Electrocrystallization and characterization of nanostructured gold and gold alloys

Dissertation

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Abstract

The kinetics of electrocrystallization of nanostructured gold is investigated and the physical properties of nanostructured materials such as thermal stability, surface roughness and hardness are improved. A new stable non-toxic electrolyte for the electrodeposition of gold and gold alloys is presented. Nanoscaling is achieved by pulse techniques. The possibility of controlling the crystallite size depending on physical and chemical process parameters such as pulse duration, current density, bath temperature, type and amount of additives is shown. A new general equation for the current transient for three-dimensional nucleation and mixed ion transfer and diffusion controlled growth with previous adsorption process based on the existing theories is reported. The theoretical predictions of this equation and its relevance for the analysis of current-time transients are discussed and compared with experimental observations. The characterizations are made by means of in situ high-temperature X-ray diffraction, scanning electron microscopy, atomic force microscopy and microindentation.

Kurze Zusammenfassung

Die Kinetik der Elektrokristallisation von nanostrukturiertem Gold wird untersucht und die physikalischen Eigenschaften von Gold und Goldlegierungen wie thermische Stabilität, Oberflächenrauhigkeit und Härte verbessert. Ein neuer, stabiler, nicht toxischer Elektrolyt für die Abscheidung von Gold und Goldlegierungen wird vorgestellt. Nanoskalierung wird durch gepulste Elektrolyse erreicht. Es wird gezeigt, dass es möglich ist die Größe der Kristallite abhängig von physikalischen und chemischen Herstellungsparametern wie Pulsdauer, Stromdichte, Temperatur des Elektrolyten, Art und Menge der Additive, zu kontrollieren. Eine neue allgemeingültige Gleichung, basierend auf bereits bekannten Theorien, die den zeitlichen Stromverlauf für dreidimensionale Keimbildung und gemischten Ladungstransfer bzw. diffusionskontrolliertes Wachstum mit vorherigem Adsorptionsprozess beschreibt, wird entwickelt. Die theoretischen Vorhersagen dieser Gleichung und ihre Anwendbarkeit zur Analyse von Strom-Zeit-Kurven werden diskutiert und mit experimentellen Beobachtungen verglichen. Zur Charakterisierung werden verschiedene Techniken wie in situ-Hochtemperatur-Röntgendiffraktometrie, Rasterelektronenmikroskopie, Rasterkraftmikroskopie und Mikroindentation angewendet.

Summary

The preparation of nanostructured materials by electroplating is highly welcomed because of the possibility to control the physical and chemical properties of the deposits by tuning of the crystallite size [Din92], [Nat03]. Gold and gold alloys are widely used in electronic devices and in dental industry, therefore, the investigations of electrocrystallization process and the improvement of mechanical properties of gold and gold alloys are of high importance.

A new stable electrolyte, free of cyanides and sulphites, is prepared for gold electroplating where Au^+ is stabilized by complex formation with 3-mercapto-1-propanesulfonic acid sodium salt. Nanoscaling is achieved by pulse techniques, nevertheless, by direct current plating the crystallites of gold samples do not exceed 100 nm. The dependence of the crystallite size on bath temperature and current density is investigated; the bath temperature is changed from 298 K to 348 K and the current density from 10 mA cm⁻² to 100 mA cm⁻². The increase of both above mentioned parameters causes the decrease of the crystallite size. The influence of organic and inorganic grain refiners on the crystallite size of gold is investigated. Organic additives like tartaric acid, benzoic acid, nicotinic acid and saccharin Na are used, however none of them brought about suitable results, probably, because of strong interactions with organic components of the electrolyte. It is shown that sulfur or arsenic containing additives decrease the gold crystallite size in the electroplating process down to 7 nm attaching to gold surfaces and preventing subsequent gold growth.

Nanocrystalline binary gold alloys with silver, palladium, platinum and copper are electrodeposited. The crystallite size is controlled by the proper choice of pulse technique, the temperature, current density and the concentration of Me salts. It is possible to deposit gold alloys with different metal contain. The alloy composition is calculated from the lattice constant which is determined by the X-ray diffraction.

The initial stage of every deposition process is the formation of nuclei on the surface. In the case of instantaneous nucleation all nuclei are formed within a short time period, then nuclei only grow and overlap. In the case of progressive nucleation, nuclei of the new phase form, grow and overlap during the whole period of observation [Mil02]. The kinetics of electrocrystallization of nanostructured gold on a glassy carbon electrode from mercapto- containing electrolyte is investigated using electrochemical potentiostatic techniques and SEM. The nucleation behaviour of gold at different potentials is determined, it is shown that the nucleation can be described by 3D progressive model. During the deposition process side reactions, especially hydrogen evolution can occur and, therefore, can cause

the deviation of the current-time curves from theoretically predicted ones. Changing the applied potential it is possible to control the size of deposited gold domains. The deposition process can occur through the adsorption of the gold complex followed by charge transfer at more positive potentials and through direct charge transfer at more negative potentials. The fits of experimental results with new proposed theoretical equation due to the combination of charge transfer and diffusion control of nucleation and growth are performed; some kinetic parameters such as exchange current density, nucleation rates, growth constants, diffusion coefficient are determined and possible reasons for the inconsistency between the experimental results and the theoretical predictions are discussed.

The thermal stability of the electrodeposited gold and gold alloys at high temperatures is investigated using the X-ray diffractometer. The X-ray patterns were recorded in reflection $(\theta-2\theta)$ mode, at the following temperatures: 553, 573, 623, 673, 723, 743 and 773 K. The resulting volume-weight average diameters at high temperatures show a fast increase in the grain size value. At lower temperatures, only a moderate and comparatively smooth grain growth can be observed, which stops after a short period of time. The fits with the generalized parabolic grain-growth model and the growth model with impediment do not yield acceptable results, therefore, the extended Arrhenius evaluations were performed using the model with the retarding term proportional to the size. The activation energies for the gold, the gold-silver alloy and the gold-palladium alloy samples are determined from the Arrhenius plot. The problems of disagreement between the data obtained from the fits and the literature results are discussed.

