with the water molecules in the surrounding atmosphere as the organic carbon contamination layer repels the water from the atmosphere and the sample keeps its hydrophobic SCA. For hydrophobic surfaces Freund et al.⁷¹ found out a reduced reaction with water below 50% relative humidity, but a slightly increased layer growth around 80% humidity of 50 nm with strong scattering. We believe that for the hydrophobic samples prolonged storage time in high humidity atmospheres would be necessary for the evolving thin water film to show any effect on the measured SCA. For low humidity around 2% barely any water film could be detected⁷¹ suggesting that the two week storage of the wrapped samples with silica gel beads suppressed the formation of a water layer and allowed the samples to adsorb the aliphatic carbon groups responsible for the hydrophobic behavior.

While for stable wetting states like fully aged hydrophobic samples exposure to high humidity atmospheres does not seem to influence the contact angle, metastable samples regarding wettability and surface composition might be influenced by a saturated atmosphere. An extended study focusing on the influence of different humidity levels on the adsorbate layer and therewith on the resulting contact angle would be necessary to quantify these effects.

The experiment conducted in Fig. 9 shows that the setup introduced by Drelich²³ can be applied to hydrophobic samples but must be handled with care if the wetting behavior of the sample is still unknown or a hydrophilic behavior is expected.

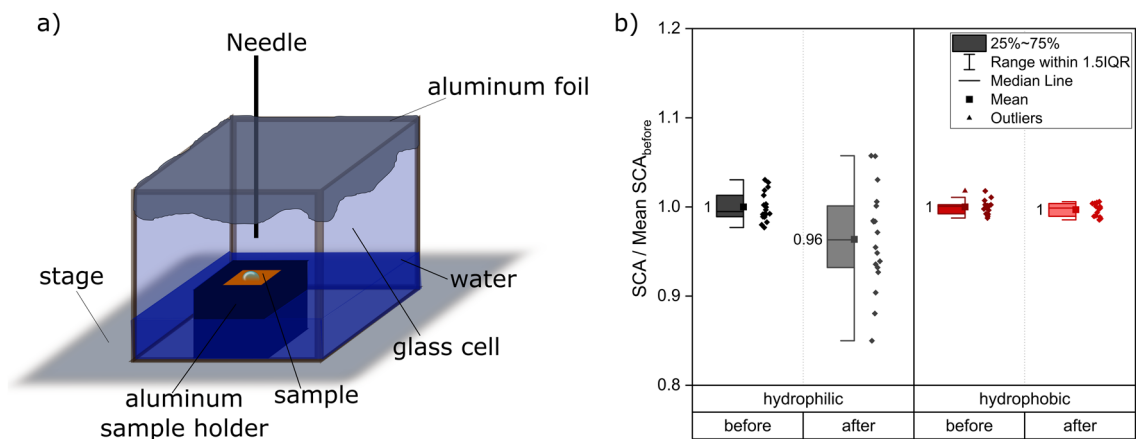


Figure 9. (a) Schematic of an experimental setup to avoid droplet evaporation as suggested by Drelich²³. (b) Contact angle of hydrophilic and hydrophobic samples before and after 15 min of exposure in setup (a). The experiments were repeated on three samples for the hydrophobic wetting condition with five droplets each and on four samples for the hydrophilic wetting condition as some samples could only fit four droplets due to the enhanced spreading. The reference data for normalization is “before”. For both wetting types a separate normalization was carried out.

Time of measurement. Once the droplet is applied on the surface under investigation, the change in contact angle with time must be considered. As mentioned in Ref.²², it can take some time for a droplet to reach a stable state on the surface but at the same time droplet evaporation is continuously decreasing the contact angle.

Figure 10 shows the development of the SCA and volume during evaporation of a 3 μ l water droplet under ambient conditions (“atmosphere”), with increased surrounding humidity produced by droplets placed next to each other (“adjacent droplets”) and wet lens paper placed underneath the sample (“lens paper”). In general, the hydrophilic surface (Fig. 10a) shows a more pronounced reduction of the SCA under all conditions compared to the hydrophobic sample in Fig. 10b. In contrast, the reduction of droplet volume is similar for both sample types suggesting similar evaporation rates, independent of the initial wetting behavior of the surface. The hydrophilic samples seem to follow the constant-contact-radius evaporation mode introduced by Picknett and Bexon^{76,77} with a strong decrease of the SCA through evaporation. For the hydrophobic samples, the contact area between water and substrate might be subjected to a stronger reduction. For both sample wetting states the placement of adjacent droplets reduces the evaporation and therewith the reduction of the SCA and the volume effectively. A wet lens paper placed underneath the sample reduces the effect of evaporation even more. These two examples suggest that a high humidity micro-atmosphere created in immediate vicinity of the analyzed droplet can effectively reduce the negative effect of droplet evaporation on the measurement of SCAs without exposing the sample to the saturated atmosphere for several minutes before the measurement can take place.

Modern contact angle devices offer climate chambers to saturate the atmosphere and therewith avoid droplet evaporation. These chambers can be very expensive and especially for self-built contact angle devices hard to adapt. Moreover, as shown in Fig. 9, the exposure of surfaces to high humidity atmospheres before the measurement might alter the measured SCA depending on the initial wetting state of the sample. Therefore, we aimed at constructing a setup that allows for a suppression of droplet evaporation by creating a saturated micro-atmosphere around the droplet after droplet application. This is realized by a small cover fabricated out of glass or aluminum with glass inlets to allow for droplet acquisition after covering the sample. Additional sources of water under the cover should be provided either as small aluminum basins filled with water or by wet cotton placed next to the sample once all droplets are applied. A construction plan for a rotatable sample stage already equipped with integrated basins, together with a plan for an aluminum cover can be found in Supplementary Fig. S1c,d together with photographs of the setup (e and f). Schematics of the setup with experimental results to prove its success in the reduction of droplet evaporation are displayed in Fig. 11.

The reduction of the SCA after ten minutes is 0.3% for the hydrophobic samples and 0.6% for the hydrophilic samples. The volume is reduced by 0.7% and 0.5% respectively. These reductions are in the range of the standard deviation of the three measurement replicates and therewith negligible. The cover method displayed in Fig. 11 therewith successfully suppresses droplet evaporation as no relevant changes in the SCAs can be observed even after 10 min and allows for an observation of the SCA for several minutes, which can be especially important for patterned surfaces¹¹.

For the experiments in Fig. 11 single droplets were applied on the surface and measured. In a detailed wetting analysis, multiple droplets usually are applied on the surface for statistical reasons and results are averaged. In that case for the “cover”-method all droplets must be applied before covering the sample, which should be done as quickly as possible to avoid evaporation. To assess the applicability of the setup under such real wetting analysis conditions, six droplets per sample were applied and measured right after droplet application and one minute and three minutes after droplet application. The first measurement 2 s after droplet application took place without the cover. Afterwards the sample was covered, and the remaining measurements (1 and 3 min) were conducted. The first droplet applied showed a reduction in droplet volume as it was exposed to the atmosphere without the cover for the longest time of all droplets. Therefore, the first droplet was not analyzed and served

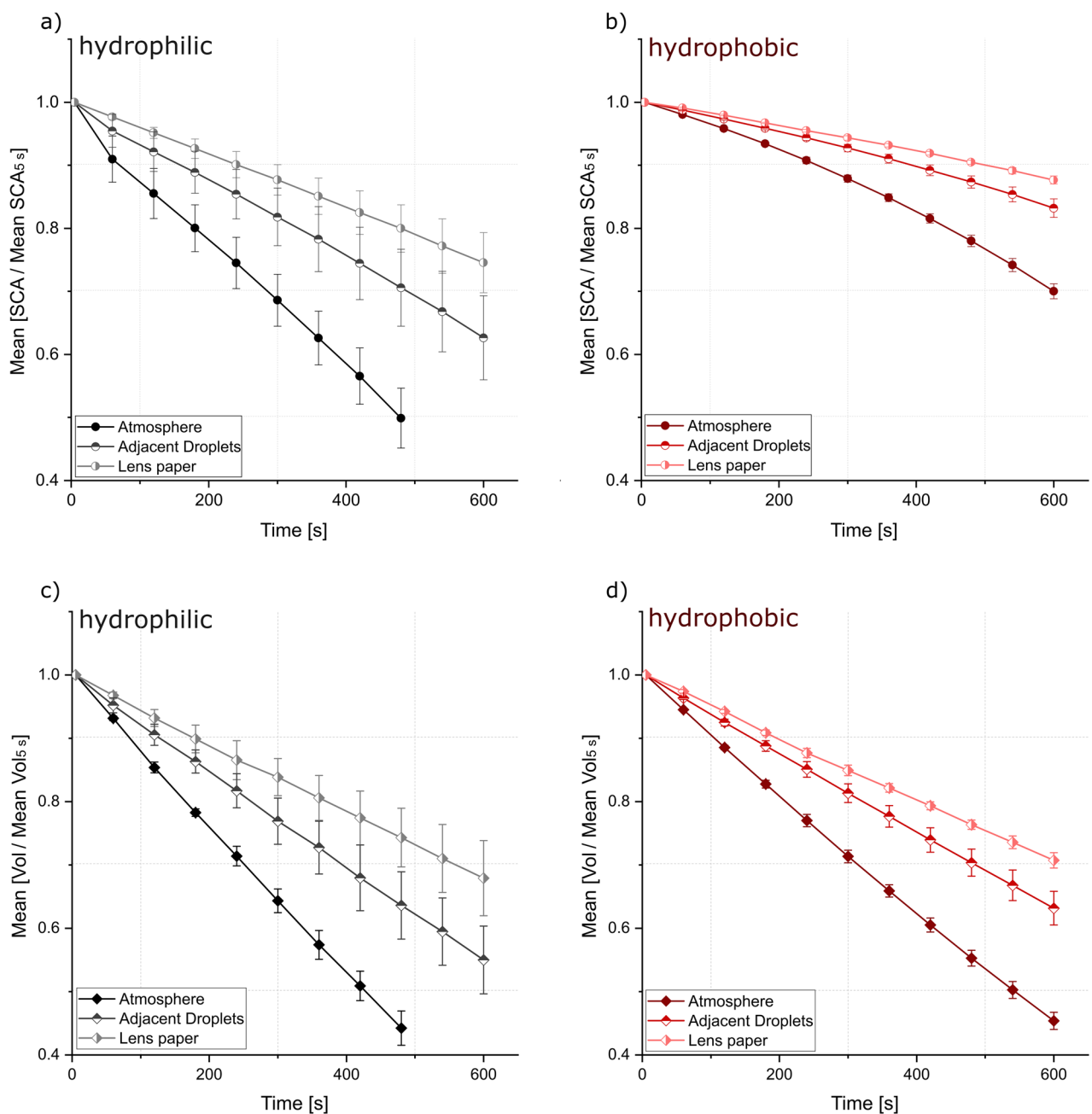


Figure 10. Change of the contact angle and volume for hydrophilic (a,c) and hydrophobic (b,d) copper surfaces through evaporation of 3 μ l droplets under atmospheric conditions (Atmosphere), with adjacent droplets (Adjacent Droplets) and with wetted lens paper (Lens paper). Each experiment was repeated three times on different samples. Data for normalization is the contact angle/volume five seconds after droplet application. For better data visualization the normalized data for each of the three samples was averaged for every time step. Error bars show the standard deviation.

only as an adjacent droplet for the following ones which can further suppress evaporation as shown before in Fig. 10. Normalized results for the SCA and the volume are summarized in Fig. 12.

No relevant decrease in the SCA or the volume could be observed. The SCA of the hydrophilic samples decreases by only 1% while no change can be observed for the hydrophobic samples. On the hydrophilic samples, spreading is more likely to occur and could be a possible reason for the slight decrease of the SCA. The volume is reduced for both wetting types by 1%. The mentioned reductions are again below the typical standard deviation of multiple measurements. The conducted measurements prove that the newly presented “cover”-method is applicable in the wetting analyses for an observation of contact angles and droplet volume throughout several minutes. The “cover”-method aims at droplet application under ambient atmosphere, which is the relevant setup for any application. The cover design and combination with additional water sources next to the sample allows for

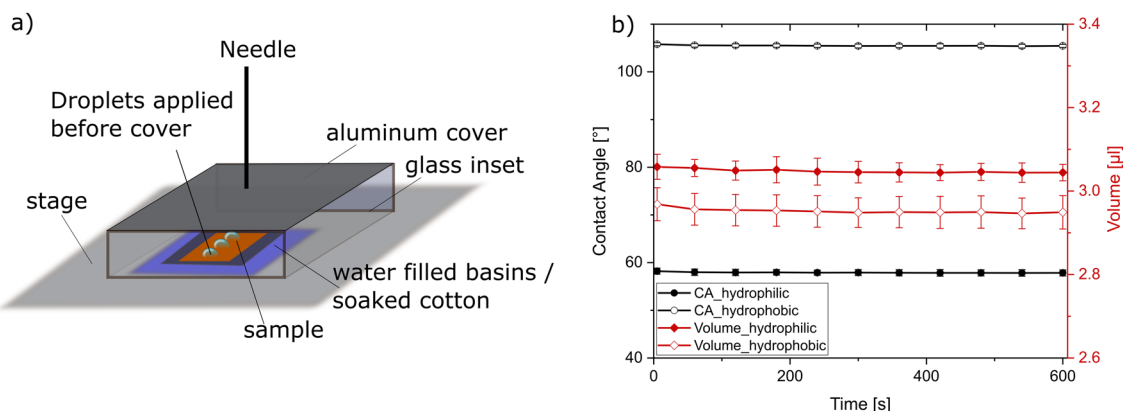


Figure 11. Schematic overview of the “cover”-setup (a). Change of the contact angle and the droplet volume, (b) over time with the designed setup (a). Each experiment was repeated three times on different samples.

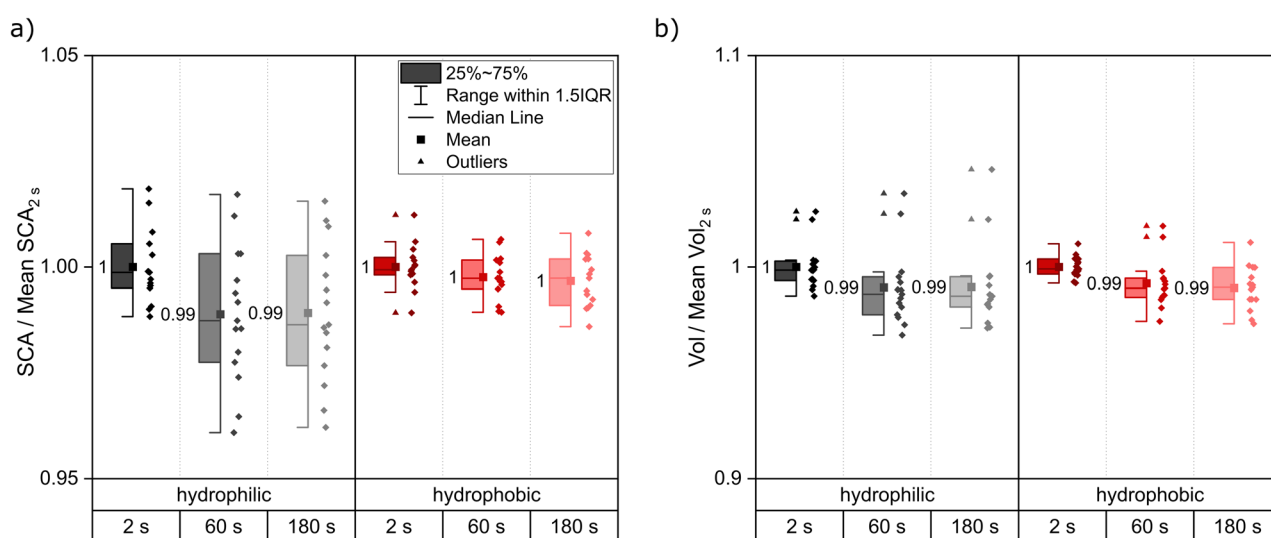


Figure 12. Static contact angle measurements with 3 μl of water. Five droplets per sample were analyzed on three samples each for both wetting states. Static contact angle (a) and volume (b) were measured 2 s, 60 s and 180 s after application. The reference data for normalization is “2 s”. For both wetting types a separate normalization was carried out. No significant differences were observed between the different measurement times suggesting stable measurement conditions.

a saturation of the atmosphere and therewith the observation of time dependent contact angle/droplet spreading behavior without exposure of the surface to high humidity before droplet application.

Conclusions

This paper provides collected information on the possible influences on SCA measurements, which is the main method to analyze the wetting behavior of various materials and shows best practice examples as an approach towards reproducible SCA measurements in literature. Sample induced influences like preparation, cleaning and storage were discussed and experiments showed the extent of their influence on contact angle results for hydrophilic as well as hydrophobic samples. The two different wetting states were achieved by different storing conditions and times. Cellulose based wrapping paper proved to act as a carbon donor for the hydrophobization of copper surfaces.

For sample induced influences, a universal and objectively correct procedure is hard to be established. Therefore, it is in the responsibility of the researcher to provide defined sample states by controlling sample preparation, storage, and cleaning to ensure comparable conditions. In contrast, for the methodology of SCA measurements like applied droplet volume, application method, surrounding humidity and time of measurement clear experimental guidelines are necessary to ensure comparability of different studies. The quality of the water used for the measurement only showed an effect on the hydrophilic samples, where a stronger interaction with the substrate is assumed in contrast to the hydrophobic samples with a more pronounced protection layer of adventitious carbon. Increasing the droplet volume from 3 to 6 μl already decreases the contact angle due to gravity effects. We recommend dosing 3 μl of purified water as a standard measure between larger volumes that are influenced by gravity and lower volumes that might be heavily distorted by the needle²². However, sample surface condition

must be considered especially for topographically or chemically heterogeneous surfaces as the droplet should be large enough to equal out local inhomogeneities²⁵. It was further shown that droplet application can either be conducted by the needle approaching the sample until the droplet wets the surface or by the stage picking up the droplet. Pipetting of droplets should only be performed, if needle and stage application are not possible as the enhanced pressure applied by the researcher can lead to droplet spreading and smaller SCAs especially on hydrophilic samples. The presented results show that evaporation affects the contact angle results drastically within a few minutes. Hence it is important to perform measurements as quickly as possible after droplet application if no measures are taken to suppress evaporation. Still, a few seconds are needed to balance out vibrations from droplet applications - 5 s proved useful here. If evaporation is to be reduced e.g., for the time dependent observation of the droplet, placing a wet lens paper underneath the sample can be helpful. If a longer observation of the droplet is desired to, for example examine spreading behavior or to allow for the droplet to reach a stable wetting state, evaporation should be controlled. Exposing samples to a saturated atmosphere before droplet application as suggested by Drelich²³ proved to potentially influence the contact angle for hydrophilic samples. Aged hydrophobic samples did not show a visible reaction to the high humidity. In general, the conducted experiments showed that hydrophobic samples seem most robust against environmental influences. It is believed that this is due to the adventitious carbon layer covering the substrate and acting as a protection against environmental influences. To avoid any possible influence of droplet evaporation or high humidity exposure, this paper demonstrates a new measurement setup allowing for droplet application under atmospheric conditions often equal to sample storage conditions and therewith offers the chance to correlate results to other measurements like XPS. Covering the applied droplets after application in the shown setup appears reliable in terms of reproducible contact angle measurements. This study not only discusses possible influences on the analyses of wetting properties, but also experimentally proves the extent of the effects and gives clear advice for setting the measurement parameters. The newly introduced “cover”-method allows for a droplet application under atmospheric conditions and an observation of the wetting behavior for several minutes by successfully suppressing droplet evaporation.

Data availability

Data is available upon reasonable request from the corresponding author.

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Author contributions

S.M.L. conceived the idea for the manuscript and conducted sample preparation, the wetting experiments, data analyses and interpretation. The manuscript was written by S.M.L. R.M. conducted XPS measurements and interpreted the XPS and TOF-SIMS findings and also supported with paper writing. D.W.M. assisted with discussion and proofreading. M.K. and F.M. oversaw the project.

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Competing interests

The authors declare no competing interests.

Additional information

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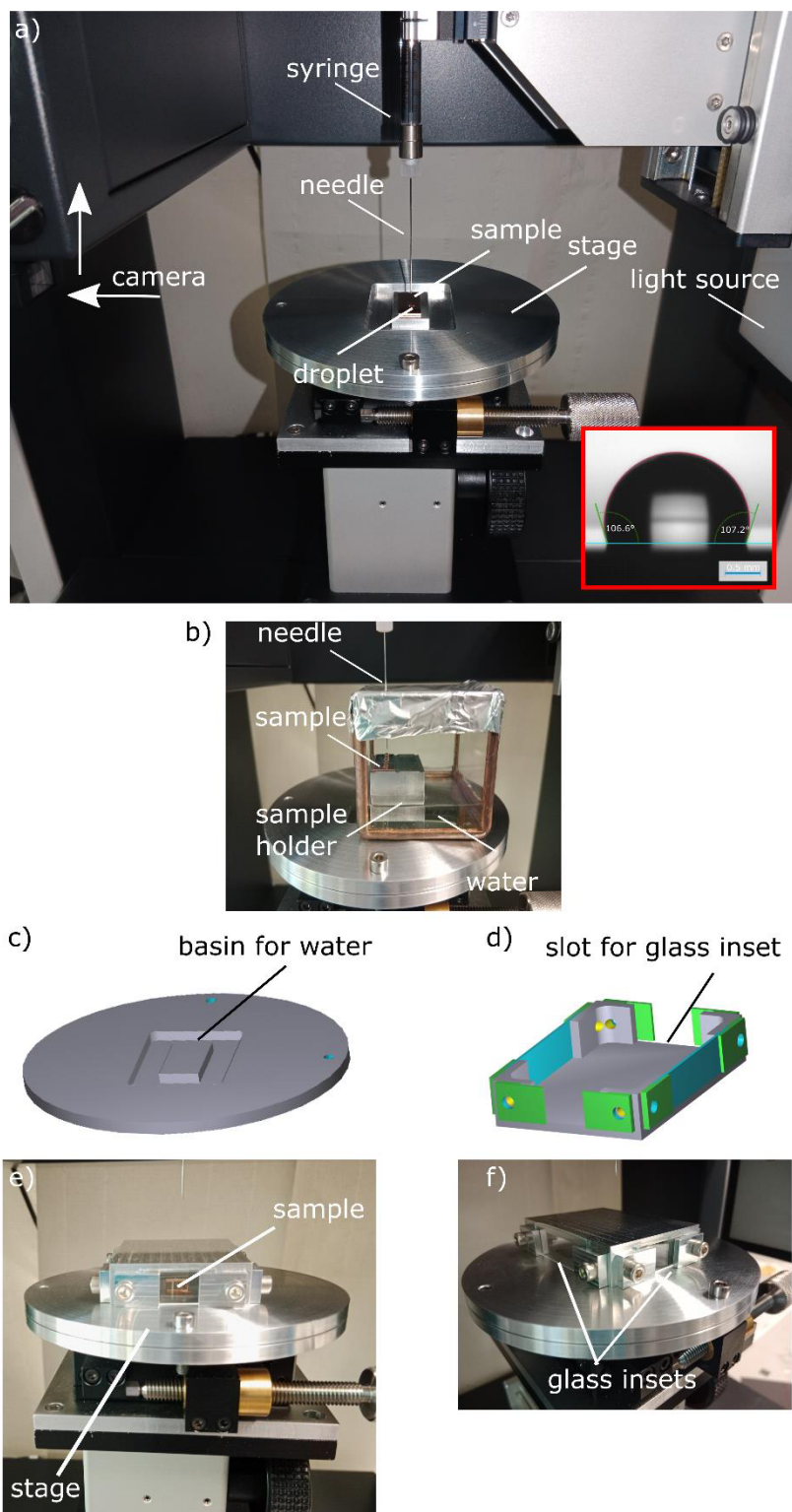
Supplementary Material

An in-depth Evaluation of Sample and Measurement induced Influences on Static Contact Angle Measurements

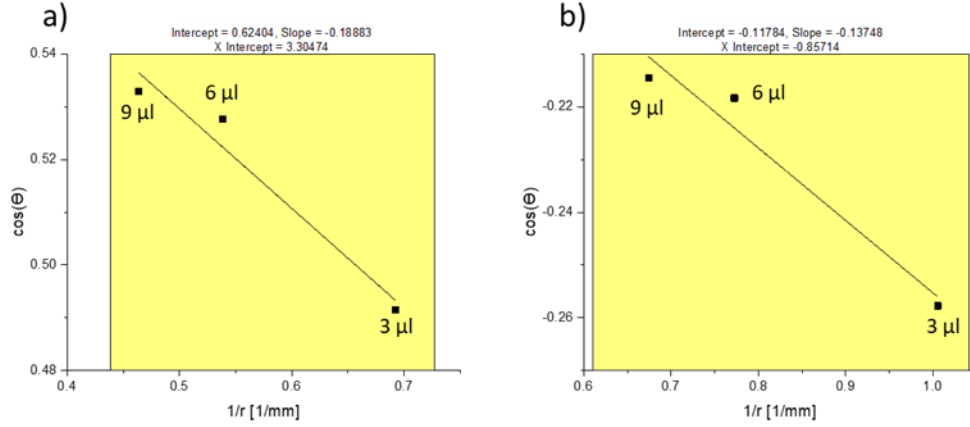
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Supplementary Figure S1: (a) Photograph of the experimental setup used for static contact angle measurements on a *Krüss DSA 100*. The inset shows a recorded image of a droplet applied on a hydrophobic copper surface with an ellipse fit in the *Krüss Advance* software. (b) Photograph of the experimental setup suggested by Drelich¹ to suppress droplet evaporation. (c) CAD-file of an aluminum stage for static contact angle measurements with milled basins for water. (d) CAD-file of an aluminum cover with slots for glass insets. Sizes should scale with sample size keeping the cover height and width as small as possible and the basins as big as possible. (e, f) Photographs of the stage filled with water and droplets placed on a copper sample covered with the designed aluminum cover.



Supplementary Figure S2: Cosine of the averaged SCA for hydrophilic (a) and hydrophobic (b) samples over the inverse droplet radius as a measure for line tension. For both wetting types a linear correlation can be assumed supporting the thesis of a constant line tension and therewith independence of the shown droplet volumes ².