The physical properties such as surface structure, roughness and hardness are investigated by means of SEM and AFM techniques. The cauliflower surface structure and, therefore, the big surface/volume ratio of the deposited gold makes it attractive for miniaturized bio-medical applications. The investigated gold samples have higher hardness as those reported in the literature.

Combining electro-analytical and physical techniques with different theories it is possible to receive new information and, therefore, to control the structure as well as the properties of nanocrystalline gold and nanocrystalline gold alloys.

Zusammenfassung

Die Herstellung nanostrukturierter Materialien durch Elektroabscheidung ist von großem Interesse, da durch Variation der Kristallitgroße eine Kontrolle der physikalischen und chemischen Eigenschaften des Materials möglich ist [Din92], [Nat03]. Die Untersuchung des Elektrokristallizationsprozesses und die Verbesserung der mechanischen Eigenschaften von Gold und Goldlegierungen sind von großer Wichtigkeit da diese Materialien in elektronischen Geräten und der Dentalindustrie oft verwendet werden.

Ein neuer, stabiler Elektrolyt ohne Cyanide und Sulfite wird in der vorliegenden Arbeit vorgestellt. In diesem Elektrolyt wird Au⁺ durch Bildung eines Komplexes mit dem Natriumsalz der 3-mercapto-1-propansulfonsäure stabilisiert. Nanoskalierung wird durch Pulstechniken erreicht, allerdings überschreitet auch bei Gleichstromelektrolyse die Kristallitgröße nicht 100 nm. Die Abhängigkeit der Kristallitgröße von Badtemperatur und der Stromdichte wird untersucht. Die Badtemperatur wird zwischen 298 K und 348 K, die Stromdichte von 10 mA cm⁻² bis 100 mA cm⁻² variiert. Sowohl die Erhöhung der Temperatur als auch die Erhöhung der Stromdichte führen zu eines Abnahme der Kristallitgröße. Der Einfluss von organischen und anorganischen Additiven auf die Kristallitgröße von Gold wird untersucht. Organische Additive wie Weinsäure, Benzylsäure, Nikotinsäure und Natriumsaccharin werden eingesetzt, allerdings entsprechen die Kristallitgrößen nicht den erwarteten Werten. Die Verwendung von schwefel- oder arsenhaltigen Additiven vermindert der Kristallitgröße beim Abscheidungsprozess auf 7 nm durch Adsorption an die Goldoberfäche, was weiteres Kristallitwachstum unterdrückt.

Nanostrukturierte binäre Goldlegierungen mit Silber, Palladium, Platin und Kupfer werden ebenfalls abgeschieden. Die Kristallitgröße wird durch geeignete Wahl der Pulsparameter, der Temperatur und der Konzentration an Metallsalzen kontrolliert. Eine Abscheidung von Goldlegierungen mit verschiedem Goldgehalt ist möglich. Die Zusammensetzung aus röntgenographisch erhaltenen Gitterkonstanten der auftretenden Mischkristalle bestimmt.

Der Erste Schritt des Abscheidungsprozesses ist die Keimbildung auf der Oberfäche. Im Falle gleichzeitiger Nukleation werden alle Keime innerhalb einer kurzen Zeitspanne gebildet, danach tritt nur noch Wachstum und Koaleszens der Keime auf. Im Falle fortschreitender Nukleation können Keime einer neuen Phase, Wachstum und Koaleszens während der ganzen Zeit beobachtet werden [Mil02]. Die Kinetik der Elektrokristallisation von nanostrukturiertem Gold auf einer Glaskohlenstof-Elektrode unter Verwendung eines mercaptanhaltigen Elektrolyten wird mit elektrochemischen Techniken und REM untersucht. Das Nukleationsverhalten von Gold bei verschiedenen Potentialen wird verfolgt und kann durch ein dreidimensionales fortschreitendes Wachstumsmodell beschrieben werden. Während des Abscheidungsprozesses können Nebenreaktionen, besonders Wasserstoffentwicklung auftreten und dadurch Abweichungen der Strom-Zeit-Kurven von dem theoretisch vorhergesagten verhalten verursachen. Durch Variation der angelegten Spannung es möglich, die Größe der abgeschiedenen Golddomänen zu kontrollieren. Die Abscheidung kann bei positiveren Potenzialen durch Adsorption der Goldkomplexe und darauf folgenden Ladungstransfer oder bei negativeren Potenzialen durch direkten Ladungstransfer vonstatten gehen. Eine neue theoretische Gleichung, die Ladungstransfer und Diffusionskontrolle der Nukleation und des Wachstums verbindet, wird auf die experimentellen Ergebnisse angewandt. Dadurch können kinetische Parameter wie Austauschstromdichte, Nukleationsgeschwindigkeit, Wachstumskonstante und Diffusionskoeffizient bestimmt werden. Abweichungen zwischen experimentellen Ergebnissen und theoretischer Vorhersage werden diskutiert.

Durch Röntgendiffraktometrie wird die thermische Stabilität des abgeschiedenen Goldes und der Goldlegierungen untersucht. Die Röntgendiffraktogramme werden bei 553, 573, 623, 673, 723, 743 und 773 K in Reflektionsgeometrie $(\theta - 2\theta)$ aufgenommen. Die daraus folgenden volumengewichteten mittleren Durchmesser weisen bei hohen Temperaturen einen starken Anstieg auf. Bei tieferen Temperaturen kann nur ein vergleichsweise geringes Kristallitwachstum beobachtet werden welches nach kurzer Zeit endet. Die Anpassung mit dem parabolischen Wachstumsmodell und dem Wachstumsmodell mit Retardierung erzielen keine akzeptablen Ergebnisse. Deswegen wird das Arrhenius Gesetz unter Verwendung eines Wachstumsmodells mit grössenabhängiger Retardierung angewendet. Die Aktivierungsenergie für Gold, Gold-Silber-Legierungen und Gold-Palladium-Legierungen werden ans der Arrhenius-Auftragung erhalten. Abweichungen von Literaturwerten werden diskutiert.

Die physikalischen Eigenschaften wie Oberfächenstruktur, Rauhigkeit und Härte wurden durch SEM und AFM Techniken untersucht. Die Blumenkohl-Strukturen und das daraus resultierende große Oberfäche/Volumen-Verhältnis des abgeschiedenen Goldes kann in miniaturisierten biomedizinischen Anwendungen von Vorteil sein. Die hergestellten nano-Goldproben besitzen eine größere Härte als Bulk-Materialien.

Die Kombination von elektroanalytischen und physikalischen Techniken mit verschiedenen Theorien führt zu neuen Erkenntnissen, die eine gezielte Kontrolle von Struktur und Eigenschaften nanokristallinen Goldes und nanokristalliner Goldlegierungen ermöglichen.

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Chapter 1

Introduction and motivation

Nanocrystalline materials differ in some physical and chemical properties from polycrystalline materials of the same chemical composition. The dependence of some properties on the crystallite size opens a possibility to create materials with new properties simply by adjusting the crystallite size appropriately during the preparation process [Nat03].

Electrodeposition is an extremely important and cheap technology. Covering inexpensive and widely available base materials with plated layers of different metals with superior properties extends their use to applications which otherwise would have been prohibitively expensive. However, it should be noted that electroplating is not a simple dip and dunk process. It is probably one of the most complex unit operations known because of the unusually large number of critical elementary phenomena or processes. Electrodeposition involves surface phenomena, solid state processes, and processes occurring in the liquid state, thereby comprising many scientific disciplines [Paun98], [Bud96], [Bard01].

Gold and gold alloys are important in electronic devices for electrical contacts, bonding and are of wide use in dental industry for the production of crowns of teeth. With further miniaturization of the electronic structures on integrated circuits also the diameter of the bond wires has to decrease. For future wire diameters below 1 μm the grain size must be below 100 nm in order to avoid a bamboo-like microstructure with grain boundaries extending over the whole diameter and with correspondingly low mechanical stability. For those reasons the improvement in mechanical properties of gold, as brought about by nanoscaling, is highly welcome: generally, with decreasing crystallite size a metal becomes harder [Nat03], [Din92], [Rob99]. Simultaneously, sufficient thermal stability must be assured: if grain growth takes place during operation, i. e., at the operation temperature of the device, the mechanical properties deteriorate.

Cyanide containing baths for gold and gold alloy electrodeposition are minutely described in the literature [Bek03], [Rey02]; however, cyanide is very poisonous even at very low concentration. The production of gold electrolytes from thiomalat, mercaptoethanol, iodide, hydroxide, thiosulfate, sulphite, tetramminnitrat and phosphoric acid were made by several authors [Nat03], [Osa97], [Gre03] but most of them are instable, toxic and water sensitive [Sim00]. Therefore, a stable and non-toxic electrolyte for gold electrodeposition is of high importance.

Electrochemical technique is a power tool to investigate in situ electrocrystallization processes [Bud96], [Bard01], [Paun98]. The investigation of the kinetics of electrodeposition leads to deep understanding of the processes like ions movement in electrolyte solution, formation of adatoms, nucleation and crystal growth, and, therefore, to the possibility of creating materials with adjusted physical and chemical properties.

An increase of the temperature causes crystal growth and therefore the physical and chemical properties to change [Li97], [Caro03], [Kan04]. For this reason the thermal stability of nanocrystalline materials is one of the most important properties which are of interest for basic research as well as for industrial applications at elevated temperatures. The kinetics of grain growth can be studied by means of in-situ high-temperature X-ray diffraction [Nat97], [Nat00], [Nat01], [Ina98]. The X-ray diffraction lines contain information about the crystallite size, the structure, packing order of the atoms in the lattice, microstrain etc. The advantage of an in-situ experiment is the analysis of the same part of the sample and the observation of changes in X-ray line shapes due to only the increase of the temperature.

The aim of the following work is the preparation of a non-toxic electrolyte for the electrodeposition of nanostructured gold and gold alloys with further characterization of physical properties of the deposit. The kinetics of electrocrystallization of nanostructured gold on glassy carbon electrodes will be investigated by means of the electrochemical techniques in order to obtain the information about the mechanism of the formation and growth of gold nuclei. The attempts to describe the kinetics of electrodeposition with theoretical equations based on the existing theories will be made. The theoretical predictions of these equations and their relevance for the analysis of experimental transients will be discussed and compared with experimental observations. The kinetics parameters describing early stages of gold electrocrystallization will be determined and a deep discussion of obtained results with following conclusion will be presented. The possibility of metallic gold and gold binary alloys deposition from the prepared electrolyte and the influence of the deposition parameters and the bath composition on the crystallite size and thermal stability of samples is to be investigated. The kinetics of high temperature crystallite growth of gold and gold alloys will be analyzed at isothermal conditions and described by means of different growth models. Mechanical properties of nanocrystalline gold will be improved and characterized by means of AFM, microindentation, nanoindentation and SEM. The comparison of the results obtained from different techniques can help to explain physical and chemical processes occurring during the electrocrystallization process and during the thermal annealing of the investigated samples.