Supplementary Table S1: Example for calculation of sample wise data normalization for three samples (α , β , γ) with three applied droplets each. Three images were taken from each droplet averaging to the SCA of the droplets. The mean of these individual SCAs on the reference samples delivers the *Mean SCA_{Reference}* (per sample). Whenever possible, on the same sample, the parameter under investigation was applied and new droplets were measured (SCA). The normalized data was calculated by dividing SCA by *Mean SCA_{Reference}* of the respective sample.

Sample	Reference				Measurement				Normalized Data
	Single image SCA			SCA	Single image SCA			SCA	
α	a ₁	a ₂	a ₃	Mean [a ₁ ;a ₂ ;a ₃] = a	A ₁	A ₂	A ₃	Mean [A ₁ ;A ₂ ;A ₃] = A	A/x
	b ₁	b ₂	b ₃	Mean [b ₁ ;b ₂ ;b ₃] = b	B ₁	B ₂	B ₃	Mean [B ₁ ;B ₂ ;B ₃] = B	B/x
	c ₁	c ₂	c ₃	Mean [c ₁ ;c ₂ ;c ₃] = c	C ₁	C ₂	C ₃	Mean [C ₁ ;C ₂ ;C ₃] = C	C/x
	Mean SCA _{Reference} = Mean [a;b;c] = x								
β	d ₁	d ₂	d ₃	Mean [d ₁ ;d ₂ ;d ₃] = d	D ₁	D ₂	D ₃	Mean [D ₁ ;D ₂ ;D ₃] = D	D/y
	e ₁	e ₂	e ₃	Mean [e ₁ ;e ₂ ;e ₃] = e	E ₁	E ₂	E ₃	Mean [E ₁ ;E ₂ ;E ₃] = E	E/y
	f ₁	f ₂	f ₃	Mean [f ₁ ;f ₂ ;f ₃] = f	F ₁	F ₂	F ₃	Mean [F ₁ ;F ₂ ;F ₃] = F	F/y
	Mean SCA _{Reference} = Mean [d;e;f] = y								
γ	g ₁	g ₂	g ₃	Mean [g ₁ ;g ₂ ;g ₃] = g	G ₁	G ₂	G ₃	Mean [G ₁ ;G ₂ ;G ₃] = G	G/z
	h ₁	h ₂	h ₃	Mean [h ₁ ;h ₂ ;h ₃] = h	H ₁	H ₂	H ₃	Mean [H ₁ ;H ₂ ;H ₃] = H	H/z
	i ₁	i ₂	i ₃	Mean [i ₁ ;i ₂ ;i ₃] = i	I ₁	I ₂	I ₃	Mean [I ₁ ;I ₂ ;I ₃] = I	I/z
	Mean SCA _{Reference} = Mean [g;h;i] = z								

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Paper 3

The Influence of Adventitious Carbon Groups on the Wetting of Copper: A Study on the Effect of Microstructure on the Static Contact Angle

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Writing – original draft, Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization.

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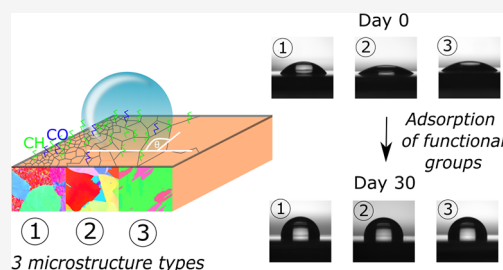


Article Recommendations



Supporting Information

ABSTRACT: Tuning of the wetting behavior of metallic surfaces by chemical and topographical modification has become popular in recent years. Still, there is a lack in the understanding of fundamental relations between intrinsic properties of the material and its resulting water contact angle. It is widely accepted in the literature that transitions from a hydrophilic to increasingly hydrophobic behavior upon exposure to ambient conditions happen due to the adsorption of adventitious hydrocarbons. In order to investigate the role of metallic bulk microstructure in the wetting behavior and its transition properties, we created three different grain sizes and deformation states on copper by preparation combined with heat treatment. We found that for freshly prepared surfaces, differences in the wetting behavior show a higher static contact angle for mechanically prepared surfaces with a fine-crystalline deformation layer compared to the electropolished cold-rolled copper sheet and the annealed defect-free coarse-grained surface. Already after five days of storage time, most of this difference vanishes, and all surfaces show a wetting behavior with a contact angle in the range of 97–100° after 30 days. Though long-term wetting behavior seems largely independent of microstructure, correlated XPS measurements showed an increased adsorption of organic contaminants of the mechanically polished surface. Preparation-induced near-surface defects seem to accelerate adsorption, while varying grain size and slight bulk deformation from rolling processes did not show significant effects. Complex relations between the amount of adsorbed carbon and the polarity of the adsorption film were found to depend on the sample age and influence the contact angle.



INTRODUCTION

The wetting properties of surfaces are crucial for a wide range of applications, e.g., for filtering^{1–3} and corrosion.^{4,5} Lubrication and tribology are also greatly influenced by the wetting behavior,^{6–8} which can lead to anisotropic spreading of lubricants in combination with surface roughness.^{9–11} Recently, the development of surfaces with certain wetting characteristics has also gained attention for the design of antimicrobial surfaces.^{12–14} Especially, topography modification by laser treatment is widely applied to tune the contact angle of technical surfaces.^{15–20} Achieved wetting states range from hydrophilic with a static contact angle (SCA) smaller than 90° to hydrophobic (SCA > 90°) or even superhydrophobic (SCA > 150°, small contact angle hysteresis).²¹ Also, the freezing behavior and the production of anti-icing surfaces pose a challenge that researchers have focused on.^{22,23} This proves that a wide range of application-oriented studies has been conducted to successfully implement a certain wetting behavior on surfaces needed for the respective use. Still, there is a lack of understanding the fundamentals leading to the resulting wetting behavior. Understanding the different wetting phenomena on metallic surfaces has been a challenge in science for many years. In general, the Young equation²⁴ describes the contact angle of an ideally flat surface in

dependence of the surface energy between the droplet, the solid substrate, and the gas phase surrounding the system. As technical surfaces can only approximate an ideal surface as they always depict a certain roughness, Wenzel²⁵ as well as Cassie and Baxter²⁶ proposed theories for the wetting of rough surfaces either by the liquid penetrating the surface topography in the Wenzel state or by encapsulating air pockets between the liquid and the substrate in the Cassie–Baxter wetting state. In reality, a clear distinction between both can be difficult due to metastable transition states.^{27,28} It is accepted in the literature that the adsorption of hydrocarbons from ambient air leads to a decrease of surface polarity and surface energy with time and an increase in SCA.^{29–31}

Though previously conducted studies aimed at finding correlations between surface topography, chemistry, and the wetting behavior,^{15,32} little attention was paid to the intrinsic substrate properties like microstructure and deformation and

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how they influence the SCA. Microstructure can refer to different properties depending on the material under investigation. For cast iron, the graphite content can be a parameter to alter microstructure: Behera et al.³³ investigated the influence of the microstructure of an iron-graphite composite on the contact angle by means of varying graphite nodule contents and showed an increase of the SCA with the graphite content. Riahi et al.³⁴ on the other hand kept the composition of their cast iron constant but varied the roughness and cast iron type (gray vs white) and found different dependencies of the SCA on preparation methods for both types. They observed an increase in SCA by ambient air exposure due to growing surface layers but did not conduct further characterizations. They also cleaned their surfaces in an ethanol ultrasonic bath before SCA measurements, which can influence SCAs.³⁵ Dasgupta et al.³⁶ observed an increase in surface energy with decreasing grain size of sintered hydroxyapatite compacts and therefore stronger wettability. The effect of the grain size of copper serving as a substrate for nickel film electrodeposition revealed a more hydrophilic behavior of the nickel film deposited on bigger copper grains. This was traced back to an indirect influence of the substrate grain size as the deposited nickel films were more homogeneous on the smaller copper grains.³⁷ Noorbakhsh Nezhad et al.³⁷ also mentioned adsorbed hydrocarbons as a source for wetting differences. On copper thin films, Platzman et al.³⁸ found higher contact angles on annealed films with less defects and grain boundaries and therefore expected reduced surface energy. Only a few details on the measurement were given, and it remains unclear if the adsorption of adventitious carbon groups plays a role in the observed grain size dependency of the contact angles. Also, roughness differences between the sputtered films must be considered.

Though some of these studies consider the effect of grain size on the resulting contact angle and wetting behavior, no detailed investigation was conducted also taking the dynamics of (hydro)carbon adsorption into account to the best of our knowledge. For application purposes, the wetting behavior of aged samples in contact with ambient air is relevant as freshly prepared surfaces can hardly be conserved without native oxidation and possibly adsorption of functional carbon groups.

In this study, we investigated the effect of microstructure involving grain size, deformation, and defects on the development of the water SCA in the long-term wettability of polycrystalline bulk copper. Near-surface defects were incorporated by mechanical polishing. The slightly bulk-deformed microstructure of the as-received copper sheet was exposed by electropolishing. High-temperature heat treatment was applied to significantly alter the defect state and grain size therewith reducing grain boundary density.

These three strongly different microstructure types are analyzed by microscopic and crystallographic characterization. The wetting behavior is assessed by SCA measurements and correlated with XPS analysis in order to observe microstructure dependencies of the carbon adsorption process, therewith providing an extensive overview of the fundamental relations between bulk microstructure and wetting development. As for the copper–water interaction, long-ranged van der Waals forces are of importance;^{39,40} it was of interest how strong differences in microstructure affect the interface properties in the presence of adsorbate layers and if the observations made by Platzman et al.³⁸ with a more hydrophilic behavior of

nonannealed copper thin films can be transferred to our copper bulk material.

EXPERIMENTAL SECTION

A cold-rolled sheet of oxygen-free copper ($\geq 99.95\%$ Cu, CW008A, Wieland) of 1 mm thickness was cut into 10 mm $\times$ 25 mm coupons. The samples were divided into three groups: Group one was polished to a mirror finish following the routine presented in ref 41, where also images of the surfaces after the different polishing steps can be found. The final 1 μ m step had to be repeated twice in order to achieve the portrayed smooth surfaces. Sample cleaning was conducted with desalinated water and ethanol; details can be found in the [Supporting Information](#) for all sample types. Samples were dried by an ambient air stream from a fan to avoid oil contamination from compressed air.⁴² For the second sample group, polishing was followed by electropolishing in 85% *ortho*-phosphoric acid (Grüssing GmbH) with the setup presented in ref 41 for 20 min at 1.5 kV to remove deformation layers previously induced via mechanical polishing with subsequent cleaning. The third group of samples underwent a strong heat treatment after mechanical polishing (pressure below 10^{-4} mbar; heating: 1 $^{\circ}$ C/min; annealing: 12 h at 900 $^{\circ}$ C; cooling: 1 $^{\circ}$ C/min). In ref 41, an image of the annealed surface before polishing can be found. The samples were then mechanically polished again and finally electropolished in the abovementioned setup for 40 min. Cleaning was performed analogous to the other sample sets. The three sample types were named according to their preparation: MP for the mechanically polished samples, EP for the electropolished samples, and AEP for the high-temperature annealed (A) electropolished (EP) samples. As shown in an earlier work, MP copper samples agglomerate functional carbon groups on their surface by contact to the atmosphere.³⁵ To ensure reproducible conditions, all samples were stored under the same conditions by controlling the contact material and atmosphere. Details can be found in the [Supporting Information](#). Samples were stored for 5, 10, 20, or 30 days. For each measurement day, a new storage box was prepared. The wetting behavior of the different samples was characterized by static contact angle measurements on a Krüss DSA 100 equipped with a 100 μ L Hamilton syringe. Prior to the measurement, the samples were again cleaned with an ambient air stream by a fan to remove dust particles. A droplet volume of 3 μ L of purified water (Thermo Fisher Scientific, HPLC gradient grade, conductivity of <1 μ S/cm) was applied, and images of the droplets were taken directly after application as well as one minute and three minutes after deposition. Droplet deposition was conducted at atmospheric conditions (22 ± 1 $^{\circ}$ C; $43 \pm 5\%$ relative humidity). To avoid droplet evaporation, the samples were covered with a small glass cover, and wet cotton was placed next to the samples as additional water sources for atmosphere saturation underneath the cover after droplet application. Details on the cover method and its successful suppression of droplet evaporation can be found in an earlier work.³⁵ Measurements were conducted on three samples per type with five droplets each for statistical purpose. Details on average calculation can be found in the [Supporting Information](#). Droplets breaking out of a regular shape that did not allow for correct contour fitting were not considered in mean value calculation.

Topographic characterization of the samples was conducted by confocal laser scanning microscopy on an Olympus LEXT OLS4100.

Surface analysis was complemented by scanning electron microscopy using a FEI Helios FineLab600 FIB (5 kV, 1.4 nA). For focused ion beam (FIB) characterization, a protective platinum layer was deposited on the samples first to avoid surface damage by the 30 kV gallium ion beam.

Microstructural characterization was conducted by electron backscatter diffraction (EBSD) using a fast CMOS detector (EDAX Velocity Plus with EDAX Apex 2.0) for large-area montage mapping and a CCD detector (EDAX Hikari with OIM Data Collection v7) for conventional maps. An acceleration voltage of 20 kV was used. Details on the step sizes are given in the results section with the respective maps. The grain size was determined with OIM Analysis v7 software,

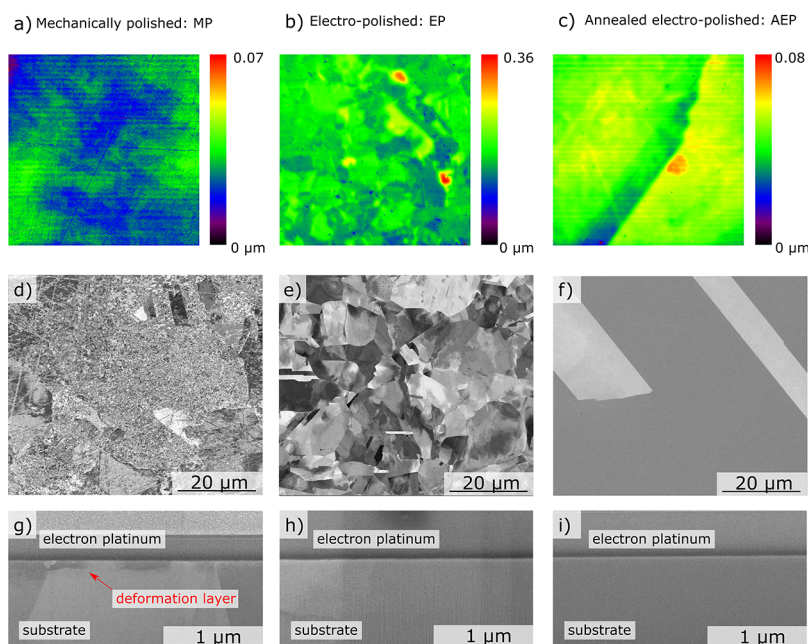


Figure 1. Optical characterization of the three sample types. Height information of an MP sample (a), an EP sample (b), and an AEP sample (c). Mechanical polishing reduces the roughness (a), while electropolishing results in a stronger topography due to the exposure of the sheet microstructure (b). Annealing enhances the grain size giving a flat surface after electropolishing (c). Electron backscatter SEM contrast of an MP sample (d), an EP sample (e), and an AEP sample (f). The MP samples show the fine-crystalline deformation layer, while after electropolishing, the sheet microstructure with its deformation is visible. Annealing leads to massive grain coarsening and a reduction of deformation. FIB cross sections of an MP sample (g), an EP sample (h), and an AEP sample (i). The deformation induced by mechanical polishing is only visible at the platinum copper interface of the MP sample.

where grains intersecting the margin of the scan were not included in the calculation. The grain tolerance angle was set to 5° .

For near-surface chemical characterization, X-ray photoelectron spectroscopy (XPS) was conducted linked to the static contact angle measurements on day 5, 20, and 30. Samples measured with XPS were prepared on the same day and in the same sample batch as the corresponding samples for wetting characterization. Samples were as well packed analogous, but an extra airtight box was used for the XPS samples due to sample transportation. XPS measurements were conducted with an Axis Nova spectrometer manufactured by Kratos Analytical Ltd. Three spots of $350 \times 700 \mu\text{m}^2$ per sample were analyzed with monochromatic Al $K\alpha$ of 1486.6 eV. The detector was positioned perpendicular to the sample surface. For the overview spectra, a pass energy of 160 eV was applied and reduced to 20 eV for the detection of the detailed spectra. Elemental concentrations were calculated by means of standard sensitivity factors provided by the manufacturer. Depending on the detected elements and the substrate, the information depth in XPS varies between 3 and 5 nm.⁴³

RESULTS AND DISCUSSION

Surface Characterization. The topography of the different surfaces measured by LSM is shown in Figure 1a–c. The MP sample shows slight topography resulting from the final 1 μm polishing. The BSE contrast in Figure 1d shows scratches and the fine-crystalline deformation layer resulting from the mechanical polishing. The structure of layers on mechanically polished copper was already characterized in 1981 by Turley and Samuels who observed a combination of “slab-shaped cells”, “very small subgrains”, and “recrystallized grains” after diamond polishing.⁴⁴ The FIB cross section below shows the spread of the deformation layer from the surface into the bulk material. Electropolishing successfully removes this deformation layer and reveals the microstructure of the cold-rolled copper sheet. Schreiber et al.⁴⁵ showed an orientation-

dependent dissolution of iron grains during electropolishing. Similar effects might be occurring on the copper samples depending on the polishing procedure and were already witnessed in ref 41. The BSE contrast in Figure 1e does not only reveal the individual grains but also their slight bulk deformation introduced by the cold-rolling process. The electropolishing process successfully removed the deformation layer as shown in Figure 1h. The AEP sample (Figure 1c, f, and i) shows a smooth surface finish only interrupted by microstructural features displaying different removal in the electropolishing process. The BSE contrast shows that the deformation layer has been completely removed by electropolishing and only exhibits considerably enlarged grains. Also, the FIB cross section shows a clean interface without any visible deformation. Laser scanning microscopy was also applied to measure the surface roughness S_a for three images of each sample type. The MP sample displays a roughness of $3 \pm 0.8 \text{ nm}$ and therewith is in a similar regime to the AEP sample with $5 \pm 0.8 \text{ nm}$. As discussed earlier, the EP sample shows the greatest roughness with $14.7 \pm 1.3 \text{ nm}$. The surface enlargement was determined by the S-ratio and resulted in 1 ± 0 for all sample types.

Figure 1 shows the changes in grain size and roughness induced by the three different preparation methods. To gain a deeper understanding of the resulting microstructure, EBSD inverse pole figure scans were performed on the three sample types. The scan of the MP sample reveals a poor signal due to the deformation layer that becomes visible in the higher resolved scan in the inlet in Figure 2a. Figure 2b shows the inverse pole figure maps of the EP sample conducted with the same step sizes as in Figure 2a. A clean surface free from preparation-induced deformation layers can be observed. Though it is a cold-rolled sheet, no significant grain elongation

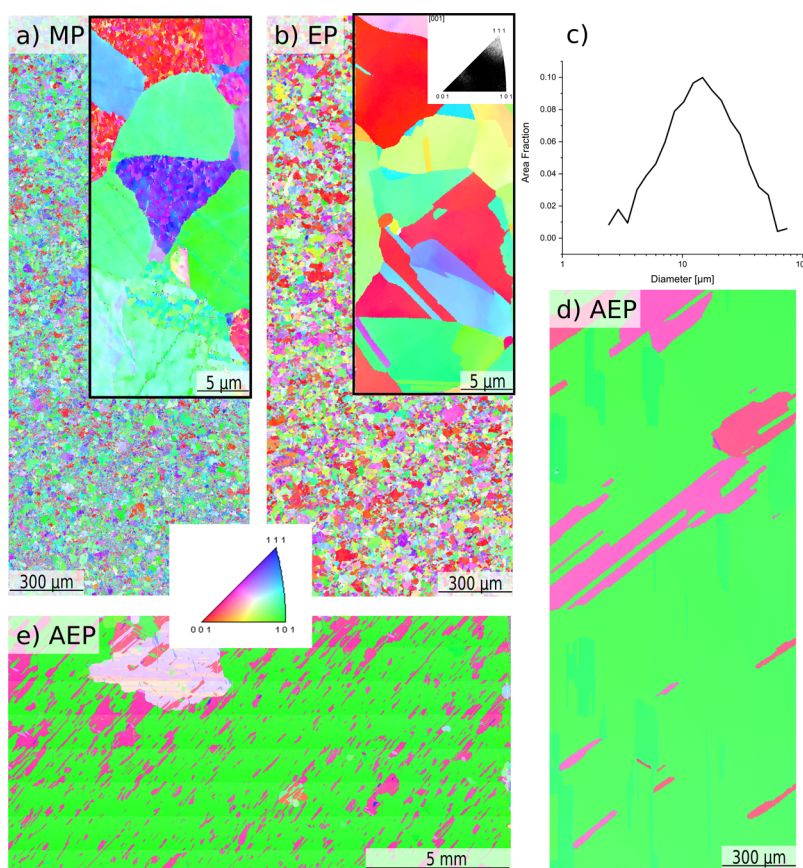


Figure 2. EBSD characterization of the three sample types. (a) Inverse pole figure map of the MP sample with a step size of $1.5\ \mu\text{m}$ showing the fine-crystalline deformation layer. The inlet was scanned with a step size of $75\ \text{nm}$ revealing surface deformation and scratches originating from the mechanical polishing process. (b) Inverse pole figure map of the EP sample with a step size of $1.5\ \mu\text{m}$ showing the microstructure of the cold-rolled copper sheet with an averaged grain diameter of $10\text{--}20\ \mu\text{m}$. (c) The inlet was scanned with a step size of $75\ \text{nm}$. (d) Inverse pole figure map of the AEP sample with a step size of $5\ \mu\text{m}$ suggesting uncontrolled grain growth. An inverse pole figure montage map of the entire sample area (e) with a step size of $10\ \mu\text{m}$ from 34×9 tiles reveals the huge grain spreading over nearly the entire sample area.

is observed, and only slight bulk deformation originating from the cold-rolling process can be seen. A dominance of the (101) and (001) orientation becomes visible. Grain size calculation showed the biggest area fraction for grains in the range of $10\text{--}20\ \mu\text{m}$ diameter. Kilpadi and Lemons⁴⁶ did not find a significant difference in surface energy for passivated titanium samples with a grain size of $23\ \mu\text{m}$ compared to $70\ \mu\text{m}$. They claimed that at the uppermost surface layer, the oxide and contaminations are present instead of the bulk material, which might be a reason for the similar surface energies. Therefore, with the high-temperature annealing, we aimed at stronger differences in grain sizes to strongly reduce grain boundaries as much as possible, which also influences the oxidation rate according to ref 38. The inverse pole figure map of the AEP sample reveals what was already visible in the BSE image in Figure 1f. A huge grain developed with some annealing twins, which are known to be formed by deformed and/or heat-treated fcc metals.^{47,48} Details on the twinning and grain growth mechanism are not in the scope of this work but can be found in the literature.^{48–50} Different samples were scanned, and all showed (101)-near orientations of this grain. During static contact angle measurements, droplets can spread over an area of multiple mm^2 .³⁵ Therefore, it was of importance to analyze the spreading of the strong grain growth over the sample area. An inverse pole figure map of the entire sample surface is portrayed in Figure 2e. It proves the formation of a

grain covering nearly the entire sample area. Only one bigger grain is left at the upper margin of the map growing from the sample edge. Since the samples were previously cut into their coupon shape, higher deformation and a different microstructure can be assumed prior to heat treatment compared to the sample center. Nonetheless, the EBSD analysis proved the success of the different preparation and heat treatment methods: A sample type with a deformed fine-crystalline layer introducing near-surface defects can be compared to the inherent microstructure of the cold-rolled sheet with grains of $10\text{--}20\ \mu\text{m}$ in diameter. The high-temperature heat treatment produced samples with a highly reduced grain number, grain boundaries, and defects as expected from the literature.³⁸

Wetting Properties. The time dependency of the wetting behavior due to the adsorption of organic molecules from the ambient atmosphere of metallic surfaces has been widely discussed in the literature, especially for laser-treated surfaces.^{12,16,51,52} Long et al.²⁹ were able to prove that for laser-patterned copper samples, storage in CO_2 did not lead to pronounced hydrocarbons on the surface and also preserved the hydrophilic properties of the surface. Storing in the vicinity of grease on the other hand strongly enhanced the adsorption, indicating that airborne organic contaminations are adsorbed on the samples during atmospheric storage. Adsorption of hydrocarbon therefore plays a major role in the wetting transition.^{29,31,51,53,54}

Recently published studies observed this transformation from an initially hydrophilic to a more and more hydrophobic behavior also on flat surfaces that did not undergo laser treatment.^{30,35} Not only the atmosphere surrounding the samples under investigation can influence the adsorption of hydrocarbons and the wetting transition. Also, sample packaging and storage play a crucial role in the transition and should be kept the very same for all samples under comparison to each other.^{35,54} Therefore, all samples, except the ones measured immediately after preparation, were wrapped in cellulose-containing cleanroom tissues and stored as described in the methods section. Figure 3 shows the results

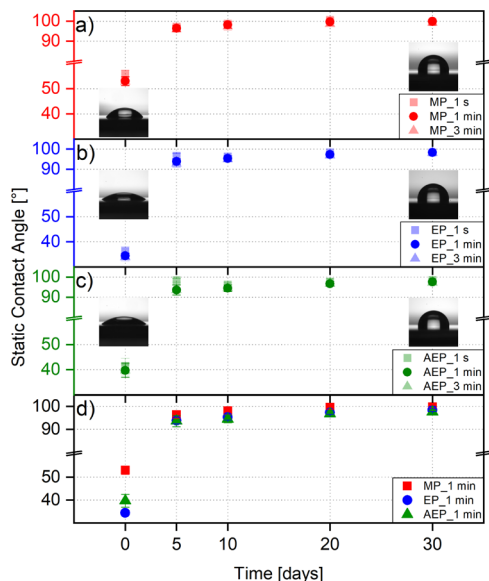


Figure 3. Static contact angle measured on the three sample types MP (a), EP (b), and AEP (c) one second, one minute, and three minutes after droplet application. In (d), the results of the three sample types one minute after droplet application are compared. Strong differences are visible directly after sample preparation with the MP sample showing a significantly higher SCA than both electropolished sample types. Throughout aging, most of the differences in SCA vanish.

of the SCA measurement conducted over a period of 30 days. Figure 3a–c gives the individual results for each sample type directly after droplet application as well as one minute and three minutes later. Measurement of the hydrophilic droplets on day 0 posed a challenge for droplet fitting as they tend to break out of a round shape. Therefore, for all droplets applied, the recognized droplet shape was checked manually, and droplets that did not show a clean fit were dismissed. With at least 7 droplets per sample type, sufficient statistics were still ensured on day 0. In addition to slight droplet spreading and the settlement of the droplet, this can also explain the minor changes in SCA directly and one/three minutes after application on the fresh samples.

Starting off with a contact angle of approximately 50°, the MP samples show a steady development toward more hydrophobic wetting behavior. Already after five days, they reach the hydrophobic state, and only gradual changes occur from day 5 to day 30. The two other sample types show a very similar development of the wetting behavior starting at hydrophilic behavior right after preparation. The (101)-dominated AEP samples show an SCA of approximately 40° right after preparation, which is in agreement with previous

findings by Korczeniewski et al.³⁰ who found an SCA of 34–52° for clean copper single crystals depending on the crystal plane via simulations. Figure 3d compares the wettability of all three sample types by displaying the SCA one minute after droplet deposition. The direct comparison unveils that shortly after sample preparation, a strong difference in the wetting behavior of the differently prepared copper samples occurs. MP samples show the most hydrophobic behavior followed by AEP samples. EP samples characterized by smaller grains and slight bulk deformation compared to AEP samples exhibit the strongest wettability. Still, the difference between EP and AEP samples is smaller than between MP and AEP. Considering the effect of grain size on the SCA, Platzman et al.³⁸ conducted experiments on sputtered copper films and found annealed films to be wetted less by water due to a reduction in surface area and energy. Annealing leads to grain growth due to energy minimization as it reduces the fraction of high energetic grain boundaries.⁵⁵ Unfortunately, only limited information on the measured contact angles was provided, and it must be considered that Platzman et al.³⁸ observed a reduction in surface roughness by the annealing procedure. Increased roughness is expected to further lower the SCA of hydrophilic surfaces.²⁵ This is true as well for the EP and AEP samples in this work, as EP samples not only have smaller grains but are also characterized by a slightly increased roughness induced by the electropolishing. Still, an increase in the surface area cannot be assessed for both sample types within the resolution of the LSM measurement indicating a negligible role of topography. Interestingly, MP samples exhibiting both the smallest grain size and the highest deformation in the near-surface region show the most hydrophobic wetting behavior right after preparation and therewith deviating from the trend observed between EP and AEP samples, which would rather indicate the most hydrophilic behavior for MP samples. It seems that the surface energy of the bulk copper surfaces might be influenced by dynamic processes like native oxidation or ambient adsorption processes. An indication is provided in the fact that already five days after sample preparation, the difference in the wetting behavior of the three sample types is greatly reduced. Kilpadi and Lemons⁴⁶ mentioned in 1994 that grain size dependencies on the free surface energy might not be detectable due to growing native oxide layers and ambient contamination films. Independent of the sample type, a similar trend can be observed that stabilizes at an SCA of approximately 100° in agreement with other works.³⁰ The MP samples depict a final SCA of 99.9 ± 0.6 , and the EP samples level at 98.4 ± 0.6 and the AEP samples at 97.6 ± 0.8 . Longer storage times or storage in an atmosphere with a higher concentration of adventitious carbon groups might lead to a further gradual increase in SCA, where angles up to 108° for polished copper surfaces were observed as previously reported.³⁵ The aging-related wetting behavior of the samples and the leveling of the three sample types suggest a heavy influence of the adsorption of adventitious carbon groups. Therefore, we assume that the differences in the wetting behavior observed directly after sample preparation are rather due to slightly deviating adsorption rates of adventitious carbon groups that might more likely arise from the different preparation routines with varying near-surface defect density and surface deformation than from grain size differences or macroscopic homogeneous bulk deformation as induced by cold-rolling processes of the samples.

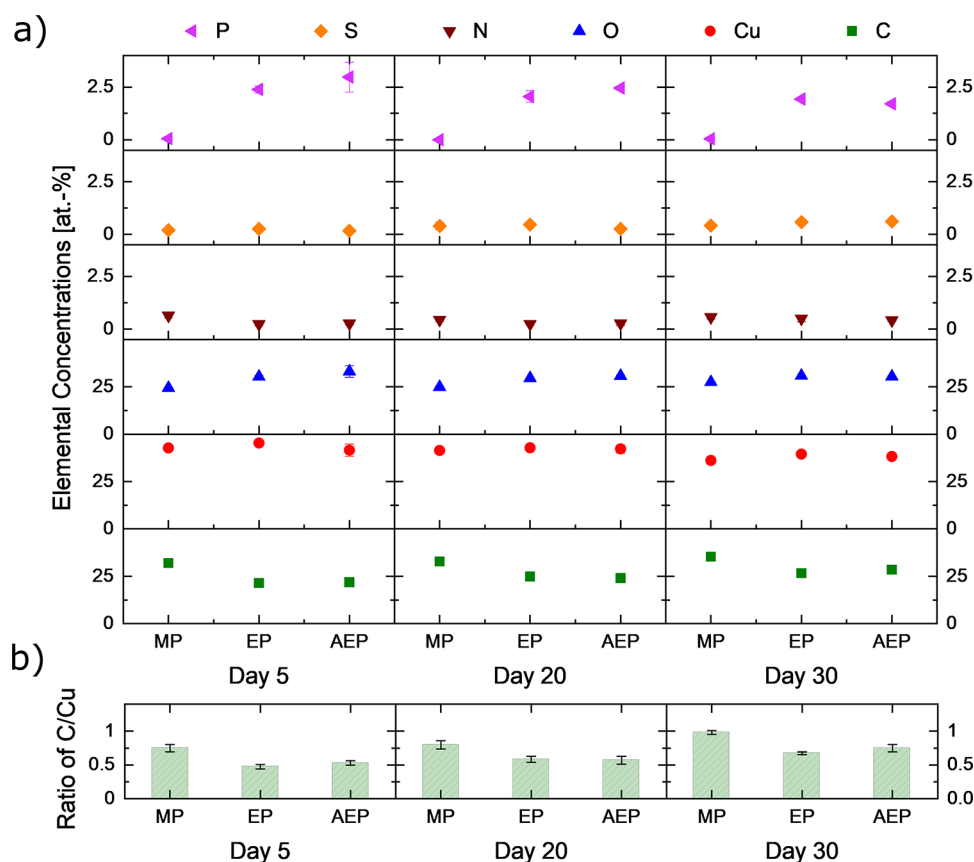


Figure 4. (a) Elemental concentrations of the atoms measured in the overview spectra in atomic percent. Only a slight contamination of the samples with phosphorus, sulfur, and nitrogen is present. The overview spectra are dominated by oxygen (oxides and organic compounds), copper, and carbon, which is most present on the MP samples. (b) Ratio of elemental concentrations of C and Cu. The measured elemental concentration of C and the ratio C/Cu reveal that the MP sample shows a stronger affinity to carbon adsorbates than the other two sample types.

Surface Chemistry. Though the different sample types level toward a similar SCA, this does not automatically allow for conclusions about indifferent adsorption layers. Only with a detailed chemical analysis, conclusions regarding the role of microstructure during the formation of contamination films are possible. Therefore, XPS measurements were conducted on day 5, 20, and 30 after sample preparation on three spots per sample type and age. For the AEP sample on day 20, one measurement spot had to be excluded from analysis due to an interruption of the analysis by the device. The results of the overview spectra for all sample types are displayed in Figure 4a.

On EP and AEP samples, a slight phosphorus contamination was detected due to the electropolishing in *ortho*-phosphoric acid. The high viscosity of the acid leads to a challenge in surface cleaning. Though a stepwise cleaning procedure in water and ethanol was conducted, this minor contamination could not be avoided. For sulfur, an even lower contamination was detected. For nitrogen, only vanishingly small elemental concentrations were measured. The increased content on MP samples throughout all time steps might be an indication for the mechanical polishing on water-based suspension being a source for nitrogen contamination. Changes in the elemental copper concentration can be traced back to the growing native oxide layer on the one hand and the carbon contamination layer on the other hand as well as water films and metastable compounds.²⁹ For the oxygen signal, a difference between MP and EP/AEP sample types can be observed on day 5 which decreases throughout aging. It must be considered that the

total oxygen content summarized in the overview spectrum does not provide information on the fraction of oxygen bound in oxides or contamination species, metastable oxidic copper compounds, or superficial water films, which is why an evaluation of the O 1s peak is necessary in order to understand the interaction of the three surface types with oxygen. Also, the growing adsorbate layer influences the detected elemental O concentration. For oxide characterization, Cu 2p and CuLMM spectra are relevant. Peak deconvolution of both is prone to large uncertainties due to heavy peak overlap of the two oxide species (CuO and Cu₂O) with the Cu signal. Moreover, metastable states like Cu(OH)₂ are also detected in the Cu 2p spectrum, while the O 1s spectrum is also characterized by overlapping peaks, which altogether pose a great challenge in XPS characterization of oxidized copper samples.^{56,57} Also, a peak deconvolution according to ref 56 left us with uncertainties in the calculations of the copper content and the oxide concentrations. Therefore, we concluded that for a stable characterization, measurements of reference samples of known oxide composition will be helpful for future investigations. In order to still evaluate the differences in oxide composition of the sample types and to see if this affects the adsorbate layer, Figure 5 shows the CuLMM and O 1s spectrum for day 5 and day 30 of one measurement spot on each sample type (deconvolution of peaks based on ref 56). The Cu 2p spectra hardly show a difference for the three sample types and can be found in the Supporting Information (see Figure S1). Solely, the CuO peak seems slightly increased

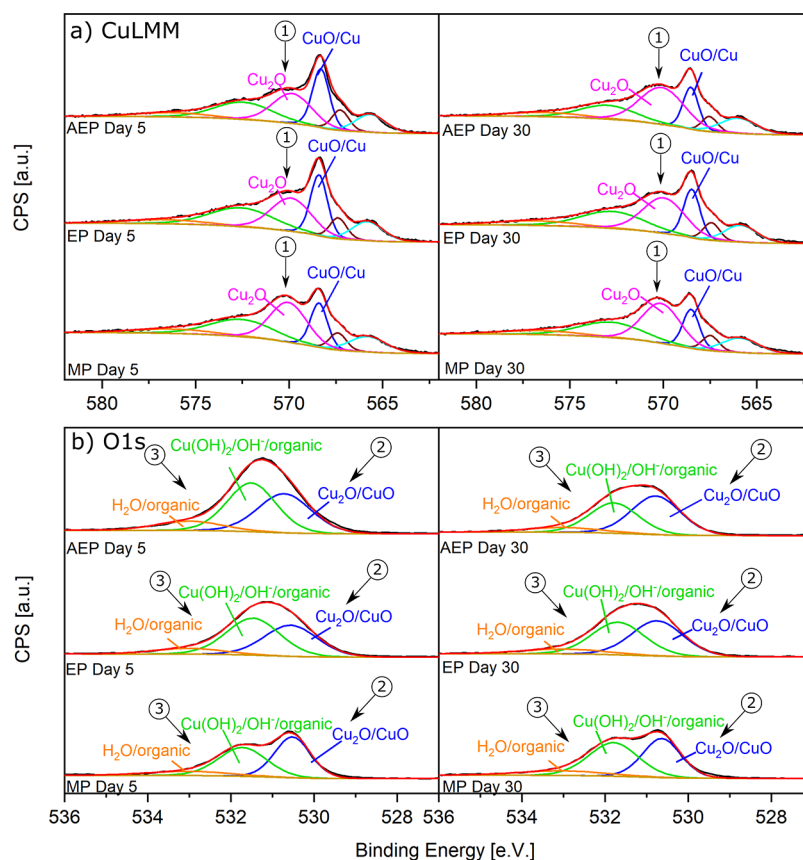


Figure 5. Detailed spectra 5 and 30 days after sample preparation for the three sample types. (a) The CuLMM spectrum reveals a more pronounced Cu_2O peak for the MP sample throughout both time steps (arrow 1). (b) The O 1s spectra show a more pronounced oxidic peak (arrow 2) for the MP sample, while a higher amount of the detected oxygen is bound in organic species and metastable compounds on both electropolished samples (arrow 3).

for EP/AEP compared to MP samples suggesting a higher relative CuO content for the electropolished surfaces, especially after 30 days of aging. The development of the CuLMM spectra shows a more pronounced difference between the sample types, as the Cu_2O peak of the MP samples is strongly increased relative to the CuO/Cu peak compared to both electropolished surfaces (compare arrow 1 in Figure 5a). While the grain size difference between EP and AEP samples and the slight bulk deformation of the EP grains from the cold-rolling process do not induce significant differences in the spectra, the deformation due to mechanical polishing seems to contribute to an increased oxidation due to a higher surface energy induced by the surface-near defects and the fine-crystalline deformation layer.³⁸ Platzman et al.⁵⁶ showed that on copper thin films already one hour after exposure to the atmosphere, about 50% of the total oxidation layer is formed. In another study, they proved that the highest oxidation rate is observed in the first six days after preparation.³⁸ Metastable $\text{Cu}(\text{OH})_2$ that has been detected converts into the stable CuO.³⁸ A significant difference between the EP and AEP samples cannot be observed, indicating that after five days of aging, the influence of grain size on the oxidation rate that is described in ref 38 is already negligible. Native oxidation relies on an electric field between the positive copper ions at the copper–oxide interface and negative ions at the oxygen–atmosphere interface and is influenced by microstructure and surface defects.^{38,56,58} While the initial theory of ion transport assumes a homogeneous oxide growth,⁵⁸ a rather inhomoge-

neous island-like oxidation seems more plausible.^{56,59} Though grain size did not show significant effects on the spectra, the fine-crystalline and defect-rich MP samples deviate from this trend. The details of the O 1s spectrum in Figure 5b reveal that for MP samples, a bigger amount of oxygen is bound in the oxidic copper-related species (compare arrow 2), while the other two sample types have more oxygen bound in metastable compounds, water films, and organic species (compare arrow 3). Throughout the aging of 30 days, the distribution for EP and AEP samples also shifts toward a higher amount of oxygen bound in oxidic copper species. Due to the broadness of the different peaks in the O 1s spectrum, for reliable estimation of the amounts of organic carbon species, a deconvolution of the C 1s spectra is necessary.

In Figure 4, the MP samples show an increased carbon uptake, indicating that near-surface deformation and its defects might accelerate the adsorption process while grain size differences seem to play a subordinate role. Figure 4b compares the ratio of elemental concentrations of C and Cu to the elemental concentration of C in Figure 4a. C/Cu is an established parameter for adsorbate layer investigations²⁹ and can be an indication for adsorbate layer thickness. As EP and AEP exhibit similar carbon contents, the grain size and slight bulk deformation of the grains originating from the cold-rolling process do not seem to strongly influence the carbon adsorption. Fine-crystalline surface deformation layers and accompanying defects at the metal–air interface instead might cause a stronger carbon adsorption. The C 1s peak was further

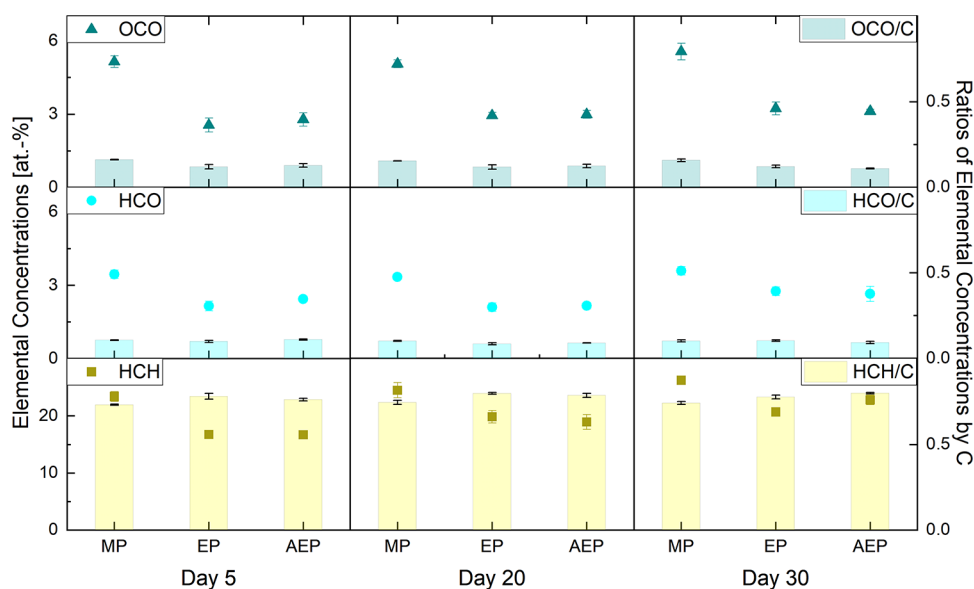


Figure 6. Elemental concentrations of the carbon bindings measured in the C 1s spectra of the three sample types in atomic percent (symbols, axis on the left) in comparison with the ratios of elemental concentrations normalized to the measured elemental carbon concentration from the overview spectra (bar charts, axis on the right). For the atomic percentages of polar and nonpolar carbon groups, the MP sample shows strong deviations from the other two sample types. The ratios of elemental concentrations deliver comparable layer composition with slightly increased amounts of polar groups in the adsorption film of the MP samples.

analyzed to detect nonpolar aliphatic carbon chains and the oxygen-containing carbon bonds. Details on the elemental concentrations as well as the ratios of elemental concentrations normalized to C are shown in Figure 6.

HCH represents the C–C and H–C–H connections, which are responsible for the hydrophobization of surfaces due to their nonpolar character, while the oxygen-containing carbon groups are polar and lead to a more hydrophilic behavior.²⁹ Carbon atoms labeled as HCO in Figure 6 have one oxygen as a direct binding partner, e.g., hydroxyl, ether, and ketone groups. OCO consists of carbon atoms with two oxygen atoms as a binding partner, e.g., carboxyl or hydroxyl groups. We refrained from resolving the different binding situations in order to avoid overfitting of the C 1s spectra as described by Gengenbach et al.⁶⁰ Taking the amount of carbon into account together with the relative amount of hydrocarbons is a proven concept in the literature for the assessment of the wetting behavior.^{29,31,61} While for the elemental concentration, the MP samples show a strong difference compared to the other two sample types, for the ratios of elemental concentrations of the polar and nonpolar carbon groups normalized to C, much smaller deviations can be observed. The OCO/C ratio is slightly increased on MP samples, and the HCH/C ratio slightly decreased therewith enhancing polarity of the adsorbate layer. Still, the wetting behavior is not shifted to a more hydrophilic character. The O 1s spectrum indicated a higher amount of oxygen bound in metastable and organic species than in oxidic species for the electropolished surfaces, but as mentioned before, we found it to be less reliable than the C 1s spectrum in regard to the characterization of organic species. The C 1s spectrum reveals that EP and AEP samples both do not show a higher content of oxygen-containing organic species compared to the MP sample. The results depicted in Figures 4 and 6 indicate comparable layer composition with no pronounced dependence on grain size and deformation as well as minor differences in surface roughness in the magnitude of 10 nm. Only the MP sample

shows slightly increased polarity. In general, adsorption can be physically (physisorption) where no chemically strong bond is formed between the adsorbate and the substrate. In this case, adsorbed particles enhance the chance for further adsorption. In contrast, chemically controlled adsorption (chemisorption) alters the chemical character of the adsorbate and has a self-limiting effect.⁶² Mostly for laser-treated surfaces, the adsorption of hydrocarbons is attributed to unsaturated binding states after the laser–material interaction leaving them in a polar and hydrophilic state. The high surface energy and polarity are reduced by the adsorption of adventitious carbon groups leading to hydrophobicity, where additional intermediate steps like hydroxylation might take place as described for aluminum surfaces.^{29,31,51,54,63–65} Often, those are described as short-ranged chains with a nonpolar alkyl group.^{29,54} Heier et al.⁶⁶ showed that the wetting behavior depends on the chemical composition of the adsorbate layer, while the substrate only shows an indirect influence by affecting this composition. However, the adsorbate layer is most strongly influenced by previous contacts with oil or solvents. They found a linear relationship between the cosine of the SCA and the ratio of polar to nonpolar adsorbates based on sputtered gold films. In a second step, they showed that this dependency and linear fit allow to approximate the wetting of steel and titanium surfaces as well. However, the wetting behavior of the aged copper samples is not described accurately by this linear fit, which may be a consequence of a different surface morphology induced by the deviating preparation techniques. The more technical copper samples are characterized by higher roughness, pronounced adsorbate and oxide layer thicknesses in contrast to the chemical inert Au model system deposited by a sputtering technique on a plain Si wafer and analyzed shortly after preparation. This suggests a more complex relation between the C/Cu ratio and the polarity of the adsorption layer ($C_{\text{pol}}/C_{\text{nonpol}}$). In order to gain a deeper understanding of the growth of the adsorbate layer and the role of both parameters, another set of MP and EP

samples was prepared for SCA and XPS analyses on fresh surfaces. They showed the strongest deviation in SCA on day 0 (compare Figure 3), indicating a minor effect of grain size even in combination with slight bulk deformation and rather observing defect density at the surface–air interface responsible for the wetting differences. Samples were stored in polystyrene boxes without the wrapping paper to lower carbon adsorption³⁵ and transferred to the XPS device as fast as possible (about 3 h after preparation). It must be mentioned though that during the preparation of this sample set, some of the phosphoric acid could not be fully removed, which is why only 8 droplets in clean areas of 4 samples could be investigated for the EP sample type. XPS revealed elemental phosphorus concentrations of 3.3 ± 0.9 at. %. In agreement with the previous analyses, MP samples showed more hydrophobic behavior than EP samples. For the XPS measurements, three samples of each type were analyzed with three measurement spots each to allow for better statistics of this metastable sample state (one outlier was removed for the MP samples). Figure 7 shows SCA over C/Cu for all

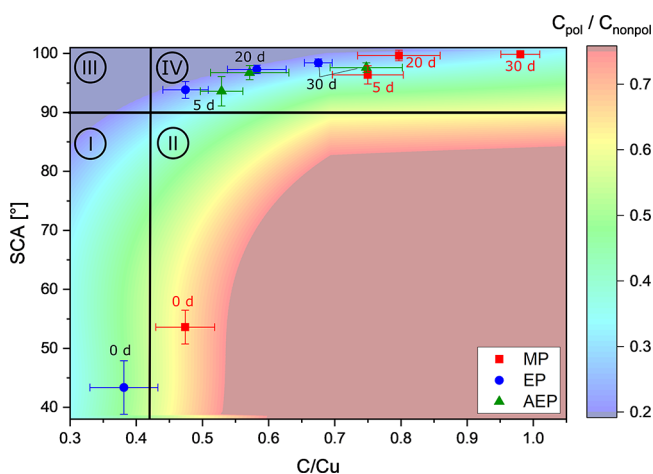


Figure 7. SCA over the ratio of elemental concentrations of C to Cu. The gradient indicates the ratio of polar to nonpolar carbon groups. Black lines divide the plot into four areas where different effects might dominate the wetting behavior. Numbers beneath/above data points indicate the age in days. In section I, C/Cu might dominate over adsorbate layer polarity. In section II, adsorbate layer polarity overrules C/Cu. In section III, low adsorbate layer polarity is combined with low C/Cu, which is unlikely to occur. In section IV, SCA seems to stabilize with growing C/Cu, and small fluctuations in adsorbate layer polarity do not seem to strongly alter SCA.

sample types combined with $C_{\text{pol}}/C_{\text{nonpol}}$. For the contour plot in the background, a factor of 200 was used to increase the data point number, and a very small smoothing factor of 0.001 was applied.

The growing accumulation of carbon correlates with the sample age for each type, and the trend resembles the SCA aging curves in Figure 3. Within the first five days of aging, it is accompanied by a pronounced reduction of $C_{\text{pol}}/C_{\text{nonpol}}$. Müller et al.⁶⁷ made similar observations on laser-patterned copper surfaces aged for 3 weeks. The diagram in Figure 7 can be divided into four sections with the hydrophilic samples (MP day 0 and EP day 0) in section I and II and the hydrophobic samples in section IV. In section I, only a small amount of carbon has been adsorbed on the surfaces, which might lead to incomplete or very thin and therefore weak adsorbate layers,

that are potentially transparent for the applied water droplets, similar to ref 39. Rafiee et al.³⁹ found that monolayers of graphene sputtered on copper substrates are transparent to the water droplet applied, while an increase in the layer number leads to a gradual transition of the static contact angle. They observed a saturation of the SCA after 6–9 monolayers were applied. For hydrocarbons, Korczeniewski et al.³⁰ found in simulations that one monolayer of adsorbed hydrocarbons already strongly influences the SCA, while additional layer growth only shows a weak influence. Based on these findings, layer thickness as well as layer density might be crucial in the case of the hydrocarbon adsorbate films. In section II, more carbon is adsorbed, but polarity is still increased. The C/Cu ratio alone might indicate hydrophobic behavior in comparison with C/Cu ratios in section IV. However, section II is characterized by an increased $C_{\text{pol}}/C_{\text{nonpol}}$ ratio, which dominates the wetting behavior over C/Cu and leads to the hydrophilic behavior of the freshly prepared MP samples. MP samples are more hydrophobic than EP samples on day 0 despite their higher $C_{\text{pol}}/C_{\text{nonpol}}$ ratio. Therefore, in section I, C/Cu is believed to dominate over $C_{\text{pol}}/C_{\text{nonpol}}$. The higher polarity of the adsorbate layers in section I and II compared to III and IV can be traced back to a higher affinity of the samples to oxygen due to native oxidation processes simultaneous to carbon adsorption. This would also explain the higher $C_{\text{pol}}/C_{\text{nonpol}}$ ratio for fresh MP samples, as they are expected to be chemically more active due to a higher near-surface defect density and the fine-crystalline deformation layer. Section III of the diagram is characterized by hydrophobic behavior due to small C/Cu and $C_{\text{pol}}/C_{\text{nonpol}}$ ratios. This combination seems unlikely due to native oxidation and hydroxylation processes in the beginning of carbon adsorption and very thin layers that are expected to be transparent for the water droplet. Samples in section IV show hydrophobic behavior due to high C/Cu ratios and low $C_{\text{pol}}/C_{\text{nonpol}}$ ratios. Our results indicate a threshold of C/Cu that leads to surface hydrophobization where a further increase still causes gradual changes in SCA but no sudden jumps as seen during the wetting transition are expected. This is in good agreement with the results in refs 66 and 68 showing a saturation of SCA with the contamination layer thickness for steel and titanium surfaces. Simulation results in ref 30 indicate as well the levelling of SCA once a monolayer of hydrocarbon is formed. The threshold may depend on sample type and could be located at 0.55–0.6 C/Cu for MP samples and at lower C/Cu ratios (0.4–0.45) for EP samples due to lower polarity. With further growing C/Cu, a gradual increase in SCA is expected, as we characterized an MP sample with 108° in an earlier study in ref 35. Different storage conditions were applied, which is why there is only limited comparability to the data from this study, and a higher C/Cu content combined with a lower $C_{\text{pol}}/C_{\text{nonpol}}$ ratio was reached after 10 weeks. Small fluctuations in polarity in section IV do not seem to alter the wettability significantly within the standard deviation of the SCA measurement for dense C/Cu layers. We want to highlight though that also, after a longer storage time than 30 days, differences in the oxide layer of copper can occur,^{38,56} which could affect the polarity of the growing adsorption layer. From the results shown, we can conclude that MP samples are characterized by increased C/Cu ratios. Especially, but not exclusively for lower C/Cu ratios, higher $C_{\text{pol}}/C_{\text{nonpol}}$ ratios can occur compared to the other sample types. In fact, defects have previously been described as preferred adsorption sites⁶⁹ possibly influencing hydrocarbon

adsorption rates.⁵³ The grain size does not seem to significantly alter adsorption due to the comparable behavior of EP and AEP samples even though EP samples did not only show smaller grain sizes but also slight bulk deformation introduced by the cold-rolling process. The latter shows to play a subordinate role compared to near-surface defect-rich fine-crystalline deformation layers.