Chapter 2

Electrochemical deposition of metals

Electrochemical deposition of metals and alloys involves the reduction of metal ions from aqueous, organic, or molten salt electrolytes. During the deposition from aqueous solutions the reduction of metal ions M^{z+} is represented by

$$M_{solution}^{z+} + ze^- \to M_{lattice}$$
 (2.1)

This can be accomplished via two different processes: (1) an electrodeposition process in which z electrons (e) are provided by an external power supply and (2) another, electroless (autocatalytic) deposition process in which a reducing agent in the solution is the electron source. The deposition reaction presented by Eq. 2.1 is a reaction of charged particles at the interface between a solid metal electrode and a liquid solution. The two types of charged particles can cross the interface: a metal ion and an electron.

2.1 Electrolysis and direct current plating

An ionic compound is dissolved with an appropriate solvent, or otherwise melted by heat, so that its ions are available in the liquid. An electrical current is applied between a pair of inert electrodes immersed in the liquid. The negatively charged electrode, where the reduction takes place is called the cathode, and the positively charged one, where the oxidation takes place the anode. Each electrode attracts ions which are of the opposite charge. Therefore, positively charged ions (called cations) move towards the cathode, whereas negatively charged ions (termed anions) move toward the anode as shown in Figure 2.1. The energy required to separate the ions, and cause them to gather at the respective electrodes, is provided by an electrical power supply.



Figure 2.1: Schematic sketch of electrolysis.

2.2 Pulsed current plating

Pulse plating is a method of depositing metal on a substrate using interrupted direct current. Modern electronics has greatly enhanced the advantages of electrolysis by allowing current or voltage to be applied as almost any function of time. The typical waveform of cathodic pulses is shown at the Fig. 2.2. It should be noted that due to the fundamental nature of the phenomena involved in the deposition process it is not possible to make full use of the range of conditions that would be allowed by modern electronics. There are two main limiting factors: the charging of the electrical double layer at the metal-electrolyte interface and the



Figure 2.2: Typical cathodic pulses. Formation of different crystallite structure due to the pulse duration.

mass transport considerations. The electrical double layer at the electrode-solution interface can be approximated to a plate capacitor with a distance of a few angstroms and therefore with a high capacitance [Bard01]. Charge must be provided to this double layer in order to raise its potential to the value required for metal deposition at the rate corresponding to the applied pulse current which is supplied by the generator. The electrode behaves like a capacitor with a resistance in parallel as schematically represented in Fig. 2.3, the resistance being a function of the current density. The charging of the double layer requires a certain time which depends on the current density and on other parameters of the system. For practical purposes the charging time should be much shorter than the pulse duration, otherwise the current pulse is strongly distorted. Moreover, the time required for discharge of the double layer should be much shorter than the off-time between two pulses. The current required at the beginning of the pulse for



Figure 2.3: Equivalent circuit of an electrode.

charging the electrical double layer is not lost for the metal deposition, since the charge is recovered at the end of the pulse while the capacitor is discharging. Pulses in a frequency range where capacitive effects are relevant do not significantly influence the current efficiency, but affect the amplitude of the pulse and hence the energy of the electrodeposition reaction. In fact, the potential benefit of pulse plating, for example, in influencing the structure and therefore the properties of deposits, is lost. In most cases one should avoid working with onand off-times shorter or of the order of magnitude comparable with the charging or discharging time of the double layer.

The limitations [Puip79] of the useful range of pulse conditions due to mass transport effects arise from the depletion of cations in the diffusion layer. In pulse plating with short pulse durations, two distinct cathodic diffusion layers can be defined instead of one as in DC. In the immediate vicinity of the cathode the concentration pulsates with the frequency of the pulsating current, decreasing during the pulses and relaxing in the interval between them. Thus a pulsating diffusion layer exists close to the cathode. If the duration of the pulse is short, the diffusion layer does not have time to extend very far into the solution and in particular does not extend to the region where convection takes over the mass transport. Therefore the metal deposited during the pulse must be transported from the bulk of the solution towards the pulsating diffusion layer by diffusion, which means that a concentration gradient also builds up into the bulk of the electrolyte. The thickness of this diffusion layer corresponds essentially to that which would be established under the same hydrodynamic conditions in DC electrolysis. Through this outer diffusion layer cations are also supplied towards the cathode during the offtime, and it is this supply that allows the relaxation of the pulsating diffusion layer during the off-time. The outer diffusion layer is essentially stationary. The two distinct diffusion layers are related to two kinds of limitations. The depletion of the cationic concentration in the pulsating diffusion layer limits the pulse current density, and the depletion of the cationic concentration in the outer diffusion layer limits the average current density. Since the concentration gradient in the pulsating diffusion layer can be very high, increasing with shorter pulse length, the pulse current density can reach extremely high values without decrease of current efficiency because of hydrogen evolution. To sum up, the first limitation due to the mass transport effect in pulse plating is that the pulse duration should not exceed the transition time, whereas the second is that the maximum average current density cannot exceed the DC limiting current density.

The crystallization of the electrodeposited metal is a very important step of the electro growth since it influences directly the structure of the deposit and therefore its properties which represent the main interest for the user. The crystallization is the process by which the adatoms or adions incorporate in the crystal lattice. Crystallization (as schematically represented in Fig. 2.4) occurs either by the build-up of old crystals or the formation and growth of new ones. These two processes are in competition and can be influenced by different factors. High surface diffusion rates, low population of adatoms, and low overpotentials are factors enhancing the build-up of old crystals, while conversely low surface diffusion rates, high population of adatoms, and high overpotentials on the surface enhance the creation of new nuclei. In pulse plating, since the pulsed current density is usually considerably higher than the corresponding DC density, the population of adatoms on the surface during pulse deposition is higher than during DC deposition, resulting in an increased nucleation rate and therefore in a finer grained structure. As will appear in the chapters describing practical applications, grain refinement has quite often been observed by experimenters. Grain refinement in pulse plating is also favored by the enhancement of nucleation rates due to high overpotentials which result from high pulse current densities. While adatom population and overpotential can be directly influenced in a predictable direction by external factors, e.g., by adjusting the electrical parameters of the system, this is not the case for surface diffusion, which in plating baths is greatly influenced by adsorbed species at the electrode, such as organic brighteners, stress reducers and many other possible molecules present in the bath. Another phenomenon that might occur in pulse plating during the off-period is recrystallization. Small grains are thermodynamically less

stable than large ones because of high surface energy, and as in bubble coalescence, small grains tend to recrystallize. For this to occur, the surface should remain active during the off-time. Again depending on different adsorbed species, the surface may be inhibited, in which case no recrystallization will occur, and the fine grains obtained during the on-time of electrolysis are stabilized.