CONCLUSIONS

The conducted study shows a systematic investigation of the microstructural influence on the long-term wetting behavior of polycrystalline metallic bulk material. A fine-crystalline near-surface deformation layer induced by mechanical polishing (MP samples), the coarser microstructure of the cold-rolled copper sheet (EP samples), and the deformation-free coarse-grained structure of annealed samples (AEP) were under comparison.

The defect-rich fine-crystalline MP surface showed the highest SCA on day 0 indicating an enhanced adsorption of nonpolar carbon groups due to an increased chemical activity, which was confirmed by XPS analyses. In the case of the other two sample types, the SCA measured immediately after preparation showed a slightly more hydrophilic behavior of EP samples compared to the coarse-grained AEP samples, which is in agreement with the results from Platzman et al.³⁸ It was shown that strong differences in the wetting behavior between the three sample types (especially MP to EP/AEP) appear immediately after sample preparation and that SCAs converge upon extended atmospheric exposure. Initial differences in microstructure induced by the different preparation routines are overruled by surface energy minimization through hydrocarbon adsorption. While a fine-crystalline deformation layer with high near-surface defect density proved to enhance carbon adsorption, differences in grain size did not show a significant effect on the adsorption behavior. Even though the EP samples showed some bulk deformation through the cold-rolling process, no significant adsorption differences could be observed compared to the AEP samples. Therefore, especially near-surface defect-rich layers like the fine-crystalline deformation layer of the MP sample are favorable for hydrocarbon adsorption. For aged samples, the adsorbate layer shows comparable composition with a slightly increased polar ratio for the mechanically polished samples, which is expected to be a result of the higher affinity to oxygen and native oxidation. As after five days of aging, a further accumulation of carbon only alters SCA by a few degrees, a threshold concentration might exist for the wetting transition from hydrophilic to hydrophobic behavior. A comparison of the SCA with the C/Cu ratio combined with the ratio of polar to nonpolar carbon groups allows for a systematic assessment of the adsorption processes. For freshly prepared samples, the total amount of adsorbed carbon seems to have a stronger influence on the SCA than the ratio of polar to nonpolar molecules. Thin layers might be transparent to the water droplet³⁹ resulting in hydrophilic behavior. Surfaces with a higher chemical activity therefore exhibit more hydrophobic behavior in early-stage aging despite higher polarity as they form thicker adsorbate films (compare MP samples). Once a sufficient carbon concentration is reached to induce water interaction, the composition of the layer shows a stronger influence in early-stage aging. During ongoing aging, the amount of adsorbed carbon further increases, stabilizing the wetting states. A saturation of C/Cu was not observed. Further growth of the

adsorbate layer can increase the SCA gradually, while small fluctuations in polarity do not seem to strongly alter the wetting behavior for aged samples.

Based on these findings, differences in the microstructure do not strongly affect long-term water wettability of copper surfaces since initial differences in SCA are expected to fully vanish after prolonged storage times. However, the transition rates can be affected especially for surfaces rich in defects at the metal–air interface due to accelerated hydrocarbon adsorption.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.3c01060>.

Details on sample preparation, cleaning, packaging, storage, and SCA calculation; exemplary XPS Cu 2p spectra (PDF)

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Notes

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Supporting Information

The Influence of Adventitious Carbon Groups on the Wetting of Copper – A Study on the Effect of Microstructure on the Static Contact Angle

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Details on sample preparation and cleaning

Sample cleaning was conducted by rinsing the samples in desalinated water and ethanol. Subsequently, they were immersed in an ethanol ultrasonic bath for 3 minutes. For the electro-polished samples, ethanol was replaced as soon as it turned opaque from participation of the phosphoric acid. After ultrasonic cleaning, the samples were again rinsed in desalinated water and ethanol before drying with an ambient air fan.

Details on sample packaging and storage

Samples were stored in air-tight boxes filled with silica gel beads to keep humidity low during storage and placed in an air-conditioned room (20-22°C). To accelerate the adsorption of adventitious carbon and protect the polished surfaces during sample transportation, a cellulose containing clean room tissue (VWR Spec-Wipe 21914-758) was used to wrap the samples. It should be noted that not a fresh pack of wipes was used but instead wipes that have had contact to the atmosphere before as well to collect carbon groups that can be transferred to the sample surface as shown in reference ¹.

Details on average calculation of the static contact angle

Three images were taken of each droplet and the static contact angle was determined on both sides of the droplet by the tangent fit method with the Advance 1.14 software. The SCA of the individual droplet was calculated by averaging the results from the three images. For each sample type and measurement day, the results from the droplets on the three individual samples were averaged and standard deviation was calculated.

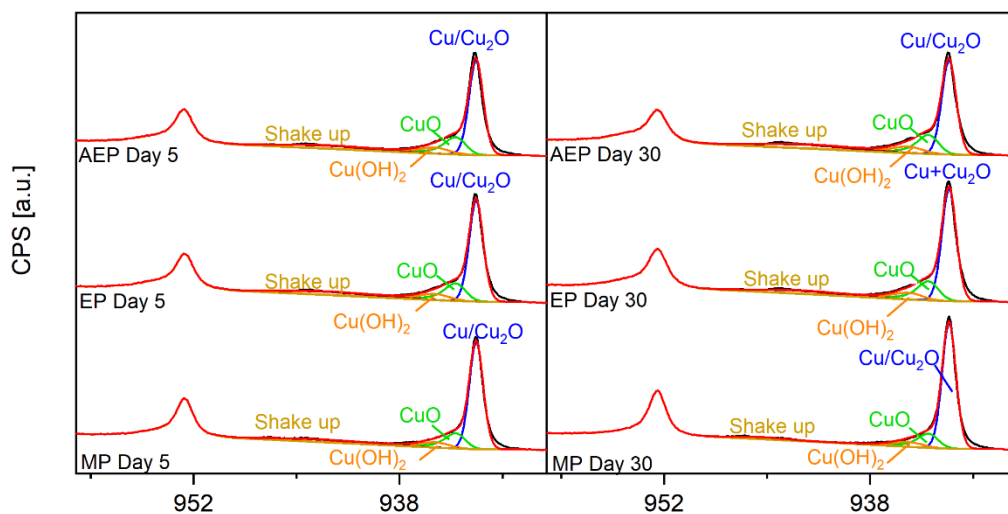


Figure S1: Cu₂p spectra of the three sample types 5 days and 30 days after preparation. Only the CuO peak (green) shows a slight increase for EP/AEP samples in comparison to MP samples especially on day 30.

A comparison shows a slight increase of the CuO peak on both electro-polished samples compared to the MP sample especially on day 30.

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Paper 4

Influence of chemistry and topography on the wettability of copper

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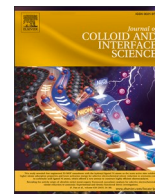
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Influence of chemistry and topography on the wettability of copper

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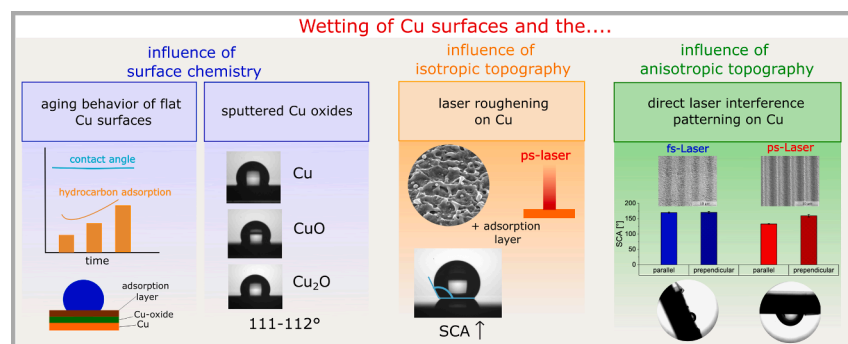
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GRAPHICAL ABSTRACT



ABSTRACT

To understand the complex interplay of topography and surface chemistry in wetting, fundamental studies investigating both parameters are needed. Due to the sensitivity of wetting to minuscule changes in one of the parameters it is imperative to precisely control the experimental approach. A profound understanding of their influence on wetting facilitates a tailored design of surfaces with unique functionality.

We present a multi-step study: The influence of surface chemistry is analyzed by determining the adsorption of volatile carbonous species (A) and by sputter deposition of metallic copper and copper oxides on flat copper substrates (B). A precise surface topography is created by laser processing. Isotropic topography is created by ps laser processing (C), and hierarchical anisotropic line patterns are produced by direct laser interference patterning (DLIP) with different pulse durations (D).

Our results reveal that the long-term wetting response of polished copper surfaces stabilizes with time despite ongoing accumulation of hydrocarbons and is dominated by this adsorption layer over the oxide state of the substrate (Cu, CuO, Cu₂O). The surfaces' wetting response can be precisely tuned by tailoring the topography via laser processing. The sub-pattern morphology of primary line-like patterns showed great impact on the static contact angle, wetting anisotropy, and water adhesion. An increased roughness inside the pattern valleys combined with a minor roughness on pattern peaks favors air-inclusions, isotropic hydrophobicity, and low water adhesion. Increasing depth of the primary topography can also induce air-inclusions despite increasing peak roughness while time dependent wetting transitions were observed.

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1. Introduction

The production of copper has been increasing continuously within recent years. The U.S. Geological Survey estimates an increase of approximately 30 % in the world wide copper production (by mining, smelter, and refinery) from 2010 to 2020 [1,2]. The Copper Development Association Inc. states that “Copper Is ... The Metal of Civilization” [3]. Many of the unique properties of copper and its alloys that make copper so vital for a wide range of applications are linked to their wetting behavior. For instance, the antimicrobial efficiency depends on the wetting properties [4] as bacterial adhesion is influenced by the surface hydrophobicity [5,6]. Furthermore, Liu et al. [7] found that superhydrophobic coatings can improve the corrosion resistance of copper, which is especially important due to its frequent application in electrical connections. Wen et al. [8] produced hydrophobic copper nanowires to accelerate droplet removal for improvement of condensation heat transfer. Chemical treatments to grow copper oxides in combination with chemical hydrophobization also showed to increase heat transfer coefficients as well as critical heat flux [9]. Chemical surface functionalization of copper combined with laser treatment allows for the fabrication of superhydrophobic/hydrophilic hybrid surfaces to alter droplet condensation [10]. Kim et al. [11] equalized surface chemistry of copper samples by a hydrophobic coating to evaluate the influence of roughness on heat transfer. Unidirectional scratches were applied leading to wetting anisotropy but sandpaper scratching can induce very irregular topographies in contrast to laser patterning of surfaces and therefore limit the possibilities of roughness evaluation on wettability. Zupančič et al. [12] found indeed that laser patterning of steel foils and the formation of non-uniform patterns induces non-uniform wetting behavior which in turn greatly affects boiling heat transfer. Li et al. [13] altered copper chemically and topographically to increase hydrophobicity and improve self-cleaning behavior as well as water–oil separation performance.

The classic Young equation considers the contact angle on ideally smooth surfaces Θ_{ideal} following equation (1) [14] as a function of the surface tensions between liquid (L) and gas (G) σ_{LG} , solid (S) and gas σ_{SG} as well as solid and liquid σ_{SL} :

$$\cos(\Theta_{ideal}) \cdot \sigma_{LG} = \sigma_{SG} - \sigma_{SL} \quad (1)$$

Later approaches also considered the role of topography in the wetting behavior. Wenzel [15] postulated equation (2) for a system where the roughness is penetrated by the liquid. r represents the ratio of the area of the actual surface by the projected surface area and is > 1 for rough surfaces:

$$\cos(\Theta_{Wenzel}) = r \cdot \cos(\Theta_{ideal}) \quad (2)$$

Only for ideally smooth surfaces $r = 1$ and Θ_{Wenzel} transforms into Θ_{ideal} described in equation (1). Cassie and Baxter (CB) derived an equation for calculating the contact angle on rough surfaces for the case of water trapping air with the surface roughness [16]. While nowadays different forms of this equation find application in the scientific community, Milne et al. [17] recommend sticking to the original CB equation (3):

$$\cos(\Theta_{CB}) = f_1 \cos(\Theta_{1ideal}) - f_2; \quad (3)$$

f_1 is defined as the area of the solid in contact with the liquid per projected area of the unit cell, Θ_{1ideal} as the contact angle on the smooth reference surface of material 1, while the subscript 2 represents area fraction of air (with an analogous contact angle of 180°).

In recent years, besides topography, the surface chemistry and its effect on wetting arose growing interest in the investigation of the wetting behavior of surfaces under ambient conditions. Different studies showed that the adsorption of volatile carbonous species leads to a transition of a hydrophilic behavior right after preparation of metallic and/or oxidic surfaces (e.g., by laser processing or simple grinding and polishing) to an increasingly hydrophobic behavior over time [18–21].

The earliest representation of a technical surface in contact with the atmosphere we were able to find is depicted in a review from J. E. Castle [22] and originally stems from a symposium contribution by F.R. Eirich [23] in 1968 (primary source was not accessible). He depicted a layered system of the metal surface with a growing oxide layer, an OH^- termination of the oxide induced by atmospheric H_2O and a subsequent attachment of polar and finally non-polar organic groups rendering the surface hydrophobic. Long et al. [18] did pioneering work in this field showing that storage of laser processed copper surfaces in organic rich atmospheres significantly increases the contact angle. More recent studies also showed that not only the atmosphere, but even sample packaging can lead to great deviations in the resulting contact angles [24,25]. Korczyński et al. [21] conducted a systematic study of the wetting transition of copper, based on controlled desorption and subsequent adsorption of hydrocarbons by exposing the surfaces to the atmosphere throughout 2 weeks and conducted simulations to explain the observed transition which showed that once a monolayer of hydrocarbon is formed, additional adsorption does not change the static contact angle significantly. In one of our previous works we were not able to find a saturation of adsorption within 30 days of storage [20]. In our current study, we present a long-term investigation of the adsorption of volatile carbon species throughout 43 weeks under controlled storage conditions and show a comparison to storage under ambient conditions.

Regarding the influence of the oxidation state of copper on the wetting behavior, recently Zhao et al. [26] showed that both CuO and Cu_2O turn out hydrophobic upon exposure to C-rich atmosphere. The production of the two oxide states also introduced roughness to their surface and the storage time differed for both oxide types. Therefore, in our study we aimed at investigating the influence of oxide states (metallic Cu, CuO and Cu_2O) on flat samples stored under controlled conditions.

This approach allows for an assessment of the influence of surface chemistry separately from topography, which both have proven to influence the wetting behavior [27]. This is especially important for laser-processed copper surfaces, as both chemistry and topography form a complex interplay regarding the observed time-dependent wetting response. While different studies in literature investigated the wetting of laser-patterned copper surfaces [28–31], sample storage and packaging often are not or only vaguely (“ambient conditions”) described. Also, in one of our previous studies [27], we stored laser patterned steel samples with and without PVD coating in ambient air and cleaned the samples in ethanol with the intention to create comparable surface conditions before measuring their wettability. We observed that both surface topography and chemistry are crucial for the wetting behavior. However, we also concluded that more detailed studies on both effects taking the adsorption of volatile carbon species into account will be necessary in the future to fundamentally understand the dependence of wetting properties of surfaces on these effects. While important insights have been gained during recent years into the interdependence of chemistry and topography on the wetting properties of copper surfaces, the detailed contributions are not clear yet. Therefore, in this work, we want to give a comprehensive overview of the wetting behavior of copper considering chemical as well as topographical surface modifications in a detailed multi-step analysis. Particularly, our approach takes the role of surface chemistry and of isotropic as well as anisotropic surface topography into consideration (compare Fig. 1). First, the aging behavior of bulk copper samples and the adsorption film forming was investigated. In a next step, the influence of the oxide state of copper on flat surfaces was investigated and finally to understand the influence of topography in the wetting behavior of copper, laser treatment was applied. First, isotropic roughness was created by ps laser treatment. Complex hierarchical patterns were created by direct laser interference patterning (DLIP) in a last step and their wetting response to water was analyzed based on the findings from the previous experiments.

2. Methods

2.1. Experimental Work

An oxygen-free copper sheet (CW008A, Wieland) of 1 mm thickness was mirror polished on an automated *Struers Tegra-Pol 21* with very light forces of 10 N in the final polishing steps of 3 μm and 1 μm as suggested in ref. [32] in order to achieve a mirror polished finish with an arithmetical mean height S_a of 3–4 nm. Cleaning was performed by immersion in an ethanol ultrasonic bath for three minutes. Samples were dried by an ambient air stream.

2.2. Chemical surface treatment

Copper and copper oxides depositions were conducted by reactive DC magnetron sputtering. Polished copper samples were rinsed with ethanol, dried, and placed on a circular holder facing a copper target (purity of 99.99 %, Kurt J. Lesker Company) at a distance of 5 cm. The distance between the samples and the center of rotation of the holder (rotation frequency of 3.5 Hz) was 7.5 cm. After evacuation, argon was introduced with a flow rate of 50 sccm (3.5×10^{-3} mbar of pressure) and sample surface etching was performed during 1 min by radiofrequency polarization. Parameters for the deposition of Cu and the oxides can be found in the [supplementary material \(Table S1\)](#).

2.3. Laser surface treatment

Isotropic laser roughening (LR) of the polished surfaces was conducted with an *Edgewave (PX50-1-GF)* PX-series laser in a single beam setup with a pulse duration of 12 ps and a wavelength of 532 nm. Additionally, direct laser interference patterning (DLIP) with two different lasers was employed to create line-like patterns. A femtosecond laser (*SOL ACE100F1K HP from Newport Spectra-Physics GmbH*) with a wavelength of 800 nm and a pulse duration of 100 fs was split into two beams by a diffractive optic element (DOE) and brought to interference subsequently on the sample surface in order to produce line patterns with a periodicity of 6 μm . The *Edgewave* picosecond laser was used equipped with an optical head from *Fraunhofer IWS Dresden* splitting the beam with a DOE, parallelizing the sub-beams with a prism and focusing on the sample surface to cause interference (see ref. [33] for a schematic overview of the beam path). A mask was installed to block two of the four sub-beams to create line-like patterns. Parameters for the laser patterning in the LR as well as the DLIP set up are summarized in [Table S2](#) in the [supplementary material](#). Details on sample storage for the individual sample sets can be found in the [supplementary material \(Table S3\)](#).

2.4. Surface characterization

For surface characterization, confocal laser scanning microscopy

(LSM) was conducted on an *Olympus Lext OLS4100*. Analyzed roughness parameters include the arithmetical mean height S_a , the mean height of the profile elements R_c , the root-mean-square deviation R_q and the S-ratio, which is defined as the ratio of the rough surface by the projected area and therewith resembles r in equation (2). Atomic force microscopy (AFM) was conducted on a *Bruker Dimension Icon*. Triangular-shaped silicon nitride SCANASYST AIR probes with a nominal radius of 2 nm were used for peak force tapping in the ScanAsyst Mode. For scans with a size of $5 \times 5 \mu\text{m}^2$ a scan rate of 0.248 Hz was applied and increased to 0.988 Hz for bigger scans of $20 \times 20 \mu\text{m}^2$. Imaging of the surface topography was performed by scanning electron microscopy (SEM) on a *FEI Helios FineLab600 FIB* at an acceleration voltage of 5 kV and 1.4 nA beam current in the secondary electron mode. High resolution micrographs were taken with an in-lens detector at 5 kV and 86 pA. For focused ion-beam (FIB) cross-sectional characterization, platinum layers were sputter-deposited to avoid damage of the surface, like rounding of the edges during cutting with a 30 kV gallium ion beam. Chemical characterization was conducted by grazing incidence X-ray diffraction (XRD; PANalytical X'Pert Pro-MPD; Cu K_α X-ray source; wavelength: 1.54 Å, 1° grazing angle). Samples were also characterized using a Bruker D8 Advanced diffractometer (Cu K_α X-ray source, wavelength: 1.54 Å) with a Bragg/Brentano configuration.

Surface chemistry was analyzed by X-Ray photoelectron spectroscopy (XPS). For this, an Axis Nova small spot electron spectrometer (Kratos Ltd.) was used. Three oblong spots of size $350 \times 700 \mu\text{m}^2$ per sample were chosen. All measurements were done with the detector axis set parallel to the surface normal of the sample. Only for a XPS tilt experiment, the detector axis was inclined from the 90° angle, measured between detector axis and surface, to 30° to reduce the information depth. By directly comparing the results of the two detector viewing directions, information concerning the elemental depth distribution can be concluded. Elemental concentrations were calculated from survey spectra (electron pass energy: 160 eV), using standard sensitivity factors, given by Kratos. Ltd. and Shirley shape fits for background subtraction. The binding states of detected elements are characterized by detailed core level spectra (electron pass energy: 20 eV) of the relevant elements (C1s, O1s, Cu2p). For Cu an additional detail spectrum of the Cu LMM Auger electron line was recorded. For details on the fitting procedure please refer to [supplementary material](#). Additionally, XPS depth profiles were recorded, by sputter removal of surface layers with a 2 keV argon ion beam. The depth scale was calibrated according a Ta_2O_5 reference sample, giving a sputter velocity of around 3 nm/min.

For wetting analysis, static contact angles (SCA) were determined on a *Krüss DSA 100* equipped with a gastight Hamilton syringe (100 μl). On flat and LR samples, 3 μl droplets of purified water (spec. conductivity $\leq 1 \mu\text{S}/\text{cm}$) were applied and images were taken 10 s after droplet deposition from two sides. On DLIP samples, droplet volume was increased to 6 μl to allow droplet deposition on the highly hydrophobic surfaces. Additionally, measurements were conducted approximately 60 s as well as 180 s after droplet deposition, where evaporation was

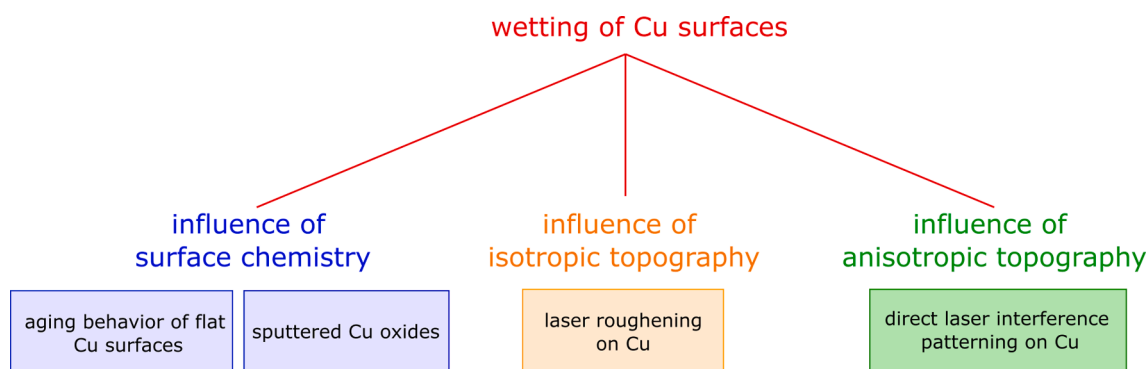


Fig. 1. Schematic describing the structure of the manuscript.

suppressed by the cover set up introduced in an earlier work [24]. SCA results are portrayed as the mean of multiple measurements with error bars indicating the standard deviation. Atmospheric conditions were controlled during SCA measurements where details can be found in the respective results section (RH refers to relative humidity during droplet deposition). For top view images of droplets an extra set of droplets was applied by a pipette under a *VHX-7000 Keyence* optical microscope. In order to distinguish between a strong and a low water adhesion, a self-designed prototype tilting stage based on a step motor was used. DLIP samples were tilted with approximately $2^\circ/\text{s}$ after application of $30\ \mu\text{l}$ of water.

3. Results and discussion

A) Aging of Copper samples

In a previous study we were able to show the strong influence of storage conditions on the development of the wetting behavior of mechanically polished copper surfaces [24]. The transition from hydrophilic to hydrophobic after sample preparation can be influenced by wrapping paper serving as a donor for hydrocarbons, which it has most likely adsorbed itself through contact with atmospheres rich in adventitious carbon before [24]. In Fig. 2 a), we present a comparison of samples stored at ambient conditions with samples wrapped in woodfree tissue. As Fig. 2 a) shows, the wrapped samples depict a steady hydrophobic SCA, while samples without the paper directly exposed to the surrounding atmosphere transition back to a more hydrophilic behavior once humidity rises. While water molecules present at the surface in initial stages of aging can support the adsorption of volatile carbonous species and therefore the transition from hydrophilic to hydrophobic SCAs, water molecules present at the surface after the hydroxylation process might form hydrogen bonds and prevent further adsorption of nonpolar groups [25,34–38]. We assume that the formation of such hydrogen bonds on the samples stored in increased humidity without the wrapping paper are responsible for the decrease in SCA and its subsequent stagnation. These results confirm the need of a strict control of the storage conditions. Fürbacher et al. [34] as well witnessed a delay in the expected wetting transition from hydrophilic to hydrophobic upon sample exposure to the atmosphere. While vacuum storage [37,38] or annealing [26,39] can be conducted in order to achieve a quick wetting transition to hydrophobic behavior, we refrain from this method due to possible side contamination and unsteady atmospheres depending on previous furnace/chamber use [34]. To investigate stable wetting states,

we decided to focus on aged samples in this study as the wetting behavior of freshly prepared surfaces might be influenced by metastable states and intrinsic material properties like microstructure [20]. In ref. [20], a saturation of adsorbed hydrocarbons could not be observed. Therefore, here we extended the storage time to investigate if a saturation is reached after prolonged times. A measurement series with mechanically polished copper surfaces packed in woodfree tissue for 3, 6, and 43 weeks was conducted with combined SCA and XPS measurements on identically stored and handled comparative samples (Fig. 2 b)).

During aging, the samples show a strong increase of the elemental concentration ratio of carbon to copper (C/Cu), a common parameter to characterize the degree of carbon coverage [18,26]. Additionally, the measurements demonstrate that the detected carbon is not bound as graphite or in form of pure hydrocarbon chains, but rather with the participation of oxygen, forming functional groups with polar character, like hydroxyls (–OH), aldehydes (–COH), ketones (C=O), ethers (–O–), carboxylic acids (–COOH), or esters (–COOC–). A second parameter was introduced, the polarity ratio of the adsorbate layer. For reasons of simplicity, the polar groups in which the carbon is bound to one or two oxygen atoms are summarized. The polarity ratio of the adsorbate layer ($C_{\text{pol}}/C_{\text{nonpol}}$) – a relevant parameter for the wetting behavior [40,41] – is then calculated as the quotient of the proportion of carbon bound in these polar binding situations to carbon bound in aliphatic hydrocarbon chains. Besides the fluctuation after 6 weeks in Fig. 2, the polarity ratio also decreases with time in agreement with ref. [20]. Despite the fluctuations in the polarity ratio occur and the amount of accumulated carbon groups differs strongly over time, the SCA measurements of the three samples under investigation depict stable wetting conditions and prove the independence of differences in the adsorbate layer once a contamination film of sufficient thickness or density is adsorbed.

In order to gain insight into the deep structuring of the adsorbate layer, a XPS tilting experiment was conducted. To compare the elemental concentrations measured at two different tilting angles (30° and 90°) relative to the sample surface, in equation (4) their contrast is calculated. It serves as an estimation of the element depth location, because with decreasing tilt angle the information depth is reduced.

$$\text{Contrast} = 100 \cdot \frac{C(30^\circ) - C(90^\circ)}{C(30^\circ) + C(90^\circ)} \quad (4)$$

As expected from the literature [23,26,42], Fig. 3 shows that the

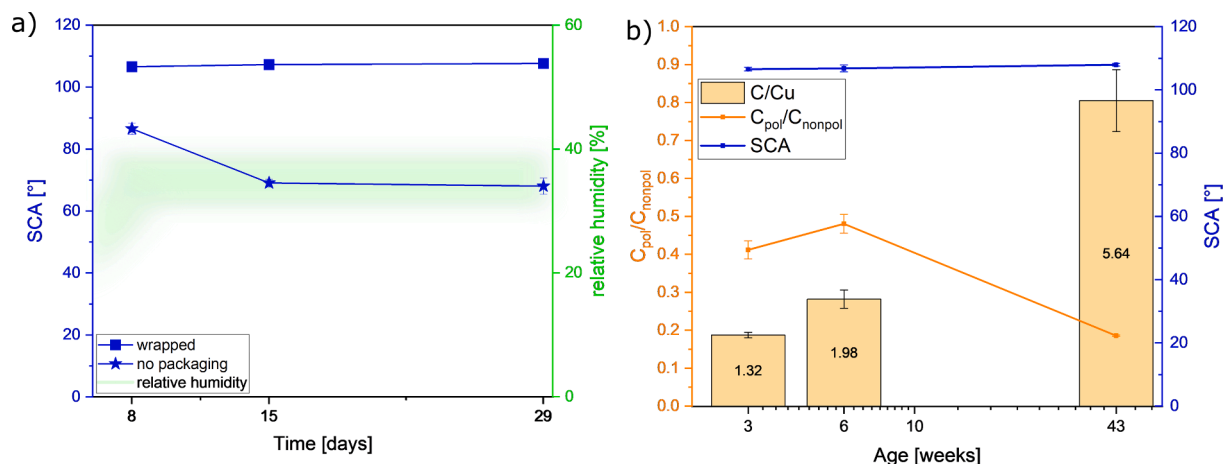


Fig. 2. Aging behavior of mechanically polished copper samples. (a) Mean value of measured SCAs with standard deviation and an indication for the relative humidity over storage time. Comparison of samples wrapped in woodfree tissue with samples stored in ambient conditions without any packaging. SCA measurement conditions: 21–23 °C; RH.: 29 % (day 8), 40–44 % (day 15 and 29); at least 9 droplets analyzed for each data point. (b) Mean value of measured SCAs with standard deviation (blue line) and mean $C_{\text{pol}}/C_{\text{nonpol}}$ (orange line) as well as mean C/Cu (orange bars) with standard deviation. Samples were wrapped in woodfree tissue. The SCA is stabilized while changes in the surface chemistry still occur. SCA measurement conditions: 21–23 °C; 35–40 % RH.; at least 7 droplets analyzed for each data point.

adsorbed nonpolar hydrocarbon groups form the outermost layer of the samples with oxygen and copper underneath. Analysis of the C1s core level spectrum indicates that the nonpolar HCH groups point outwards and therewith form the primary contact to applied water droplets. The polar groups are deeper and seem to be responsible for the adhesion of the adsorbate to the metal or rather oxide surface. This may be an explanation why in Fig. 2 b) all samples show a similar SCA, although the ratio C/Cu as well as $C_{\text{pol}}/C_{\text{nonpol}}$ change. The hydrocarbon coverage ratio and layer thickness/density seem to be sufficient to dominate the water-substrate interaction with a nonpolar and, therewith, hydrophobic termination of the adsorption layer.

These results show that once an adsorption layer of sufficient thickness or density is grown, a further accumulation and even slight fluctuations in the polarity ratio do not significantly affect the SCA. Korczeniewski et al. [21] conducted simulations showing that the strongest change in SCA is observed after formation of a monolayer of hydrocarbons on copper single crystals, whereas additional layer growth only shows little effect, which is in good agreement with our experimental observations regarding C/Cu. This supports our results from an earlier work [20], indicating that there might be a material and microstructure-dependent threshold concentration of C/Cu which induces a wetting transition from hydrophilic to hydrophobic. This threshold might also depend on hydrocarbon type [43]. Our results suggest that the adsorption is not solely chemically driven but that after chemisorption, physisorption of hydrocarbons continues as the latter is not characterized by a self-limiting effect [44]. We assume that chemisorption is responsible for the wetting transition from hydrophilic to hydrophobic, while subsequent physisorption causes further gradual increase in SCA until the interaction forces are fully dominated by the hydrocarbon layer. This could also explain why we saw a levelling of copper SCA around 100° in a previous study [20] observing the wetting transition due to chemisorption, while samples in Fig. 2 level around 108° due to subsequent physisorption. However, the process of hydrocarbon adsorption is highly complex and elevated theoretical models will be needed especially for the investigation of multilayer hydrocarbon adsorption [43].

B) Influence of oxide chemistry

DLIP structures are generated by complex chemical as well as topographical modifications. It is known in the literature, that during the laser patterning of copper, both CuO and Cu₂O are formed, though Cu₂O seems to dominate the oxidic surface [29,45]. To separate the influence of topography and chemistry, we prepared flat surfaces with the two different oxides and pure metallic copper in a first step by

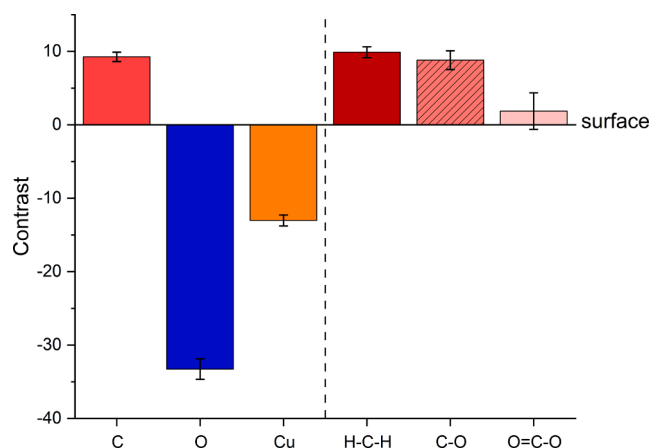


Fig. 3. Contrast calculated according to equation (4) from XPS measurements perpendicular (90°) and under an angle of 30° to the sample surface indicating the depth distribution of the measured elements on wrapped samples stored for 57 weeks.

sputter deposition. LSM measurements depict a similar roughness S_a of 3–4 nm for the sputtered surfaces which is in the range of the roughness of the polished substrates. Table 1 summarizes the roughness characterization and shows the S-ratio to be 1.000 for all surfaces within the resolution of the LSM suggesting a negligible influence of topography on the wetting behavior. FIB cross-sections displayed in Fig. 4 d) – f) allow for the measurement of the thickness of the deposited layers. To enhance the contrast between the copper substrate and the deposited layers and to avoid rounding effects of the cutting edges during FIB preparation, a Au₈₀Pd₂₀ layer was deposited before preparing the FIB cross-sections. Table 1 shows the layer thickness ranging between 130 nm and 147 nm. A thickness above 100 nm was pursued to assure a negligible influence of the underlying copper substrate in the water interaction. XRD measurements were performed to ensure the growth of the desired oxides. The star quality reference patterns shown as vertical lines in Fig. 4 d) are slightly shifted for the two oxide types compared to the peaks in the recorded spectra. Such peak shifts were also observed in other studies reporting the sputter deposition of oxidic copper layers [46]. This might depend on the oxygen pressure [47] and is an indication for deviations in the lattice constants [48,49], most likely caused by point defects and non-stoichiometry of the Cu₂O phase.

The analyses results from Fig. 4 and Table 1 confirm the production of flat surfaces differing in copper oxide states. After aging the samples, wetting as well as near surface chemical characterization were conducted. Instead of using the same samples for both analyses, only identical treated samples were used to avoid interactions respectively cross-contaminations between samples used for SCA and XPS analysis. Fig. 4 e) summarizes the SCAs measured 10 s, 60 s and 180 s after deposition of 3 μ l water droplets. The results reveal, that for each surface type, after 10 s a stable wetting state is already reached and no significant droplet spreading can be observed within three minutes after droplet deposition. The CuO samples show a very slight anisotropy of approximately 2° which could be induced by some preparation artefacts from the underlying polished substrate but is not expected to be a result of the sputter-deposition. When averaged over the two measurement directions, after 60 s, no significant differences can be observed between the sample types as they all range between 111° and 112° suggesting a negligible influence of copper oxide state on the water SCA.

Park et al. [49] found an increase in SCA on magnetron sputtered copper oxide thin films with increasing annealing temperature, which proved to not affect the oxide composition (they found a mix of amorphous Cu₂O and monoclinic CuO) but to enhance surface roughness. They attributed the increase in SCA to a lotus effect, but no details were provided on sample age or storage and the droplets with a very small volume of 0.2 μ l and corresponding short contact lines might be easily disturbed by certain roughness features. Ghotbi et al. [50] prepared SiO₂/Cu and SiO₂/CuO thin films by hydrothermalization varying in coating duration and strongly in surface morphology. They observed hydrophilic behavior with SCAs $< 40^\circ$ for all oxide films but also did not give details on the storage and measurement conditions. Zhao et al. [26] employed the hydrothermalization method to form films consisting of CuO and Cu₂O polyhedrons which both showed superhydrophobic properties after storage in C-rich atmospheres. XPS analyses revealed the adsorption of nonpolar hydrocarbon chains and theoretical calculations supported the idea of a strong chemisorption of carboxylic acid. They found that oxide composition does not influence the superhydrophobicity which is controlled by strong chemisorption of volatile

Table 1

Sputter layer thickness and roughness parameters determined by LSM for the sputter-deposited layers.

	Cu	CuO	Cu ₂ O
Layer thickness (FIB) [nm]	147 ± 14	140 ± 7	130 ± 5
S_a [nm]	4 ± 0	4 ± 1	3 ± 1
S-ratio	1.000 ± 0.000	1.000 ± 0.000	1.000 ± 0.000

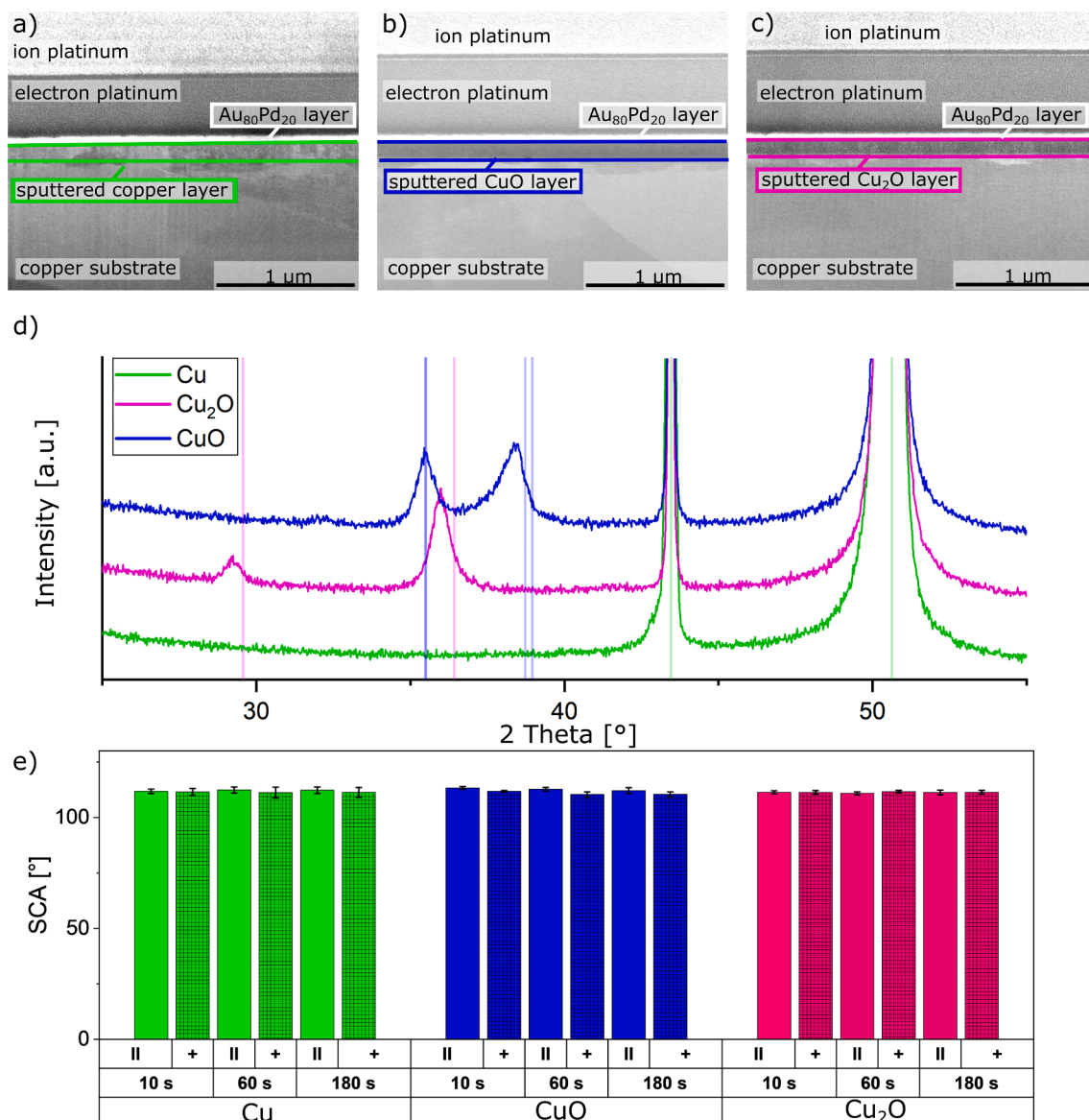


Fig. 4. FIB cross-sections of the sputtered surfaces coated with $\text{Au}_{80}\text{Pd}_{20}$ to enhance the contrast to the sputtered Cu layer (a), sputtered CuO layer (b) and Cu_2O layer (c). (d) XRD-analysis of the sputtered surfaces confirming the formation of Cu, CuO and Cu_2O . Vertical lines represent the reference patterns (Cu: 04-009-2090, CuO : 00-045-0937, Cu_2O : 04-007-9767). (e) Mean value of SCAs parallel (||) and perpendicular (+) to the sample axis with the standard deviation of aged sputter-deposited Cu, CuO and Cu_2O samples measured 10 s as well as 60 s and 180 s after droplet deposition. SCA measurement conditions: $\approx 22^\circ\text{C}$; 39–42% RH.; at least 10 droplets analyzed on 3 samples per type for 10 s measurement; at least 7 droplets analyzed on 3 samples per type for 60/180 s measurement.

carbon species, but the storage time varied greatly for the two oxide types. Our results go along with the observations made by Zhao et al. [26] as oxide composition does not seem to significantly affect the long-term SCAs on the sputter-deposited flat surfaces.

Near surface chemical characterization by XPS analysis was conducted to further verify the oxide state at the uppermost surface layer. XPS characterization of copper and its oxides is prone to large uncertainties due to rather small chemical shifts of the Cu 2p photoelectron line and strong overlaps (compare Fig. 5). Due to these difficulties in reliable copper oxide characterization by XPS, additional reference samples sputtered together with the samples from the analysis in Fig. 4 were used to obtain model spectra for the different oxide types (see Fig. 5) and used in all subsequent XPS analysis of Cu 2p and CuLMM for deconvolution to identify the contributions of different oxidation states (see [supplementary material](#) for details).

While the Cu 2p photoelectron line of CuO shows a just observable chemical shift ($< 1\text{eV}$) to metallic copper and a rather significant strong

satellite structure at about 940 eV (Cu^{2+}) as identification criteria, Cu_2O and metallic copper are nearly not distinguishable in the Cu 2p region [51]. Also, the difference of O1s chemical shifts ($< 0.5\text{eV}$) is too small to serve as criteria. The Cu LMM Auger lines in contrast show rather significant structures, for all three binding states. This offers the possibility of an identification by the peak shape of the Auger lines. Fig. 6 summarizes the elemental compositions retrieved from the Cu LMM, the Cu 2p and the O1s spectra of the aged sputter-deposited samples. Considering that the differences in peak shapes for Cu 2p are not very significant these results are only given for the sake of completeness. The same holds true for the O1s core level spectra. So as expected, the results based on analysis of Cu LMM, Cu 2p and O1s show some deviations, but all tend to confirm the identification of the sputter-deposited oxides as dominated by CuO and Cu_2O , respectively. The Cu-treated sample reveals native oxidation after aging which was not detected by XRD in Fig. 4. The quantitatively most reliable results are based on the Cu LMM analysis.

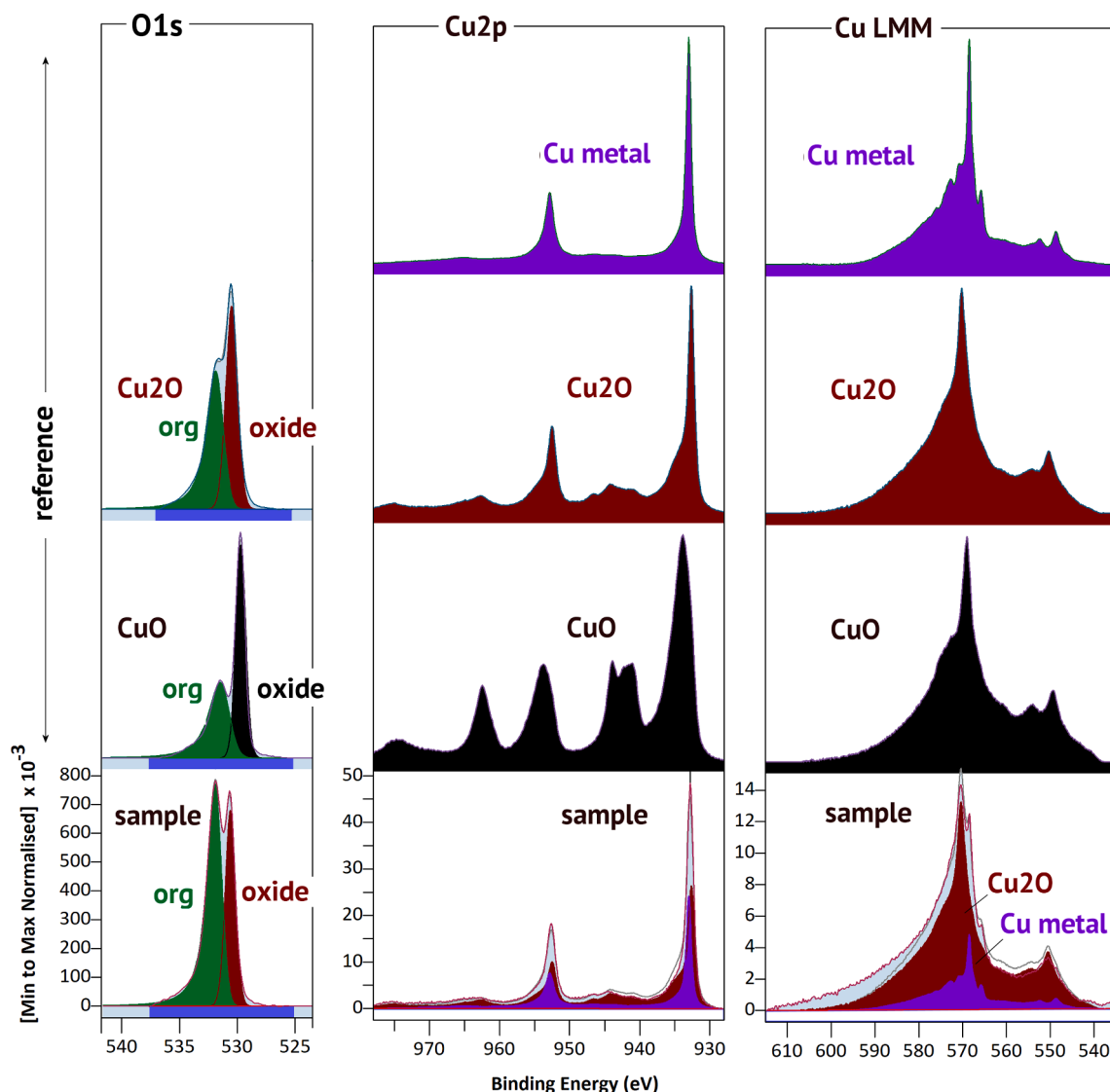


Fig. 5. Comparison of O1s, Cu2p and Cu LMM core spectra for reference surfaces of Cu (sputter cleaned bulk sample), Cu₂O respectively CuO (sputter-deposited). In the lower line the respective spectra for a polished aged Cu sample are shown inclusive a deconvolution into the distinguished distributions.

Our XPS analysis reveals negligible sulfur and nitrogen contaminations on the aged samples in the overview spectra (Fig. 7 a)). The detected carbon is predominantly bound as aliphatic hydrocarbon, and confirms the interpretation of omnipresent adventitious carbon (compare section A of the manuscript), whose nature is surprisingly still discussed [52]. Detail C1s spectra (Fig. 7b) show that besides the dominant portion of carbon bound in aliphatic hydrocarbons a significantly smaller portion has one or two oxygen atoms as direct binding partners. This suggests the involvement of organic compounds such as ethers, aldehydes, ketones, esters, alcohols, carboxylic acids, which are airborne and under typical atmospheric conditions omnipresent. These oxygen-containing organic species are subsumed and abbreviated here as OCO (carbon with two oxygen as binding partners in an aliphatic hydrocarbon chain) and HCO (carbon with one oxygen as binding partner in an aliphatic hydrocarbon chain) and form a small part of the adsorption film. The ratio C_{pol}/C_{nonpol} is similar for the sample types with 0.31 ± 0.02 for Cu compared to 0.28 ± 0.01 for CuO and 0.29 ± 0.03 for Cu₂O, while the Cu samples show a greater uptake of volatile carbons. As the Cu sample is not passivated once it comes in contact with the atmosphere after the sputter deposition, it is likely chemically more reactive than the two passivated oxidic surfaces. In a previous study [20], chemically more active samples due to an increased surface defect

density showed an enhanced uptake of hydrocarbons. We believe that surfaces with a higher affinity to oxygen like the Cu sputtered samples might also depict a higher affinity to hydrocarbons. Besides, interaction with water vapor influencing hydroxylation of the surfaces might be more pronounced for the pure copper surface than for the oxidic samples (see section A for discussion of water vapor interaction).

It must be noted that for our deposited copper films, adsorbed water molecules do not only influence hydroxylation but also native oxidation processes that can be drawn responsible for the detection of mainly Cu₂O on the Cu-treated samples (compare Fig. 6a) [53]. In order to evaluate the mechanisms of hydrocarbon adsorption on the three different sample types, high resolution analysis in early-stage aging would be necessary but was out of scope of this study as our main goal was to determine whether differently passivated copper surfaces depict varying SCAs after stable states were reached due to pronounced adsorption film formation.