Figure 2.4: Crystallization mechanism [Puip79]; a) build-up of existing crystals, b) nucleation and formation of new crystals.

Electrolysis can be controlled by regulation of either current or voltage. In current regulation mode, the reaction rate is kept constant and the potential varies as a function of time. In voltage regulation, the driving force for the reaction is kept constant and the reaction rate varies as a function of time. In current regulation, the average deposition rate can be very simply derived from the following equation [Pui86]:

$$j_m = j_p \frac{t_{on}}{(t_{on} + t_{off})}$$
 (2.2)

while in voltage regulation the average deposition rate can be predicted only from computations of a speculative nature. The main advantage of voltage regulation is a better control of the current efficiency and of alloy composition. High overpotentials resulting from excessive concentration depletions are avoided. However, from a practical point of view, regulation of pulsed voltage is very difficult to achieve. To do it properly, a third electrode, a reference electrode, should be added to the system. Moreover, to get instantaneously a given potential at the electrode, the current should start theoretically from an infinite value, which is obviously not feasible because of apparatus limitations. On the other hand, at the end of a pulse, for instantaneous reestablishment of the starting potential (which might be the rest potential of the system), some metal should be redissolved; hence a constant voltage pulse requires a short inversion of current at the end of the pulse, which is not generally desirable. Furthermore, passivation may occur during the inversion. It should be pointed out that the above remarks apply to a regulated cathodic potential and not to the voltage between the negative and positive poles of the power supply. The latter is much easier to regulate, and sometimes, in particular for very high currents, the power supply engineer prefers it to the constant current regulation. For most applications, however, current regulation is preferred. The first application of periodically interrupted current dates back to the end of the last century, when it was used by Coehn [Coehn93] to produce coherent deposits of zinc. Baeyens [Bae54] reviewed applications of various types of modulated currents up to 1952, and Dini [Dini63] has reviewed the main work carried out up to 1963 with reverse current, i.e., current comprising an anodic component in the interval between cathodic pulses. Studies on this subject have been covered by Cheh [Cheh71] and a review has also been given by Puippe et al. [Puip79]. The principal advantage of pulsed current is that it can be used to improve deposit properties. Advantages have also been claimed in respect to saving of time and reduction in energy requirements, but the former cannot be relied upon, and the latter is certainly not achievable. Gurovich and Krivtsov [Gur68] used pulsed current in deposition of copper and zinc and found an increase in the number of grains, which they attributed to passivation of growth sites by adsorption of an inhibiting species during the off-time, thus forcing the formation of new nucleation centers for continued growth. Decrease in crystallite size has often been observed [Buk04], [Nat03], [Vis76], leading to a fine and more compact structure, and hence reducing the porosity of the deposit [Pop77]. Many workers have observed an increase in smoothness of deposits using pulsed current [Gur68] and that surface roughness decreased with decreasing pulse length, which is attributable to mass transport phenomena [Nat96], [Nak01].

The main purposes of pulse plating are: the improvement of deposit properties, namely,

porosity, ductility, hardness, electrical conductivity, wear resistance and roughness; deposition of alloys, the composition and structure of which are not obtainable with DC plating; improvement of plating thickness distribution by periodic inversion of polarity; increase in average deposition rate, although this can be achieved only to a rather limited extent.

2.2.1 Influence of pulse plating on crystallization

In the electrodeposition process after the charge-transfer reaction, adatoms are formed. There is very little probability that they meet exactly at a growing step and therefore that they are immediately incorporated in the crystal lattice. Adatoms most probably land far from growing steps and have to move on the surface to reach growing steps. The adatom movement occurs by surface diffusion. At the growing steps there is an adatom concentration of c_{ad}^0 and between the growing steps there is a higher adatom concentration c_{ad} reaching a maximum in the middle of the two growing steps. For high surface diffusion rates the adatom concentration profile between two growing steps is relatively flat, but for low surface diffusion rates it is much more curved. The adatom concentration ratio c_{ad}^0/c_{ad} is related to the crystallization overpotential η by the following relationship [Puip79]:

$$\eta = \frac{RT}{zF} ln \frac{c_{ad}^0}{c_{ad}} \tag{2.3}$$

From equation 2.3 the higher c_{ad} , the more negative η will be. From these considerations it is clear that high surface diffusion rates are accompanied by low crystallization overpotentials, and vice versa. For a given surface diffusion rate and from equation 2.3, very high negative values of η can be expected. In practice, however, this will not occur because a competitive crystallization process, nucleation, is enhanced by increasing overpotentials. Nucleation decreases the average distance between neighboring growth steps and therefore reduces the surface diffusion distances and decreases the value of the maximum of the adatom concentration profile. Thus nucleation can counteract an excessive increase in crystallization overpotential resulting from high adatom concentrations. In fact, in any system a balance will be established between the two crystallization modes, building up of existing crystals or formation of

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fresh nuclei, such that the crystallization overpotential is as low as possible. The two competitive steps of crystallization, building up of existing crystals and formation of fresh nuclei, are schematically illustrated in Fig. 2.4.