Independent on oxide state, all three sample types build strong adsorption layers dominated by nonpolar hydrocarbons, which ultimately determine and dominate the wetting properties. The resulting hydrocarbon adsorbate film masks the surface and shields the metal oxide underneath. The results from Section A) and B) allow for a separation of chemical and topographical influences on laser patterned

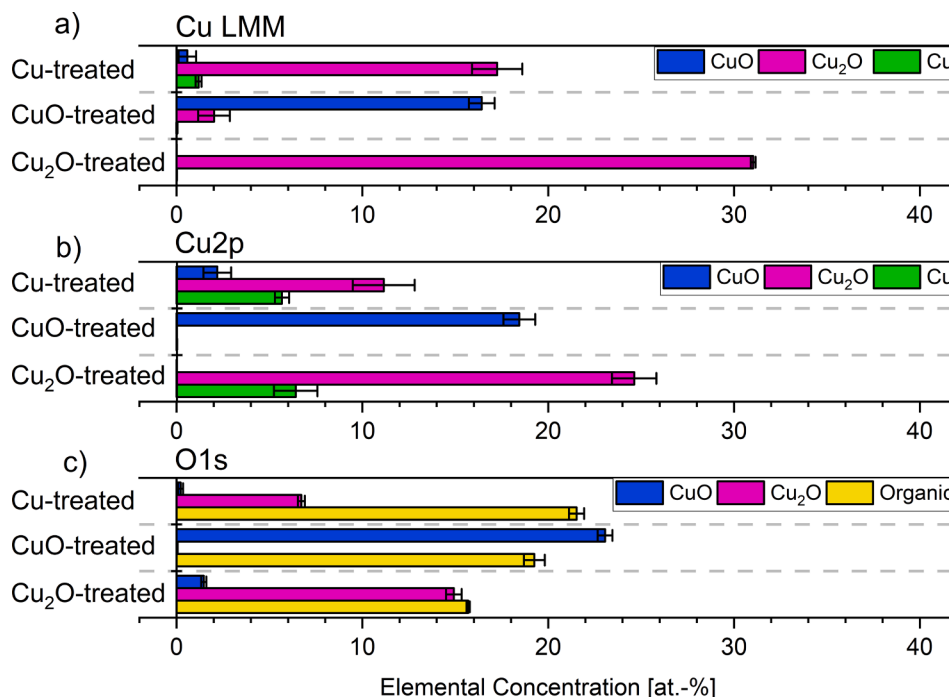


Fig. 6. Elemental concentrations in at.-% obtained from the XPS detail spectra Cu LMM (a), Cu₂p (b) and O1s (c). The sputter treatments are specified on the y-axis, the calculated concentrations are represented by colored bars.

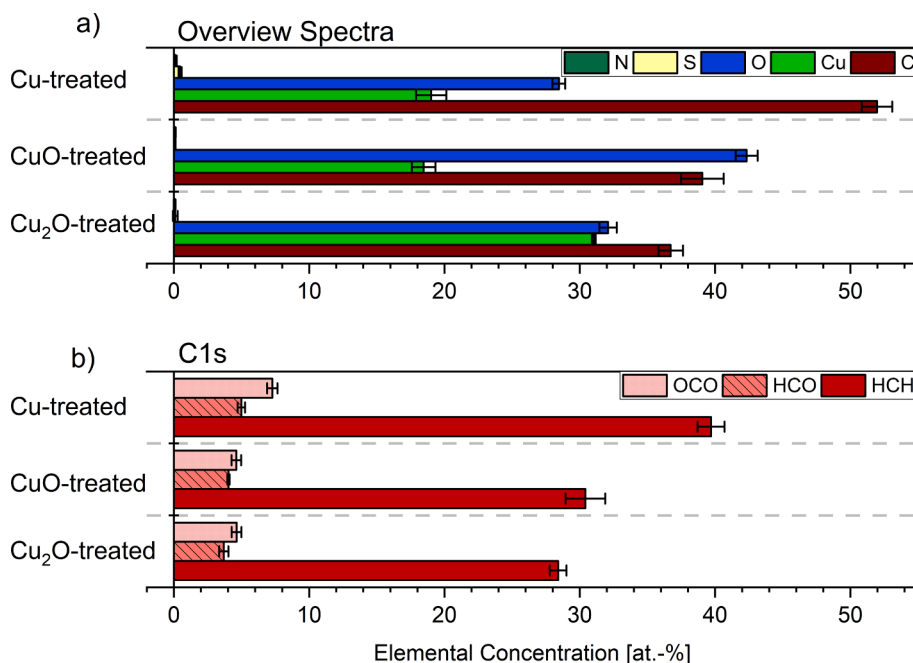


Fig. 7. Elemental concentrations calculated from XPS overview spectra (a) for all detected elements and (b) for carbon, broken down by its binding states according to the deconvolution of C1s core level spectra, of the sputtered samples. Sample sputter treatments are given on the y-axis.

surfaces. Before investigating complex hierarchical patterns, in a next step, the influence of a random topography paired with the oxidic surface was investigated.

C) Influence of topography

LR samples were produced by laser processing of polished copper samples with one ps beam and parameters were chosen in order to minimize directional topography following the laser scanning direction. Fig. 8 summarizes the topographical characterization conducted by SEM and FIB analysis, AFM, and LSM measurements.

The LR-samples show a random roughness consisting of melt structures and melt droplets varying in size forming undercuts and pores. These features complicated the AFM analysis in Fig. 8 c). The AFM tip is a non-equal-sided pyramid. The minimum angle of inclination is 65°. Thus, the maximum angle of the pyramidal shape with respect to its axis is less than 25°. Therefore, no feature with a higher aspect ratio, especially undercuts, can be characterized by AFM. Due to the irregularities of the surface, a slow scan rate was necessary. The LSM analysis in Fig. 8 f) does not depict significant differences in topography perpendicular

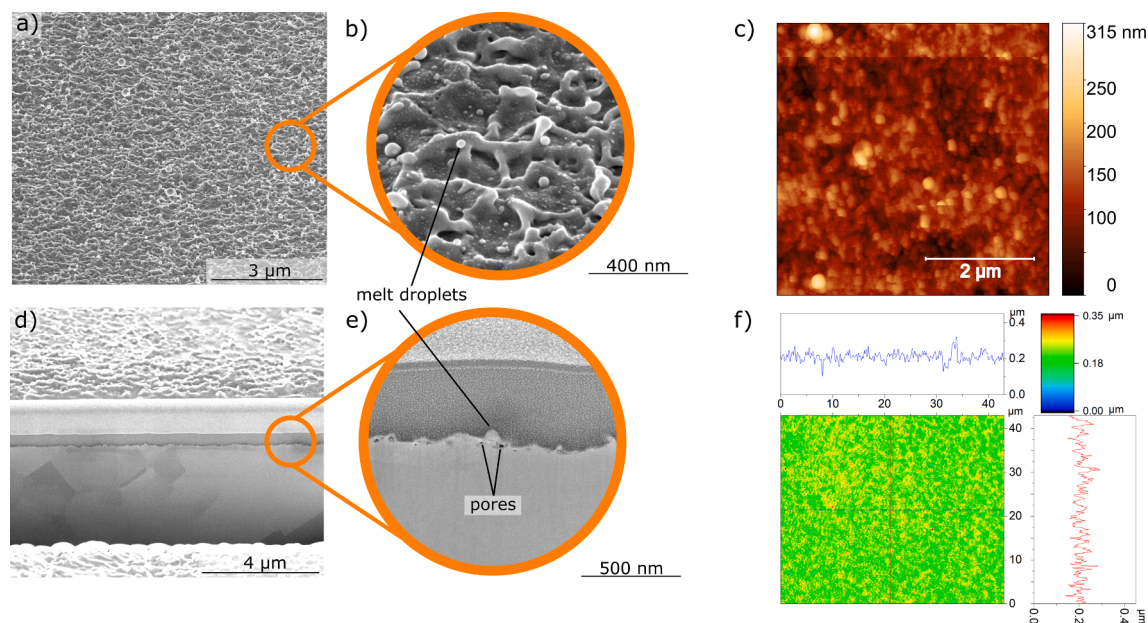


Fig. 8. Topographical characterization of a LR-Sample. (a) SEM-image of the 52° tilted surface with a magnified image in (b). (c) AFM characterization of the surface. (d) FIB cross-section with a magnified image in (e). (f) LSM characterization with height profiles parallel and perpendicular to the laser scanning direction.

and parallel to the laser scanning direction. Chemical characterization by XRD revealed the oxidic character of the melt features with a dominance of Cu_2O over CuO (compare Figure S1). Table 2 summarizes the roughness parameters obtained by LSM and AFM. The average surface roughness is 20 nm as measured by LSM, which is larger than that of the polished samples. The increase in surface area determined by the S-ratio differs greatly between the two different measurement techniques. Due to the lower lateral resolution of the LSM, the measured S-ratio is approximately 22 % lower than that measured by AFM.

Larger scale XPS analysis, that does not resolve the melt structures and melt droplets was conducted to investigate whether the picosecond laser treatment influenced the adsorption of volatile hydrocarbons with different functional groups. The analysis of the overview spectrum in Fig. 9 a) shows a clear dominance of copper, oxygen, and carbon as expected for aged laser treated copper surfaces. The detailed analysis of the C1s core level spectra (compare Fig. 9 b)) reveals, similarly to the polished and sputtered samples, a strong adsorption of hydrocarbons and considerably less oxygen-containing adventitious carbon groups leading to a polarity ratio ($C_{\text{pol}}/C_{\text{nonpol}}$) of 0.28 ± 0.1 .

Following our argumentation, that Cu LMM spectra are the most reliable source for oxide characterization, a clear dominance of Cu_2O follows. Some studies report an initial dominance of CuO right after laser processing which converts into Cu_2O upon exposure to oxygen during sample storage [31]. Cheng et al. [31] also attributed the witnessed wetting transition to the deoxidation of CuO to Cu_2O . Our results contradict this hypothesis as we found both oxide types to be hydrophobic upon exposure to ambient air due to hydrocarbon adsorption. Gaudiuso et al. [39] observed both oxide states together with $\text{Cu}(\text{OH})_2$ on femtosecond laser structured and low temperature heat treated surfaces but attributed the wetting transition to the adsorption of hydrocarbons on the hierarchical topography which was accelerated by the

heat treatment. Hydrocarbons also proved in our study to be the relevant factor for the latter discussed transition in the wetting behavior. The O1s spectrum in Fig. 9 c) reveals that most of the immediate surface oxygen detected by XPS is bound in organic species with the remaining oxygen being bound preferably in Cu_2O (see Cu LMM).

Fig. 10 shows the results of SCA measurements with the standard deviation on the LR-samples perpendicular and parallel to the laser scanning direction. The aged surfaces show a hydrophobic behavior and a slight anisotropy of the SCA appears with mildly increased angles perpendicular to the laser scanning direction (increase of approximately 2° after 10 s and of 3° after 60 s / 180 s). Though the topographic analysis in Fig. 8 does not show a visible structural anisotropy, the SCA reveals a weak direction dependency indicating that the topography has a very slight variation parallel and perpendicular to the laser scanning direction, which is below the resolution of the LSM analysis in Fig. 8. Though a parameter study was carried out to find the laser parameters, which deliver the most homogeneous pattern, the roughness can be overlaid with the trace of the single laser beam that was scanned over the samples multiple times with a hatch distance of 13.5 μm resulting in the observed wetting anisotropy. Also, the SCA parallel to the laser scanning direction shows a slight decrease with time suggesting potential capillary forces along the scanning direction of the laser beam. Still with the wetting anisotropy being in the magnitude of the standard deviation of the SCAs measured parallel, it can be considered as very mild.

As a reference, copper samples were polished, packaged, and measured on the same day as the LR-samples and depicted a SCA of $108^\circ \pm 2$, which is in good agreement with the results from Fig. 2. The minor roughness induced by the picosecond LR process increases the SCA by approximately 25 %. This is in agreement with the literature, where laser-induced surface features lead to a hydrophobization [28,30,54,55].

The S-ratios shown in Table 2 were used to calculate the theoretical SCA according to Wenzel [15], which underestimated the measured SCA greatly, indicating that either even the fine AFM tip was not able to capture enough details in order to obtain the correct increase in surface area or the droplet forms air-inclusions with the surface depicting a wetting behavior according to Cassie and Baxter [16]. For the calculation of the CB contact angle, the wetted fraction of the rough surface needs to be determined which poses a great challenge as this value is not

Table 2

Roughness parameters of the LR-Samples determined by LSM and AFM.

	LR-Sample
Sa [nm]	20 ± 0
S-ratio AFM	1.307 ± 0.07
S-ratio	1.025 ± 0.001

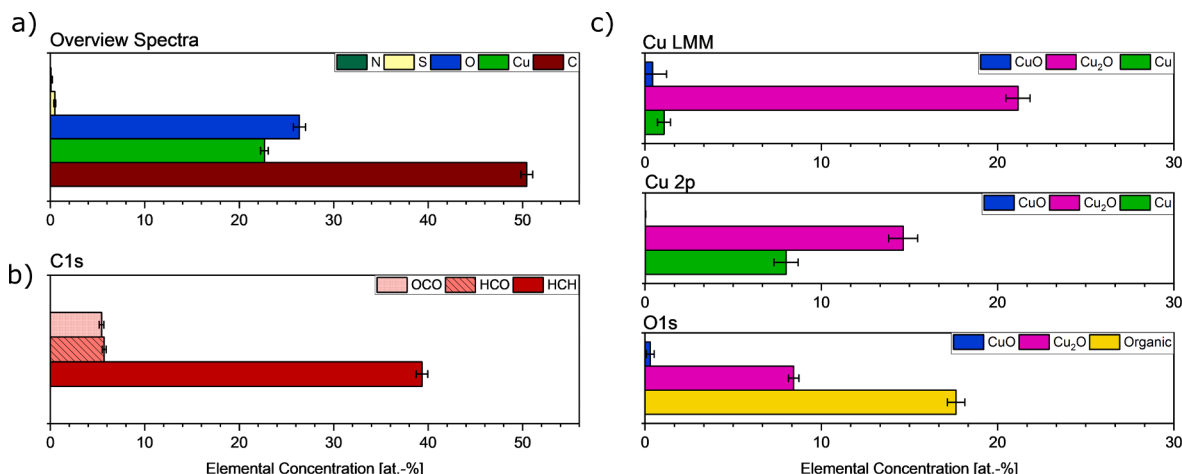


Fig. 9. Results of the XPS-analysis of the LR-Samples. (a) elemental concentrations from overview spectra, and (b) for carbon, broken down to its binding states according C1s core level spectra, as well as (c) for copper and oxygen from LMM Auger, respectively Cu 2p and O1s detail spectra.

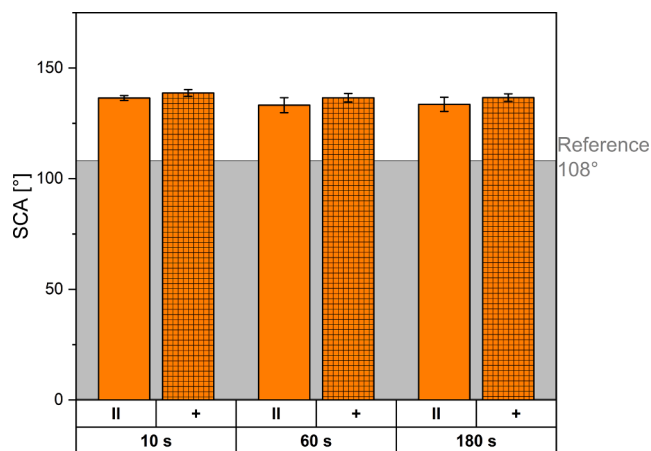


Fig. 10. Mean value of SCA measurements on LR-samples 10 s, 60 s and 180 s after droplet deposition parallel and perpendicular to the laser scanning direction with standard deviation. Only a very mild anisotropy is visible. Measurement conditions: $\approx 23^\circ\text{C}$; $\approx 39\%$ RH; 15 droplets on 3 samples for 10 s measurement; 6 droplets on 3 samples for 60/180 s measurement.

accessible via direct measurement. Moreover, transition states between CB and Wenzel exist [56]. Though the models from Wenzel and from Cassie and Baxter are very well established, it is known in the literature that there are wetting states that cannot be represented by them as not all topographic features are expected to influence the resulting wettability or show the potential to trap air [57]. According to equation (1) a r factor of 2.3 would be needed to approximate the measured SCAs around 135° for a Wenzel wetting state. As our previous investigations showed that a carbonous adsorption layer dominates the SCA over differences in the underlying oxide state, clearly topography can be held responsible for the increase in SCA. It must be mentioned though that the topography can only show its full potential after this adsorption took place. The production and detailed analysis of the sputter-deposited oxides as well as the LR-samples serve as a basis for the comprehension of complex wetting phenomena as observed on anisotropic hierarchical structures produced by DLIP. DLIP surfaces are not only characterized by the main periodic pattern, but also portray secondary roughness (sub-pattern) e.g. as LIPSS, craters, and/or a decoration with melt structures or even smaller nanoparticles [45,58,59].

D) Complex DLIP patterns

While copper oxide state does not seem to significantly alter the wetting response after adsorption of hydrocarbons, topography showed a pronounced effect even for simple structures. To determine the influence of a complex surface topography in more detail, different DLIP patterns were applied to polished copper surfaces. The structure periodicity was set to $6\ \mu\text{m}$, while the structure depth and therewith the aspect ratio was varied by laser power adaption of the picosecond laser. To fabricate a sample with changes in the nanoroughness with an identical primary line-like pattern, additionally a femtosecond laser was used to duplicate one of the pico-second laser structures. This does not only allow for the detailed analysis of the wetting response to slight topographic changes but also the characterization of surface morphology and chemistry induced by different pulse durations.

Fig. 11 summarizes the topographical characterization of the four sample types. Numbers in the sample names indicate the pattern depth of 500 nm for the fs-DLIP sample (named F500) and the ps-DLIP sample (P500) or 1000 nm respectively (ps-DLIP sample P1000). The LSM-scans in Fig. 11 a) – c) are combined with profile plots parallel and perpendicular to the main pattern. All three sample types depict periodic line patterns spreading homogeneously over the scanned area with the P1000 samples being approximately twice as deep as the other two sample types. The mean height of the profile elements R_c was measured in 9 different sample areas and results were averaged in Table 3. The desired structure depths were produced without significant differences between the F500 and the P500 samples. Also, the average roughness S_a calculated in three different sample areas, depicts comparable values for the F500 and P500 samples (147 and 134 nm, respectively) and an increased roughness of 272 nm for the P1000 samples. It must be noted that the LSM measurement cannot resolve all structural details due to its limited resolution (120 nm lateral, 10 nm in height). AFM scans in Fig. 11 which also have a limited resolution show an increased roughness in the structural valleys of F500, which might contribute to the slightly higher S_a values while the decoration with nanoparticles on the peaks of the P500 sample might not be fully detected by the LSM. Clearly, the pile-up of particles on the P1000 sample was detected though (compare Fig. 11 c). For the increase in surface area (S-ratio) the same trend can be observed. Both ps samples show more oxidic particles on the peaks and especially for the P1000 sample, the AFM scan reveals melt droplets agglomerated on the maxima of the pattern. The LSM profile scan along such a structural maximum also reveals the more pronounced roughness. The fs sample on the other hand is clearly substantially rougher inside the valleys. On the AFM scan of the polished reference sample, only a few scratches from the final polishing step are visible leading to a roughness of 4 nm. For a more detailed analysis of

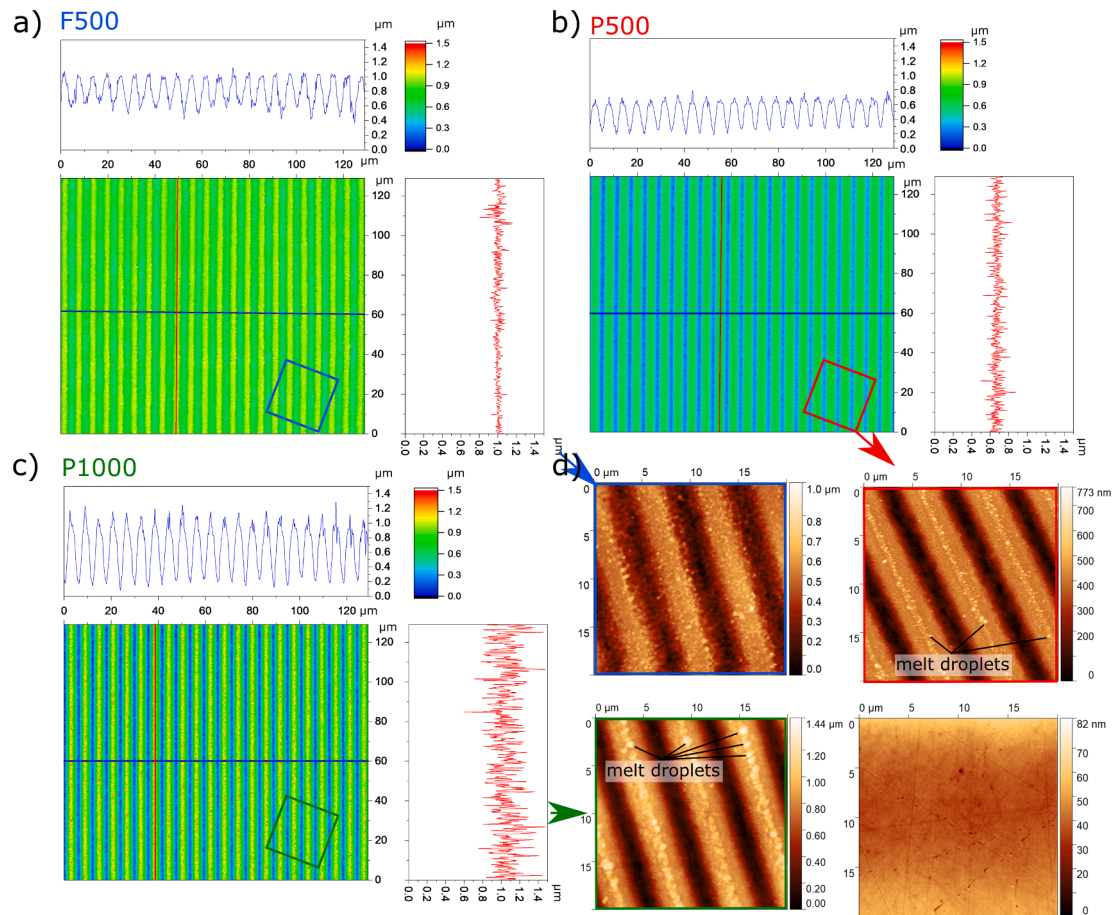


Fig. 11. Topographical analysis of the laser samples and the polished reference. (a – c) LSM-Scans of the DLIP samples with profile plots parallel and perpendicular to the main structure (F500 = fs-DLIP, 500 nm deep / P500 = ps-DLIP, 500 nm deep / P1000 = ps-DLIP, 1000 nm deep). (d) AFM-scans of the three DLIP-structures and the polished reference sample.

Table 3

Results of roughness analysis by LSM (R_c , S_a and S-ratio) as well as AFM (S-ratio AFM) for the four sample types.

	F500	P500	P1000	Reference
R_c [nm]	474 ± 22	471 ± 14	1005 ± 27	—
S_a [nm]	147 ± 3	134 ± 3	272 ± 1	4 ± 0
S-ratio	1.068 ± 0.002	1.038 ± 0.001	1.142 ± 0.002	1 ± 0
S-ratio AFM	1.132	1.122	1.192	1.001

the topographic features, SEM and FIB characterization were carried out (compare Fig. 12).

The characterization of the F500 samples in Fig. 12 a) – d) reveals topographic maxima with only a discreet secondary roughness dominated by flakelike structures reported in another study as well on DLIP-copper samples with a periodicity of 3 μm [45]. The valleys of the structures depict a pronounced roughness as a network of crater structures forms a sub-pattern (compare Table 4). The P500 surface differs mainly from the F500 surfaces through the agglomeration of oxidic particles and melt droplets arranged in a line along the structural maxima increasing local roughness and decreased roughness in the valleys ($R_q = 30 \text{ nm} \pm 4$). The FIB cross-section in Fig. 12 g) reveals a similar profile line as the F500 samples except of the decoration with oxidic features on the structure peaks. For the deeper ps samples P1000, the agglomeration of oxidic particles and especially melt structures is more pronounced than on the P500 samples. Oxidic nanoparticles are not flakelike as observed on the F500 samples but show a more regular morphology. The FIB cross-section reveals a more sinusoidal profile line

due to the stronger agglomeration of oxidic particles and melt structures on the peaks of the pattern. An increase in pulse duration from the fs to the ps-regime leads to a higher temperature impact on the copper surface. It has been reported that resolidified particles appear for ps laser treated copper surfaces along oxide layering while fs treated copper only showed a thin oxidic layer on top of the copper substrate [60]. The larger heat effected zone of the substrate treated with a ps laser pulse was accompanied by a more pronounced recast area as well as ejected and resolidified particles on aluminum [61,62], which is in good agreement with our observations for DLIP on copper. Regarding the sub-pattern morphology the more defined crater structures could be explained by the findings by Winter et al. [63]. They observed that copper irradiated with 525 fs builds a stronger “eruption structure” in the sub-μm range while the 20 ps irradiated copper showed increased bubble sizes in the μm range. Though this is expected to increase the roughness for the ps samples, the F500 samples show a finer network forming in the valleys, which might be overlayed by more pronounced melt structures for the P500 sample. Rajan et al. [61] reported stronger recast deposition after laser ablation with higher ps powers on aluminum and we can confirm these results for DLIP on copper (compare P1000).

XRD measurements were conducted in the range where oxidic copper peaks (CuO and Cu₂O) are expected and are summarized in Figure S2. Though a clear peak assignment to reference spectra was not possible, a general trend could be observed supporting the SEM findings with more oxides for F500, P500, and P1000, respectively. For near-surface characterization of the chemical composition of the surfaces, larger scale XPS analysis, that does not resolve the laser structures was conducted. Fig. 13 shows the elemental concentrations of the surface

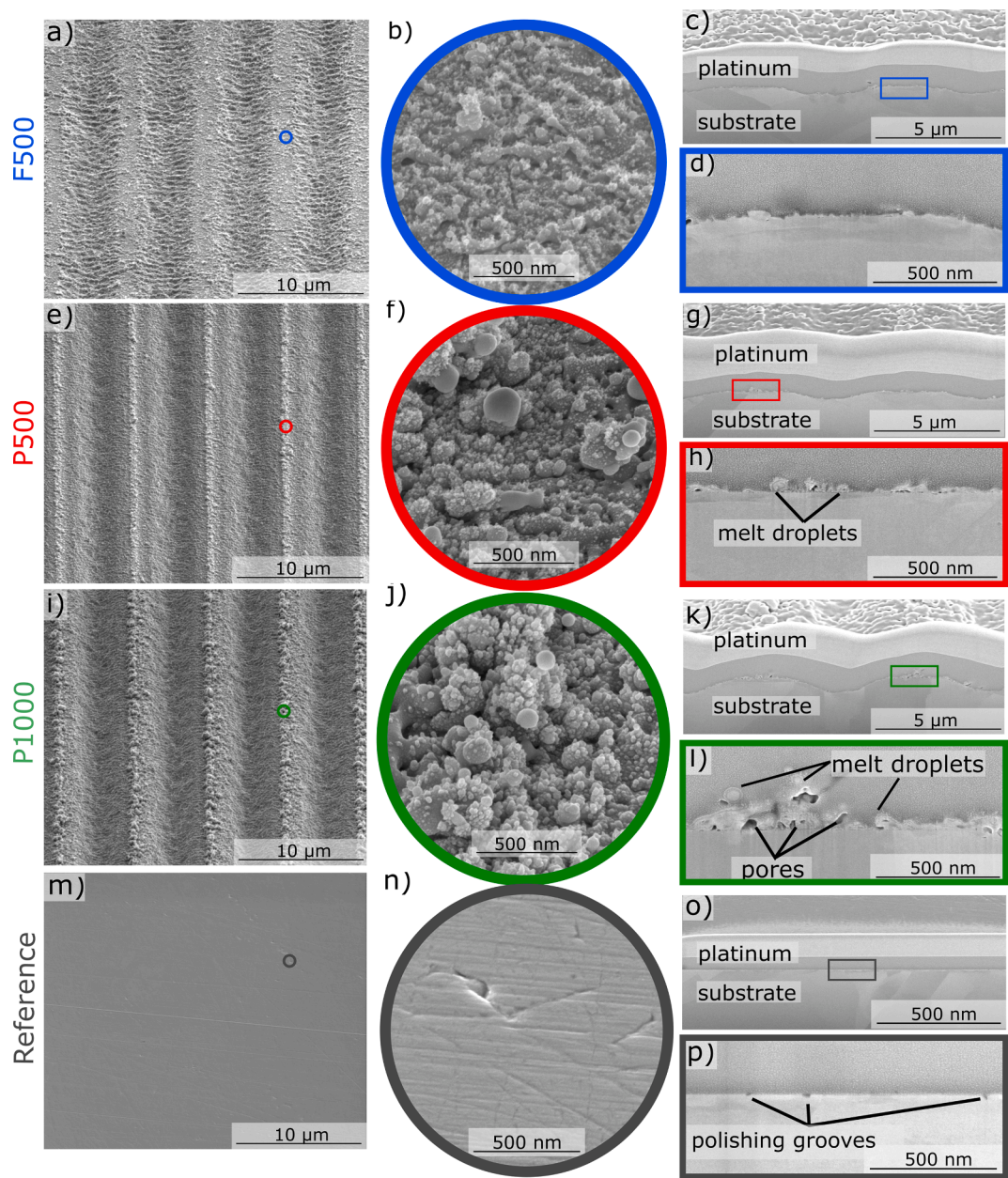


Fig. 12. SEM- and FIB characterization of the four sample types (F500 = fs-DLIP, 500 nm deep / P500 = ps-DLIP, 500 nm deep / P1000 = ps-DLIP, 1000 nm deep): (a) – (b) SE images of F500 with mild nanoroughness on the peaks and pronounced roughness in the structure valleys. (c) – (d) FIB-cross section of F500 showing the flattened peaks. (e) – (f) SE images of P500 with more pronounced nanoroughness on the peaks through melt droplets. (g) – (h) FIB-cross section of P500 showing the flattened peaks decorated with melt droplets and nanoparticles. (i) – (j) SE images of P1000 with strong nanoroughness on the peaks through melt droplets and oxidic particles. (k) – (l) FIB-cross section of P1000 showing a more sinus-like profile and a strong decoration of the structure peaks with melt droplets enclosing pores with the substrate. (m) – (n) SE images of the polished reference with some artefacts from the mechanical polishing. (o) – (p) FIB-cross section of the polished reference showing the flat profile with some polishing grooves.

Table 4
Roughness analysis of the peaks and valleys of the laser patterned samples.

R_q [nm]	Peak	Valley
F500	35 ± 5	51 ± 3
P500	51 ± 11	30 ± 4
P1000	123 ± 15	37 ± 3

composition of the DLIP-samples and a polished copper surface after aging, core level spectra can be found in Figure S3. The elemental concentrations shown in Fig. 13 a) rule out unexpected foreign contamination. The detected Cu binding states according to the results

of the analysis of Cu LMM spectra shown in Fig. 13 b) indicate that Cu_2O forms the oxidic layer for all sample types. The analysis according to the Cu2p spectra and the detail O1s spectrum confirm the domination of Cu_2O over CuO . The detail O1s spectrum additionally shows a strong signal of organic bound oxygen due to the organic adsorption layers. Fig. 13 c) depicts the detected C binding states analyzed from the C1s spectrum. Due to sample aging, a strong adsorption of aliphatic carbon groups appears on all sample types with a minor contribution of polar groups. The amount of adsorbed carbonous groups measured as C/Cu ratio is given in Table 5. The ratios are smaller than expected from Fig. 2 for samples aged for 12 weeks but all samples are still in the regime where stabilized SCAs were observed on polished surfaces (compare

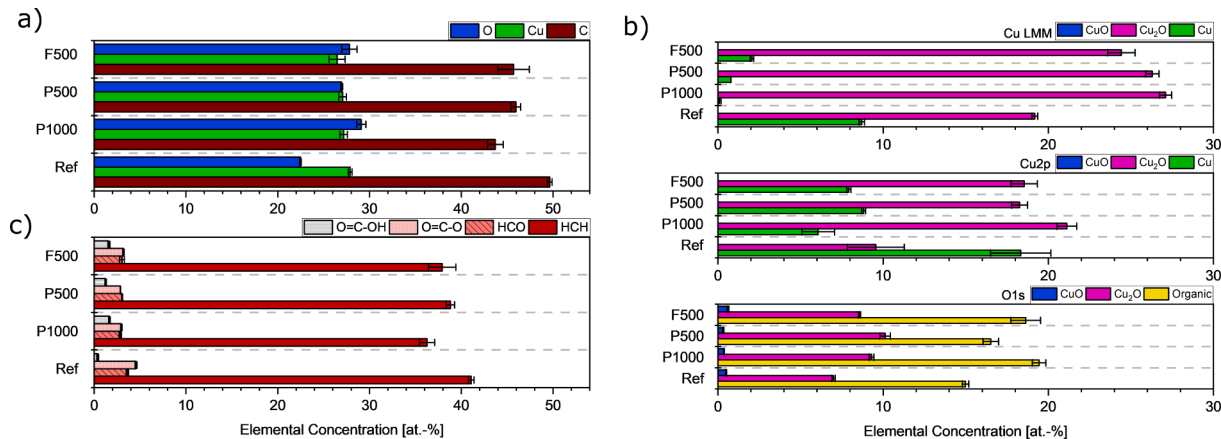


Fig. 13. XPS overview spectrum (a) and detail spectra Cu LMM, Cu2p and O1s (b) and C1s (c) of the DLIP-samples and a polished reference sample after aging. A strong hydrocarbon adsorption layer covers the copper substrate with its oxidic reaction layer dominated by Cu₂O.

Table 5

The C/Cu ratio serves here as a measure for the adsorption of volatile hydrocarbon groups and ratio C_{pol}/C_{nonpol} describes the polarity ratio of the adsorption layer for all sample types.

XPS ratios	F500	P500	P1000	Reference
C/Cu	1.73 ± 0.12	1.7 ± 0.04	1.61 ± 0.05	1.78 ± 0.02
C_{pol}/C_{nonpol}	0.21 ± 0	0.18 ± 0	0.21 ± 0.01	0.21 ± 0.01

Fig. 2). Reasons could be another batch of the packaging paper that adsorbed less carbonous species itself but also fluctuations in humidity or temperature during sample preparation could potentially influence the adsorption process. C_{pol}/C_{nonpol} delivers very comparable values for all sample types. Fig. 13 c) reveals the presence of COOH groups on the laser treated samples which are barely present on the polished reference (see Figure S3 for details). They were also found in a previous study of laser treated copper surfaces [18,45] and might be adsorbed during the laser process itself by interactions of the laser plasma with the surrounding atmosphere. The results of XPS analysis depicted in Fig. 13 and Table 5 reveal a dominance of Cu₂O for all sample types regarding the oxide state and a strong hydrocarbon adsorption with comparable

adsorption film compositions.

To increase information depth of the XPS analysis, sputter profiles were recorded for all sample types (compare Fig. 14) supporting previous results by showing a more pronounced oxide layer from F500 to P500 and P1000 and a comparable course of the C concentration.

To summarize the XPS analysis, the sample types differ in the amount of surface oxide, respectively oxide layer thickness, but not in the dominating oxide type. Also, all samples show pronounced uptake of adventitious carbon and the adsorbed hydrocarbon film covering the oxide shows a very comparable composition. Due to the coverage of all samples with the adsorption film, differences observed in the wetting behavior can be assigned to the variations in topography. Fig. 15 summarizes the wetting results of the SCA tests on the different surfaces with top-view images of the droplets. As can be seen from Fig. 15 a), the F500 samples show very high SCAs of approximately 170° parallel and perpendicular to the line pattern with no visible anisotropy. The wetting state seems stable over time and no spreading of the droplet was observed. Though the P500 samples are characterized by the same primary topography, a completely different wetting response to the applied water droplets can be observed. It is characterized by a strong wetting anisotropy with SCAs of approximately 160° perpendicular to the line

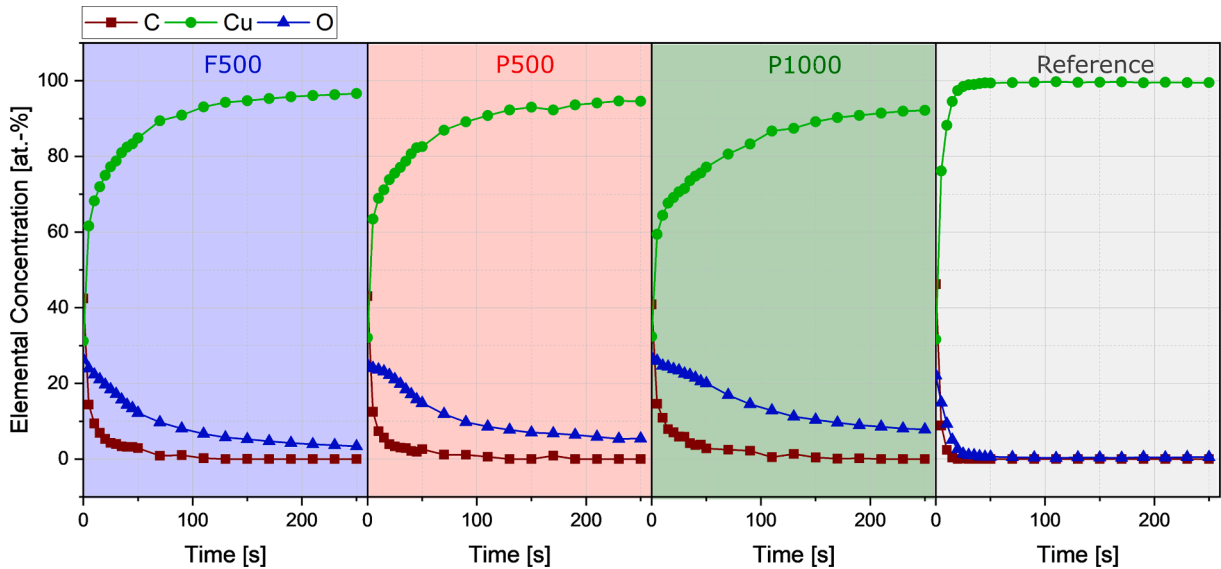


Fig. 14. In order to map the depth distribution of the detected elements, XPS sputtering depth profiles were recorded. The most pronounced difference can be found in the oxygen concentration falling abruptly on the polished reference on the one hand and decreasing progressively on the laser treated surfaces on the other hand. Results indicate a stronger oxide formation from F500 to P500 and P1000. The course of the C concentration is comparable for all sample types.

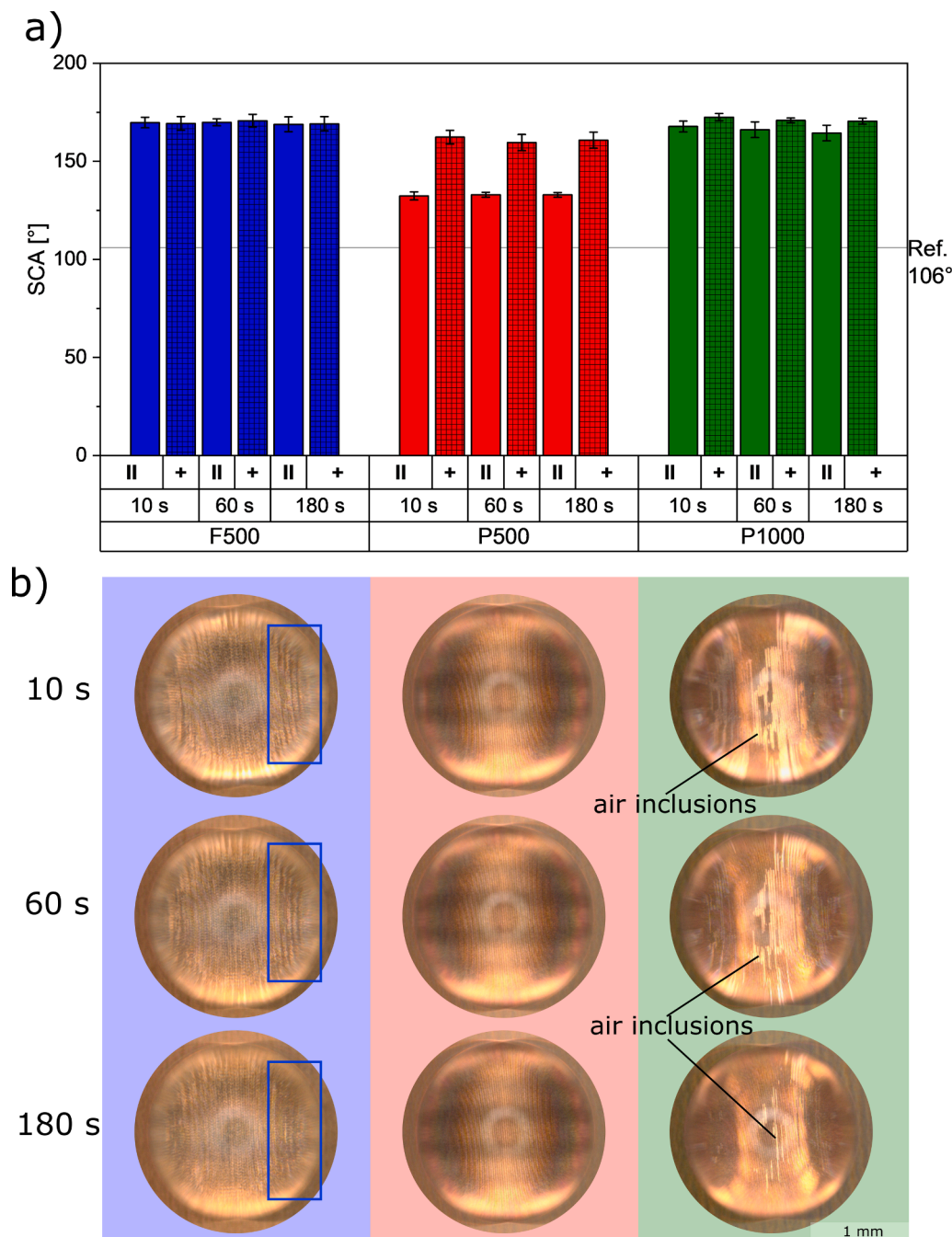


Fig. 15. (a) Mean value of SCAs of aged DLIP samples (F500 = fs-DLIP, 500 nm deep / P500 = ps-DLIP, 500 nm deep / P1000 = ps-DLIP, 1000 nm deep) 10 s, 60 s and 180 s after droplet deposition parallel (II) and perpendicular (+) to the line-like pattern with the standard deviation. Measurement conditions: $\approx 22^\circ\text{C}$; $\approx 49\%$ RH.; at least 9 droplets on 3 samples for 10 s measurement per type; 6 droplets on 3 samples for 60 s/180 s measurement per type. (b) Top view of the droplets on the different surfaces. Bright stripes indicate air bubbles trapped in the valleys of the structure due to the change in reflectivity.

pattern and 130° in the other direction. A slight settlement of the droplet along the roughness is indicated by the gentle decrease of the SCA after 60 s. The behavior of the P1000 samples is comparable to the F500 samples with SCAs in the range of 170° perpendicular to the line pattern. A slight anisotropy of approximately 5° can be observed that seems to mildly increase with time, but it must be mentioned that droplet deposition on the P1000 samples posed a challenge despite the increased volume of $6\ \mu\text{l}$ and took more time which is why the slight decrease of SCAs after deposition could also be due to a modest droplet evaporation. As XPS analysis revealed that all sample types are covered by an adventitious carbon film that is in direct contact to the water in the wetting experiments, topography can be drawn responsible for the

observed wetting differences. Especially the anisotropic wetting of the P500 samples compared to the F500 samples indicates that the same primary topography may induce different wetting regimes when combined with varying secondary roughness features. Based on previous findings [27] and ref. [64], we expect a CB wetting state for line patterns that do not demonstrate wetting anisotropy and a Wenzel wetting state for the P500 samples that do demonstrate wetting anisotropy. Thereby, wetting anisotropy is induced by the droplet entering the pattern, where capillary forces can pull the droplet along the pattern grooves. In order to better observe the existing wetting states, images of additionally applied droplets were taken in top-view with a digital microscope (compare Fig. 15 b)) without the cover set up.

Images of droplets on the F500 sample show subtle visible brighter stripes in the line pattern which are assumed to be caused by trapped air bubbles. After 180 s, margins of the droplet show less bright stripes indicating a partial transition to the Wenzel state (compare blue frame). The P500 sample depicts a Wenzel wetting state already 10 s after droplet deposition without any visible air inclusions, which matches the observed wetting anisotropy. A strong spreading is not observed. The P1000 samples show air inclusions due to their increased aspect ratio compared to P500 [56,61,65]. Here, the transition to the Wenzel state is pronounced moving from the outside to the inside of the droplet, which is in good agreement with the findings by Murakami et al. [56]. Still, no strong deviation in SCA with time occurs possibly due to droplet pinning on the increased peak roughness. Wetting of the secondary peak roughness cannot be assessed but concerning the primary pattern, the F500 samples show the most stable CB state, followed by the P1000 samples with a clear transition to the Wenzel state within a few minutes and the P500 state with a stable Wenzel wetting already after 10 s. For pattern grooves smaller than the capillary size of water (2 mm), elongation of the droplet is expected in the Wenzel state due to capillary forces reducing with increasing surface hydrophobicity and CB wetting [64]. We barely observe droplet elongation in top view for P500 despite apparent Wenzel wetting which we trace back to the high chemical hydrophobicity and a complex interplay with surface topography, e.g. droplet pinning. Our results indicate that not only the primary topography (line pattern) and its aspect ratio, but also the sub-pattern morphology play a major role regarding the wetting state due to the strong difference between F500 and P500. We believe that the increased roughness in the valleys of F500 samples favors air inclusions and isotropic wetting. We want to highlight that the formation of periodic sub-patterns in the valleys like LIPSS instead of the here observed random network structures might trigger pronounced wetting as capillary forces could be active on two scales (primary and secondary pattern). Detailed investigations on the effect of periodic sub-pattern morphologies and their orientation relative to the primary pattern will be necessary in the future.

Analysis of water adhesion by measurements of advancing contact angle (ACA) and receding contact angle (RCA) was not found suitable for our samples (details can be found in the [supplementary material](#)). In order to still be able to observe whether the samples show a high or a low water adhesion, tilting experiments were conducted parallel and perpendicular to the line pattern. Due to the use of a prototype tilting stage, we refrain from giving exact sliding angles and interpret the results in order to assign the observed wetting behavior to a low water adhesion as observed for the lotus effect or a high adhesion as shown by the rose petal effect [65]. Images of the tilted surfaces are shown in [Figure S4](#). F500 as well as P1000 samples showed rolling of the droplet independently of the tilting direction, while the droplet stuck on the P500 samples and the reference samples even after a tilt of 180°. On the F500 sample the water leaves occasional residues. On the P1000 sample only very small residues are left, which evaporate within seconds after the rolling of the droplet. High water adhesion as observed on P500 can be caused by penetration of the primary roughness with (Wenzel) or without penetration of the secondary peak roughness (Cassie impregnating wetting state) as postulated for the rose petal effect [66,67]. Rose petal behavior was already observed on DLIP patterns on steel [68] as well as on flat fs-treated copper transitioning to an increasing lotus like behavior for more pronounced structures [65] which resembles the trend we observe between P500 and P1000.

Bhushan et al. [67] depicted a wide range of possible wetting regimes for hierarchical microstructures with a primary roughness and a secondary nanoroughness. They distinguish between a lotus effect with air inclusions with the primary and secondary roughness and a Cassie state penetrating only the nanoroughness on top of the primary topography. For the F500 and the P1000 samples the water residues indicate adhesion or pinning to some topographic features whose characteristics cannot be determined in detail in our experimental setup. We expect a

further adsorption of hydrocarbons (e.g. due to continued aging) or the deposition of more hydrophobic molecules to reduce the water residues on the surfaces of F500 and P1000 and to further lower their sliding angle as higher concentrations of nonpolar surface groups are expected to increase and further stabilize trapped air and delay penetration of the water into the roughness. This is also believed to fully cancel any anisotropy on P1000 but otherwise not expected to majorly influence the SCAs. For the P500 samples, it is uncertain at this point whether a more hydrophobic surface termination might reduce the witnessed anisotropy and favor air inclusions as witnessed for F500 or if the topography prevents CB wetting independent of chemical hydrophobicity. More studies in the future will be necessary to address this question. The application of hydrophilic coatings is expected to greatly enhance the wettability of all surfaces, transferring all patterns into the Wenzel wetting state with a strong water adhesion. However, detailed analysis of these research questions was beyond the scope of this work and will be required in the future to verify these assumptions.

Clearly, very slight changes in topography can induce significantly different wetting behavior. Though an exact determination of the Wenzel factor r and the CB factor f are not possible in our experiments, indications exist regarding the wetting states. We assume that the pronounced roughness in the valley of the primary topography of the F500 samples in combination with the flattened peaks impedes the droplet from wetting the valleys, induces air-inclusions and therewith results in the roll-off behavior. The subtle decoration of the peaks with flakelike nanoparticles might push the wetting behavior even further to the superhydrophobic state [39]. A slow transition towards Wenzel state was observed. The same primary topography produced by ps-DLIP (P500) with an increased roughness on the structural peaks due to a stronger agglomeration of melt structures and a decreased roughness in the valleys induces wetting of the valleys which also causes the witnessed anisotropy of the SCAs and a strong water adhesion. Sticking of the droplet is as pronounced as on the polished reference and supports the idea of either a full Wenzel or a Cassie impregnating wetting state as shown in ref. [66]. The higher structures of the P1000 samples induce air inclusions [56,65] despite increasing peak roughness, although no stable transition is observed. Still, the present air inclusions prevent the droplet from sticking to the surface when turned upside down. Clearly, topography has a major influence on the wetting regime and even with the same primary pattern, different wetting states can be achieved.

4. Conclusions

This study provides a comprehensive insight into the wettability of copper with its multi-step experimental approach. The precise design of the experiments and the comprehensive chemical as well as topographical analysis allow for the clear separation of both effects on the wetting behavior of copper. New insight is gained into the ageing behavior of copper and the formation of carbonous adsorption films and applied to interpret the impact of topography on different scales. The adsorption of organic species from the atmosphere is known to heavily influence the resulting wetting behavior [18]. In the first set of experiments, we were able to show that upon controlled aging of polished copper surfaces in contrast to ambient storage conditions the SCA stabilizes despite ongoing increase in hydrocarbon concentration and fluctuations in the relative amount of polar adsorbates. This supports our findings from a previous study [20] that a material- and micro-structure dependent threshold of adsorbed hydrocarbons might exist after which additional adsorption only leads to gradual increase of SCA. This is in agreement with the simulative findings by Korzeniewski et al. [21] which showed that once a monolayer of hydrocarbon is formed, additional adsorption does not induce strong changes in SCA anymore, while we were able to not only determine the amount of adsorbed hydrocarbons but also the binding states and the arrangement in detail by XPS-analysis. Controlled adsorption experiments will be needed in the future to elucidate the role of adsorption layer density and thickness

regarding the wetting response. Our results suggest that after chemisorption which we draw responsible for the wetting transition, physisorption might lead to a further growth of the adsorbate layer as no saturation of C/Cu was observed.