In addition to the surface diffusion rate and to the applied overpotential, other parameters, such as the exchange current density between adatoms and cations, can also influence the adatom concentration profile. In practice, for a given system (cathode-electrolyte), the applied overpotential is the only parameter that can be easily varied externally. In pulse plating, full advantage of this possibility is taken by varying the amplitude of the pulsed voltage or pulsed current. In the simple case of a cathode-electrolyte system, where surface diffusion rate and exchange current density between adatoms and cations are constant, the influence of pulse plating on the nucleation rate can be qualitatively understood. Increased pulsed voltage or pulsed current amplitude, as compared to usual DC amplitudes, leads to increased adatom concentrations, corresponding to equation 2.3 to higher overpotentials and therefore to higher nucleation. In pulse plating, when the pulse amplitude is increased as compared to DC amplitude, the formation of new crystal nuclei is more likely than the building up of existing crystals. In pulse plating, a decrease in the grain size of deposits can therefore be expected.

There are several ways of examining the effect of pulsed current density on the grain size, of which two methods are: a) increase in pulsed current density at constant pulse length and constant average current density, b) increase in pulsed current density at constant pulse charge (number of coulombs per pulse is kept constant) and at constant average current density. Physically, this mode of investigation corresponds to the situation where constant numbers of atoms are supplied to the surface with different energies, resulting in differences in crystal growth.

The interval between two pulses, the off-time, has sometimes been called the "dead time". Evidence has shown, however, that the off-time can in fact sometimes be a very active period with respect to crystallization. The designation off-time is therefore more appropriate.

By increasing the on-time, the crystals can grow to a larger extent without being blocked by inhibiting species, resulting in larger grains.

2.3 Effect of additives

Most solutions used in electrodeposition of metals and alloys contain one or more inorganic or organic additives that have specific functions in the deposition process. These additives affect deposition and crystal building process as adsorbates at the surface of the cathode. One classification of adsorption phenomena is based on the adsorption energy : the energy of the adsorbate-surface interaction. In this classification there are two basic types of adsorption: chemisorption (an abbreviation of chemical adsorption) and physisorption (an abbreviation of physical adsorption). In chemisorption the chemical attractive forces of adsorption are acting between surface and adsorbate (usually covalent bonds). Thus, there is a chemical combination between the surface and the adsorbate where electrons are shared and/or transferred. New electronic configurations are formed by sharing of electrons. In physisorption the physical forces of adsorption, Van der Waals or pure electrostatic forces, operate between the surface and the adsorbate; there is no electron transfer and no electron sharing. Since the additive is not used up in many cases of electrodeposition in the presence of an additive (the additive is not incorporated in the deposit), one can conclude that the adsorption equilibrium is dynamic. In a dynamic adsorption equilibrium state the adsorbed molecules are continually desorbing at a rate equal to the rate at which dissolved molecules from the solution become adsorbed. If the rates of the adsorption and desorption processes are high and of the same order of magnitude as that of the cathodic deposition process, then no incorporation of additives in the deposit will occur. However, if they are much smaller, additive molecules will be entrapped in the deposit via propagating steps (growing crystallites). Thus, at a current density higher than the optimum value, additives will be incorporated into the deposit. This incorporation can result in poor quality of the resulting deposit. Adsorption of some molecules from solution produces an oriented adsorbed layer. For example, nicotinic acid (NA, or 3-pyridinecarboxylic acid, nniacinor vitamin B3) is attached to a Pt(111) surface primarily or even exclusively through the N atom with the ring in a (nearly) vertical orientation (Fig.2.5). In another example, benzoic acid (BA) is an aromatic compound that orients horizontally at a Pt(III) surface (Fig.2.5) [Paun98]. This horizontal orientation of adsorbed BA involves coordination of the carboxylic acid to the Pt surface. The coordination depends on surface potential. BA adsorbed at



Figure 2.5: Adsorbate molecular orientation at the electrode surface [Paun98]: (a) nicotinic acid; (b) benzoic acid.

negative potentials is coordinated to the Pt through the aromatic ring and (primarily) one carboxylate oxygen; when adsorbed at positive potentials, it is coordinated to the Pt surface through two equivalent oxygens. Change in adsorbate concentration in solution can also result in orientational changes of molecules on the surface. In electrodeposition the transfer of a metal ion M^{n+} from the solution into the ionic metal lattice in the electrodeposition process may proceed via one of two mechanisms: (1) direct mechanism in which ion transfer takes place on a kink site of step edge or on any site on the step edge (any growth site) or (2) terrace site ion mechanism. In the terrace site transfer mechanism a metal ion is transferred from the solution to the flat face of the terrace region. At this position the metal ion is in the adion state and is weakly bound to the crystal lattice. From this position it diffuses on the surface seeking a position with lower potential energy. The final position is a kink site. In the presence of adsorbed additives the mean free path for lateral diffusion of adions is shortened, which is equivalent to a decrease in the diffusion coefficient D (diffusivity) of adions. This decrease in D can result in an increase in adion concentration at steady state and thus an increase in the frequency of the two-dimensional nucleation between diffusing adions. Many monoatomic steps can unite (bunch, coalesce) to form polyatomic steps in the presence of impurities. Additives can also influence the propagation of microsteps and cause bunching and formation

of macrosteps. Type of deposit obtained at constant current density may depend also on the value of the surface coverage θ by an additive. The effect of the deposit brightening can be achieved through three possible mechanisms: (1) diffusion-controlled leveling, (2) grain refining, and (3) randomization of crystal growth. The effect of crystalline size decrease and the increase of the hardness by using additives during electrodeposition was observed by several authors [Nat96], [Buk04], [Din92], [Lin86], [Lin91].

Chapter 3

Nucleation and grain growth

The basic concepts of nucleation and growth during the early stages of electrocrystallization on a foreign substrate are now fairly well understood [Kash00],[Mil02],[Bud96]. A nucleus, a cluster of atoms, is only stable if it exceeds a critical size. The growth of each individual nucleus is then determined by the rate of incorporation of new atoms, i.e. ion transfer and/or diffusion. For a real surface the rate of nucleation is given by:

$$\frac{dN}{dt} = (N_0 - N)A \tag{3.1}$$

which can be integrated with N = 0 at t = 0, to yield an expression for the nuclei density as a function of time:

$$N = N_0 \left[1 - exp(-At) \right]$$
(3.2)

In these equations, A is the nucleation frequency per active site and N_0 is the density of active nucleation sites. For $A \ll 1$, this equation reduces to

$$N = N_0 A t \tag{3.3}$$

The Eq. 3.3 represents the case of *progressive nucleation* (Fig .3.1 (b)) when nuclei of the new phase form, grow and overlap during the whole period of observation. For $A \gg 1$ the equation



Figure 3.1: Deposition of nuclei due to a) instantaneous and b) progressive nucleation.

3.1 reduces to

$$N = N_0 \tag{3.4}$$

The Eq. 3.4 is the case of *instantaneous nucleation* (Fig. 3.1 (a)), i.e. the maximum number of nuclei is formed virtually immediately after the potential perturbation.

3.1 Diffusion-controlled growth

The radius r of a hemispherical nucleus that grows under pure diffusion control is obtained by combining Faraday's law

$$j(t) = \frac{zF\rho}{M}\frac{dV}{dt}$$
(3.5)

(where ρ is the density of Me ions, V is the volume of the hemispherical nuclei, other symbols have their usual meaning) with the time independent part of the hemispherical diffusion equation [Mir90], [Bard01] one receive

$$2zF\pi rDc = \frac{zF\rho}{M}\frac{dV}{dt}$$
(3.6)

where $V = \frac{2}{3}\pi r^3$. Under limiting current conditions, i.e. semi-infinite diffusion and zero surface concentration, the radius is given by:

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$$r = (2MDc/\rho)^{1/2} (t-u)^{1/2}$$
(3.7)

where u is the time at which the nucleus was born. The current corresponding to the growth of a single nucleus is then given by:

$$I(t) = 2\pi z F D c r = 2\pi z F D c \left(2M D c / \rho\right)^{1/2} (t - u)^{1/2}$$
(3.8)

3.1.1 Current transients in the absence of overlap

In the absence of the overlap the total current density for the diffusion-controlled growth of the ensemble of nuclei is given by:

$$j(t) = zFDca \int_{0}^{t} (t-u)^{1/2} \frac{dN}{du} du$$
(3.9)

where $a = 2\pi (2MDc/\rho)^{1/2}$ and $dN/du = AN_0 exp(-Au)$ (Eqs. 3.1 and 3.2). The solution of Eq. 3.9 can be written in different equivalent forms but it is convenient to write the solution as:

$$j(t) = zFDcaN_0 t^{1/2}\Phi aga{3.10}$$

where:

$$\Phi = 1 - \frac{e^{-At}}{(At)^{1/2}} \int_0^{(At)^{1/2}} e^{\lambda^2} d\lambda$$
(3.11)

For large values of the argument, $At \ge 20$, $\Phi \to 1$ and Eq. 3.10 reduces to the case of instantaneous nucleation with the current density proportional to $N_0 t^{1/2}$. For small values of $At, At \le 0.2, \Phi \to (2/3) At$ and the total current density is proportional to $(2/3)N_0At^{3/2}$, the expecting result for the limiting case of progressive nucleation. The Eq. 3.10 shows that the

total current density is equal to the value for the limiting case of instantaneous nucleation multiplied by the function Φ , which reflects the retardation of the current by slow nucleation.

3.1.2 Current transients in the presence of overlap

In the case of diffusion control a depletion zone develops around each growing nucleus and, as growth continues, these depletion zones start to overlap. The resulting diffusion problem is usually solved by introducing the concept of planar diffusion zones. In this approach each nucleus is in the center of the bottom plane of a cylindrical diffusion cylinder with radius r_d and hight δ , which corresponds to the distance from the electrode where the concentration reaches the bulk value. Analytical expressions for r_d and δ must be chosen in such a way that the flux by linear diffusion through a cross-section of the hypothetical cylinder is equal to the flux by hemispherical diffusion to the nucleus. The diffusion zone [Mil02]. The radius of a planar diffusion zone is much larger than the radius of the corresponding nucleus, so that the probability of the real physical coalescence of the nuclei can be neglected within the time scale of the experiment. To account for overlap it is then sufficient to consider the overlap of the hypothetical planar diffusion zones by use of the Avrami theorem [Avr40]:

$$\theta = 1 - exp(-\theta_{ex}) \tag{3.12}$$

where θ is the fraction of the surface covered by planar diffusion zones and θ_{ex} , the extended coverage, is the fraction of the surface that would be covered in the absence of overlap.