Based on these findings, samples in the following experimental sets were stored under strictly controlled conditions. In order to investigate the role of copper oxide in the wetting response of aged samples, magnetron sputter deposition was applied to form Cu, CuO and Cu₂O on polished copper substrates. Though XPS revealed a more pronounced hydrocarbon adsorption for Cu, SCA analysis delivered similar long-term wetting behavior for all three surface types. This finding goes along with a study published recently [26] where rough copper oxides produced by hydrothermalization showed the same hydrophobicity after storage in C-rich atmospheres for different times. While in reference [26], the impact of the copper oxide state was analyzed on topographically altered surfaces, we performed the investigations on flat samples to exclude an overlaying impact of a pronounced roughness. We kept storage conditions the same and minimized the influence of topography and therewith can disprove the hypothesis that a deoxidation from CuO to Cu₂O might be responsible for a wetting transition [31] as both oxides turn hydrophobic upon exposure to atmospheres rich in hydrocarbons. Based on these findings, the influence of topography on the wetting behavior of copper was investigated in detail by surface laser treatment. In order to understand the role of a mild isotropic roughness first, LR was implemented to uniformly roughen the surface. An increase of SCA of 25 % compared to the polished surface was reached. Again, identical storage conditions were applied to surface types under direct comparison to each other making our estimation of 25 % reliable. A strong hydrocarbon layer was detected, which allowed the topography to show its potential for further hydrophobization. For the analysis of hierarchical structures, two different pulse durations were applied in the DLIP set up to generate the same primary line-like topography with varying sub-pattern morphologies. Contrary to other studies taking different pulse durations into account [62], we aimed at keeping the primary topographies as similar as possible. As the oxide state proved to not influence the wetting in the aged state and samples were equally stored to form adsorption layers, clearly topography could be drawn responsible to the distinct difference in the wetting behavior. A more pronounced roughness in the structural valleys in combination with minor topographic features on the peaks in from of a mild decoration with flakelike nanoparticles favors air-inclusions and roll-off behavior. More pronounced roughness on the peaks induced by melt structures with reduced topography in the valleys rather induces wetting of the valleys and strong adhesion. Increasing the depth of these structures can induce air inclusions and cause rolling of the droplet despite increasing peak roughness. While a variation of the primary topography and especially the aspect ratio proved to influence water adhesion before [56,61,65], we were able to induce opposite wetting phenomena while maintaining the primary topography. A stronger hydrophobic surface termination potentially further stabilizes CB wetting which might affect especially the sliding behavior towards smaller angles. Detailed experimental studies of the dependence of the dynamic wetting behavior of hydrocarbon adsorption will be needed in the future. Also, different sub-pattern morphologies e.g. LIPSS need to be investigated in detail in systematic experimental approaches.

With these results, our work provides a comprehensive overview of the wettability of copper.

The knowledge gained in the presented study gives fundamental insight into the wetting behavior of surfaces, particularly patterned samples and allows for the detailed design of copper surfaces targeting the desired static as well as dynamic wetting behavior.

CRedit authorship contribution statement

Sarah Marie Löfflein: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal

analysis, Conceptualization. **Rolf Merz:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Yerila Rodríguez-Martínez:** Writing – review & editing, Methodology, Investigation. **Florian Schäfer:** Writing – review & editing, Methodology, Investigation. **Philipp G. Grützmaier:** Writing – review & editing, Conceptualization. **David Horwat:** Writing – review & editing, Supervision, Resources. **Michael Kopnarski:** Supervision, Resources, Project administration, Funding acquisition. **Frank Mücklich:** Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2024.04.212>.

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Supplementary Material

Influence of chemistry and topography on the wettability of copper

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Details on sputter deposition

Table S1: Parameters for sputter deposition of Cu, Cu₂O and CuO on polished copper substrates.

	Cu	Cu₂O	CuO
<i>Argon flow rate [sccm]</i>	50	50	50
<i>Oxygen Flow Rate [sccm]</i>	-	6	12
<i>Current [A]</i>	0.15	0.15	0.15
<i>Working Voltage [V]</i>	355	397	405
<i>Working Pressure [mbar]</i>	$3.4 \cdot 10^{-3}$	$3.84 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$
<i>Deposition Time [min]</i>	10	5	6

Details on laser patterning

Table S2: Parameters für laser patterning.

	LR samples	DLIP fs Laser F500	DLIP ps Laser P500	DLIP ps Laser P1000
<i>Spot diameter [μm]</i>	27*	52	83	99
<i>Power [mW]</i>	920	31	1344	1936
<i>Pulse-to-pulse distance in scanning direction Δx [μm]</i>	8.77	20	10	10
<i>Hatching distance [μm]</i>	13.5	18	18	18
<i>Acc. Fluence [J/cm^2]</i>	7.77	7.8	7.5	10.8

* For the LR process the given spot diameter is not the focus diameter as only a defocusing to 27 μm allowed for the desired surface quality.

Details on sample packaging and storage

All samples under direct comparison to each other (within one sample set) were prepared, packaged, and stored under the same conditions. Details for the different sample sets are summarized in Table S3.

Table S3: Details on sample packaging and storage for the different sample sets.

<i>Sample set</i>	Wrapping paper	Storage Time	Comments
<i>Aging set of polished samples</i>	laservision A99CLSTA1302	See Fig. 2	
<i>Sputtered Cu and Oxides</i>	VWR Spec-Wipe 21914-758*	5 months	No wetting transition was observed. Tissues did not generate C-rich atmosphere. → Repackaging
	laservision A99CLSTA1302	3 months	
<i>LR Samples</i>	laservision A99CLSTA1302	3 months	
<i>DLIP Samples</i>	laservision A99CLSTA1302	3 months	Another charge of the wrapping paper was used.

* Wrapping paper of this type which was in contact with the atmosphere before (not sealed) induced a wetting transition in a previous study [1]. Here, a fresh sealed batch was used which did not induce a wetting transition. A possible reason could be the time the tissues were in contact with the ambient air to adsorb hydrocarbons themselves before acting as a donor. We recommend performing a test run before deciding for a certain wrapping paper to accelerate the wetting transition.

The wrapped samples were stored in polystyrene boxes which were then packed in airtight boxes. Silica beads were included to assure low humidity. Temperature was controlled to approximately 20°C during storage.

Details on XPS analysis

XPS analysis was done on an Axis Nova small spot electron spectrometer (Kratos Ltd.) equipped with 165 mm radius hemispherical analyzer, combined electrostatic and magnetic lenses, DLD detector and monochromatic Al K_{α} (1486.6eV) X-ray source. The system works at an operating pressure $< 1 \cdot 10^{-8}$ mbar. The measurement spots are defined by the virtual electron optical image of the selected detector entrance aperture on the sample surface. During pump-down process inside the entrance airlock, halogen lamps irradiate the samples, and lead to moderate heating, which supports the process of removal of volatile water adsorbates.

Chemical state analysis for carbon and oxygen was performed after subtraction of a Shirley-type background by inscribing Gauss-Lorentz shaped partial peaks, localized according to the respective expected chemical shift, in reference to the NIST database [2]. Potentially occurring artefacts due to local charging effects were compensated with respect to a binding energy of the C1s partial peak of aliphatic hydrocarbons at 285eV. In the case of copper, as an alternative to the Gauss-Lorentz model peaks, measured core level spectra on oxygen-free sputter-cleaned Cu as well as CuO, and Cu₂O reference samples (produced by sputter deposition on glass) were used for the fit procedure as contributing partial peak models to reproduce the measurement curves and determine the proportions of the respective bonding states (compare Figure 5).

XRD analysis of the LR sample

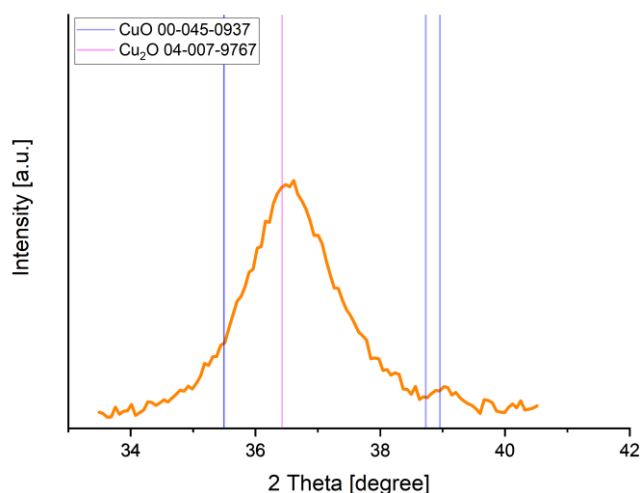


Figure S1: GI-XRD measurement of a LR sample.

The XRD analysis reveals a clear domination of Cu₂O over CuO on the LR samples. It must be noted that the XRD analysis was conducted on samples aged for more than 3 months which is why at the moment of SCA measurement a slightly increased CuO amount could be possible.

XRD analysis of the DLIP samples

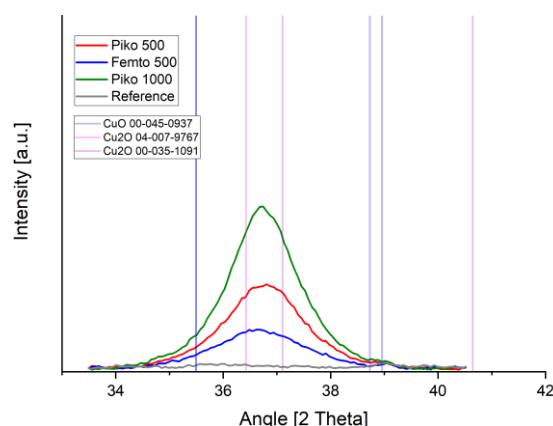


Figure S2: GI-XRD measurements of the four sample types with reference spectra (vertical lines). No clear peak assignment to the reference spectra is possible but a qualitative comparison shows an increase in surface oxidation with pulse duration and laser power.

Though highly resolved spectra were obtained, no clear peak assignment of the oxidic peak in the range of 35-38° was possible. As suggested by Ahmed et al. [3] also the reference peaks for Cu₂O obtained under high pressure [4] were included. A domination of Cu₂O over CuO can be assumed for the DLIP samples. XRD scans were obtained on separate samples within 2 weeks after the wetting and XPS analysis. We believe that strain induced by the laser treatment leads to the shift of the peak relative to the reference patterns. Still, the spectra in Figure S2 allow for a qualitative comparison of the sample types showing no detectable oxidation for the polished reference and increasing oxidation for F500, P500 and finally P1000.

XPS core level spectra for the DLIP samples

Figure S3 demonstrates core level spectra obtained on the DLIP samples and a polished reference sample.

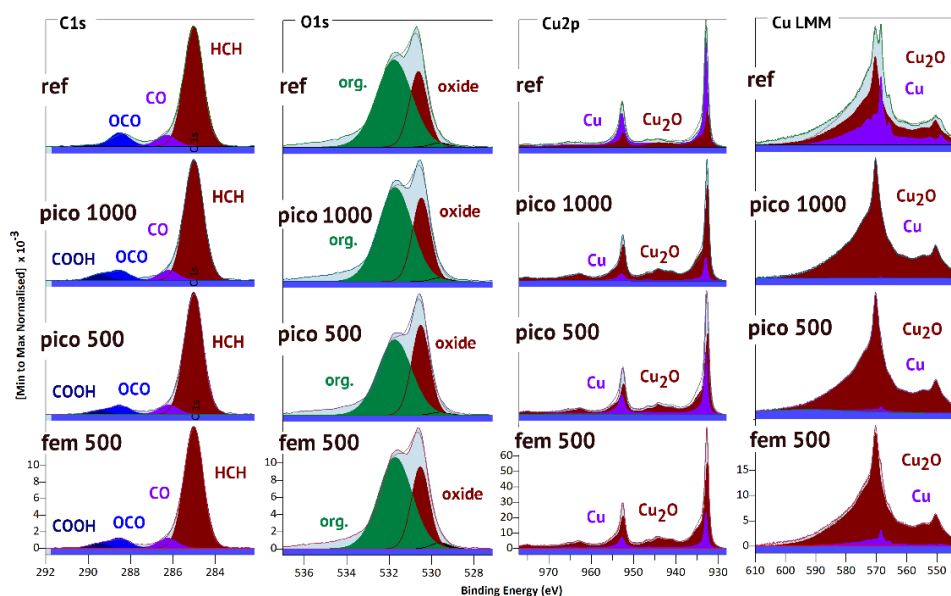


Figure S3: Core level spectra of C1s, O1s, Cu2p and Cu LMM for the DLIP samples. While for C1s and O1s spectra Gauss-Lorentz shaped partial peaks were used, in the case of Cu2p and Cu LMM spectra experimentally obtained model peaks on sputter deposited reference oxides were used to quantify the contributions of different binding states.

Details on ACA and RCA measurements

ACA and RCA measurements were tried to conduct according to the protocol by Huhtamäki et al. [5] in order to gain insight into the water adhesion of the surfaces. ACAs could only be determined by positioning the needle above the droplet as suggested by Drelich [6] as the droplet was pushed along the surface when the needle was inserted. Unfortunately, strong vibrations whenever a new droplet merged with the existing one accompanied the analysis. Measurement of RCAs was not possible due to pinning of the triple line and a collapse of the droplet before base line movement. Also, an increase of the starting volume to approximately 90 μl did not allow for RCA measurement. A time dependent dissolution of adventitious carbon groups in the applied water during the prolonged measurement might induce the severe pinning and decrease of hydrophobicity. This technique therefore was not found suitable for the analysis of our samples.

Tilting experiments

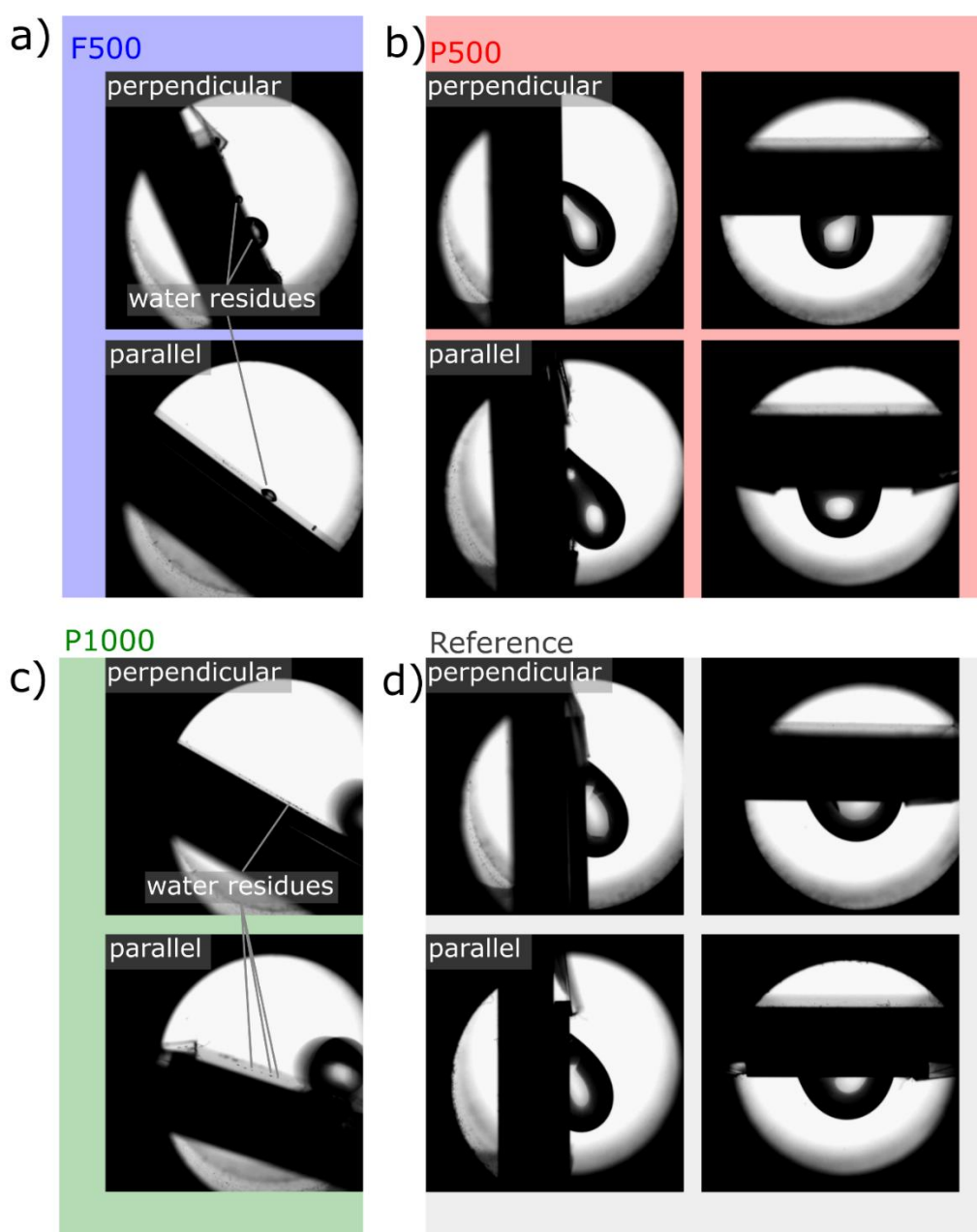


Figure S4: Images of 30 μl droplets after inclination of the surface. The F500 and P1000 samples show sliding behavior of the droplet while it sticks to the surface of the P500 sample and the polished reference even after a 180° tilt.

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6 Conclusion and Outlook

Wetting phenomena accompany not only our daily lives but are also of the utmost importance for different research areas like materials science, life science or medical technology just to name a few. While an incalculable number of research papers focus on the effect of different surface treatments like coating or patterning or a combination of both in an empirical way, there is still a lack of fundamental knowledge gained by strictly systematic investigations. Static contact angle analysis is a sample characterization method which is regularly applied in materials science to assess the wetting behavior. It is commonly believed to be a straightforward and facile measurement technique which captivates due to a rather simple measurement setup, that could even be built directly by the researcher if no device is available in the laboratory. After careful study of this thesis, readers should know better than simply accept these prejudices on static contact angle measurements.

A study of laser patterned steel substrates with subsequent chemical coating motivated to gain a deeper understanding of the impact of surface chemistry and surface topography on the wetting behavior of metallic substrates (see Paper 0, reference [167]). Copper was chosen for further investigations due to its wide application in science and industry. After creating a basis by a detailed investigation of copper preparation (see Paper 1, reference [168]) it became obvious that static contact angle analysis cannot be classified as a simple and not error-prone wetting characterization if high standards on research quality and reproduction are to be met. A variety of possible influencing factors was identified and their effects were quantified on hydrophilic as well as hydrophobic copper surfaces (see Paper 2, reference [169]). Especially, sample storage and packaging were found to crucially impact the resulting static contact angles on copper. But not only sample induced influences, also measurement related parameters affect the analysis which is why sample preparation including packaging, storage conditions and time as well as measurement conduction should always be under control especially for surfaces under direct comparison. Especially if storage times and packaging conditions vary, static contact angles might differ greatly for the very same material due to the adsorption of volatile organic compounds on the surfaces during sample aging. While in literature, static contact angle measurements are sometimes alleged with a reduced reproducibility due to thermodynamic irregularities, results in this thesis indicate a strong impact of the delicate adsorption processes of carbonaceous species as the main cause for a lack in reproducibility in SCA measurements. By controlling sample storage and packaging in the following studies and following systematic measurement protocols, high reproducibility could be met by static contact angle measurements. Before analyzing complex chemical and topographical surface states, the next investigation focused on the effect of intrinsic material properties on the resulting wetting behavior by creating different microstructures on copper (see Paper 3, reference [170]). Surfaces rich in defects show higher adsorption rates of volatile organic compounds and therefore a quicker transition to hydrophobic wetting behavior. Differences in grain size and bulk deformation do not have a major influence on the transition rate. Still, once a threshold concentration of adventitious carbon is adsorbed,

SCA results for the different microstructures converge and only gradual changes occur with time. The dynamics of the adsorption of volatile organic species to form films of adventitious carbon is especially relevant in the early stages of aging before layers of sufficient thickness are formed to dominate the liquid-substrate interaction. This finding was crucial for the following experiments as laser treatments also affect the surface microstructure but apparently this impact can be neglected if aged samples are investigated. After focusing on the microstructure, a detailed investigation of the adventitious carbon species showed ongoing adsorption with very high concentrations after storage for several months while the static contact angle levels in the hydrophobic regime. Detailed XPS-analysis proved a non-polar termination with hydrocarbons while compounds containing oxygen were found underneath (see Paper 4 part A, reference [171]). As laser patterning also impacts surface oxidation, different oxidic copper terminations and their impact on the long-term wetting behavior were investigated (see Paper 4 part B, reference [171]). Analogous to the microstructure-related experiments, differences in the oxide state do not appear to affect long-term wetting behavior due to pronounced adsorption films forming on top of the oxides. With these investigations the basis was built to analyze the complex impact of laser induced surface topography on long-term wetting behavior. Due to coverage of the surface with adventitious carbon masking microstructure and oxides, a focus on topography became possible. DLIP patterns result in complex hierarchical structures consisting of a periodic primary pattern which is complemented by secondary roughness. To analyze the effect of simple isotropic non-hierarchical patterns first, ps laser roughening was applied and already significantly increases the static contact angle after aging (see Paper 4 part C, reference [171]). DLIP brings static contact angles to extremes (see Paper 4 part D, reference [171]): Careful adaptation of the laser parameters allowed the production of similar primary line patterns by fs- and ps-DLIP with varying secondary roughness. The creation of similar topographies with different pulse durations not only allowed for the comparison of the forming patterns and oxides but also the systematic assessment of the effect of variations in the secondary topography on the long-term wetting behavior. The addition of a ps-structure doubled in depth allowed for the determination of the impact of the primary topography. It was found that not only changes in the primary pattern, e.g. aspect ratio, but also differences in the secondary roughness are sufficient to induce significant changes in the wetting response. After storage under controlled conditions, the two twin-patterns exhibit noticeable differences in the wetting response to water in terms of static contact angle and resulting wetting anisotropy, water adhesion and wetting state which was traced back to the differences in the secondary roughness inside the pattern valleys and on top of the pattern peaks. It should be noted that the determination of local roughness alone should not be the only criterium to estimate the resulting wetting behavior. Comprehensive analysis of the patterns as conducted in this study is necessary as the geometric characteristics of secondary roughness also need to be considered. Periodic secondary patterns like LIPSS might induce different wetting responses than the here observed crater-structures in pattern valleys. Only with such organized and methodical approaches, the promising effect of laser patterning on the wetting behavior can be understood and employed strategically in the

design of technical surfaces with a desired wetting behavior.

This thesis portrays a systematic study on wetting and provides deep insight into the complex relations between sample preparation, sample aging, adsorption of volatile organic compounds, measurement techniques, microstructure, chemical surface termination, simple as well as hierarchical topography and the resulting wetting behavior of copper. Taking all these effects into account, the reader might wonder if there is a single key parameter which can be identified as the most significant impact on wetting behavior. The answer to this question is based on the findings in this thesis, both surface chemistry dominated by adsorbed non-polar hydrocarbons and surface topography show complex interactions. The adsorption effects clearly overrule other material's properties like microstructure or oxidic termination and are the basis for topography to show its potential on the wetting behavior. Therefore, neither surface topography nor surface chemistry can be singularly identified as the most crucial impact – they rather form a symbiosis in the interaction of the substrate with water. DLIP patterns proved to hold great potential for the fine adjustment of desired wetting properties – e.g. line patterns with an adequate chemical termination can both result in isotropic wetting with high SCAs and reduced adhesion or anisotropic wetting in the hydrophobic regime with strong adhesion.

Though the analysis conducted already provides profound insight into the wetting of copper, there are several further research objectives to be answered in the future:

- Detailed investigations into the transferability of the results obtained on copper to other metallic substrates will be necessary. A first approach towards this research objective was made in the Bachelor thesis of Philipp Leonhard-Trautmann within this research project where DLIP was not only applied to copper, but also to brass and steel. It was found that high fluences on steel produces loosely distributed flakelike structures on the surfaces which were washed away once in contact with water and therefore induced hydrophilic behavior despite prolonged aging, whereas brass and copper showed more comparable behavior.
- Further variations of surface topography will be needed to determine the full potential of DLIP for wetting. Such studies should always follow systematic approaches instead of an empirical variation of laser parameters. More variations in the primary but also in the secondary topography are needed to further sharpen the understanding of the role of hierarchical topography.

The role of LIPSS, especially if formed as a secondary roughness e.g. in pattern valleys, needs to be assessed as they induce a second periodicity to the pattern and might thereby cause capillary forces to be active within the secondary roughness. Experiments conducted within the bachelor thesis of Philipp Leonhard-Trautmann give rise to the possibility that the formation of LIPSS in the pattern valleys perpendicular to the primary pattern of fs-structures might increase the overall wettability and induce slight wetting anisotropy but the overall pattern formation on the samples was rather uneven. Therefore, detailed

investigations will be necessary in order to make reliable conclusions on the role of LIPSS and their orientation as the secondary roughness.

- Analogous to surface topography, also for the effect of surface chemistry further studies should focus on a variety of chemical terminations which might be directly influenced by sample storage and packaging. Especially naturally adsorbed layers are of interest due to the reversibility of de- and adsorption and the accompanying switchable wetting behavior. They also do not cause environmental harm as they refrain from the use of harsh chemicals. Still, especially in combination with DLIP, artificial coatings characterized by strong (non)-polarity might be of interest to the wetting community.
- Under the appliance of sample aging to induce wetting transitions, wetting results appear to be highly dependent on sample age in early-stage aging and increasingly less dependent once a threshold concentration of adventitious carbon is adsorbed. Further investigations are needed to determine which properties of the sample influence this threshold value and to what extent. These investigations are important to gain further understanding of the adsorption processes and their impact on the wetting behavior. Experiments with even longer storage times and / or storage in higher concentrations of hydrocarbons could clarify if at one point differences in the wetting response induced by slight variations in topography, as observed on the DLIP twin patterns, could be overruled by the thickness / density of the adsorbate layer. It needs to be considered though, that measurement becomes increasingly challenging if static contact angles further approach 180° .
- While usually sample aging is combined with alteration of topography to reach highly hydrophobic states, for application favoring hydrophilicity the prevention of the adsorption of nonpolar hydrocarbon species or the development of topographies showing hydrophilic behavior despite aging is of interest.

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Figure 8: Overview of the content structure of this thesis. Paper 0 refers to reference [167], paper 1 to reference [168], paper 2 to reference [169], paper 3 to reference [170] and paper 4 to reference [171]. (Abbreviations: PVD – Physical vapor deposition, LSM – Laser scanning microscopy, SEM – Scanning electron microscopy, EDS – Energy-dispersive x-ray spectroscopy, FIB – Focused ion beam, WLI – wight light interferometry, TOF SIMS – Time of flight secondary-ion mass spectrometry, EBSD – Electron backscatter diffraction, XPS – X-ray photoelectron spectroscopy, AFM – Atomic force microscopy, XRD – X-ray diffraction)..... 30