3.1.3 Overlap model of Sharifker and Mostany.

In the model of Scharifker and Mostany [Schar84] (Fig. 3.18) the mass balance is written as:

$$zFDca(t-u)^{1/2} = zFDc\pi r_d^2 \frac{1}{[\pi D(t-u)]^{1/2}}$$
(3.13)

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where the left hand side is the current to a hemispherical nucleus (Eq. 3.8). The right hand side is the Cottrell current to an equivalent area πr_d^2 where the hight of the corresponding diffusion cylinder starts to grow from the moment that the nucleus is born. Solving for the equivalent area, with $dN/du = AN_0 exp(-Au)$, the extended coverage is calculated from:

$$\theta_{ex} = a\pi^{1/2} D^{1/2} A N_0 \int_0^t (t-u) exp(-Au) du$$
(3.14)

which can be solved to yield:

$$\theta_{ex} = aN_0 (\pi Dt)^{1/2} t^{1/2} \Theta = bAt\Theta$$
(3.15)

where $b = (2\pi)^{3/2} D(Mc/\rho)^{1/2} (N_0/A)$. The function $\Theta \equiv \Theta[At]$ is given by:

$$\Theta = 1 - (1 - e^{-At})/At \tag{3.16}$$

For the case of instantaneous nucleation $\theta_{ex} = aN_0(\pi Dt)^{1/2}t^{1/2} = bAt$, so that the function Θ reflects the retardation of the growth of the extended coverage as the result of slow nucleation. In the model of Scharifker and Mostany [Schar84] the current density is calculated from Cottrell's equation or planar diffusion with fractional coverage θ so that:

$$j(t) = zFDc(\pi Dt)^{-1/2}\theta$$
(3.17)

and by using the virtue of Avrami's theorem (Eq. 3.12):

$$j(t) = zFDc(\pi Dt)^{-1/2}(1 - exp[-aN_0(\pi Dt)^{1/2}t^{1/2}\Theta])$$
(3.18)

Making the substitutions and using the Tailor series expansion one receives:



Figure 3.2: Scharifker-Mostany model for the electrochemical nucleation with diffusion - controlled growth [Per03].

$$j(t) = \frac{zF\sqrt{D}c}{\sqrt{\pi}\sqrt{t}} \left(1 - exp\left(-N_0\pi kDt\right)\right)$$
(3.19)

$$j(t) = \frac{zF\sqrt{D}c}{\sqrt{\pi}\sqrt{t}} \left(1 - exp\left(-\frac{1}{2}J\pi kDt^2\right)\right)$$
(3.20)

Where $J = AN_0$ is the nucleation rate constant and $k = (8\pi cM/\rho)^{1/2}$.

3.1.4 Analysis of the current maximum

The current described by Eqn. 3.18 passed through a maximum and therefore the current j_{max} and the time t_{max} corresponding to the maximum can be evaluated by equating the first derivative of Eqn. 3.18 to zero [Schar84]. Experiment transients can be qualitative analyzed due to the dimensionless form of Eqn. 3.18 (Fig. 3.3):

$$\frac{j}{j_{max}} = \frac{t}{t_{max}} exp\left[-\frac{1}{2}\left\{\left(t^2 - t_{max}^2/t_{max}^2\right)\right\}\right]$$
(3.21)

for 2-dimensional instantaneous [Hwa00]

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$$\frac{j}{j_{max}} = \left(\frac{t}{t_{max}}\right)^2 exp\left[-\frac{2}{3}\left\{\left(t^3 - t_{max}^3/t_{max}^3\right)\right\}\right]$$
(3.22)

for 2-dimensional progressive [Hwa00]

$$\left(\frac{j}{j_{max}}\right)^2 = \frac{1.9542}{t/t_{max}} \left\{1 - exp\left[-1.2564(t/t_{max})\right]\right\}^2 \tag{3.23}$$

for 3-dimensional instantaneous [Mos84], [Dep03]

$$\left(\frac{j}{j_{max}}\right)^2 = \frac{1.2254}{t/t_{max}} \left\{1 - exp\left[-2.3367(t/t_{max})^2\right]\right\}^2 \tag{3.24}$$

and 3-dimensional progressive [Mos84], [Dep03] nucleation and growth, respectively.



Figure 3.3: Theoretical current-time transients for instantaneous and progressive nucleation [Paun98].

3.2 Charge-transfer-controlled growth

In the case of charge-transfer-controlled growth we shall suppose in what follows that the three dimensional centers are right circular cones in order to ease the mathematical difficulties. Consider a cone cut into a series of thin cylinders of height dx at a distance x from the electrode (Fig. 3.2). Assume a growth velocity, V_2 (cm sec⁻¹), perpendicular to the plane and a rate constant, k' parallel to the plane. Then the radius of the conical nucleus is given by:

$$r_{cone} = \frac{Mk'(t-u)}{\rho} \tag{3.25}$$

The rate constant of electrochemical process is interpreted on the basis of the statistical mechanics and is given by the expression [Paun98]:

$$k' = \frac{k_B T}{h} \left(\frac{-\Delta G_e^{\neq}}{RT}\right) \tag{3.26}$$

where k_B is the Bolzmann constant, T is the absolute temperature, h is the Planck constant, ΔG_e^{\neq} is the electrochemical activation energy, and R is the gas constant. Applying Avrami's theorem (Eqn. 3.12) due to a phase change occurring through the random distribution of nuclei in a large volume (such that boundary effects could be neglected), followed by uniform growth of the centers in 1, 2 or 3 dimensions

$$V_0 = 1 - exp(-V_{ex}) \tag{3.27}$$

where V_0 is that fraction of the total volume occupied by the new phase, taking into account of the overlapping regions, and V_{ex} is the fraction of that volume with neglect of overlap (note that $V_{ex} \to \infty$ as $t \to \infty$, whereas $V_0 \to 1$).

Applying the Avrami formula to a layer comprising all the cylinders of height dx at a distance x to the electrode, the current due to these will be given by [Arm66].



Figure 3.4: Evaluation of the overlap for right circular cones growing on an electrode under charge-transfer-controlled growth.

$$dj = f(x)dx = 2zFN_0Mk'^2\left(t - \frac{x}{V_2}\right)exp\left\{-\frac{\pi N_0}{\rho^2}k'^2M^2\left(t - \frac{x}{V_2}\right)^2\right\}(dx)$$
(3.28)

for the case of instantaneous nucleation. Then

$$j = \int_0^t dj = \int_0^{V_2 t} f(x) dx$$
 (3.29)

Integrating by change of variable gives

$$j = \frac{zF\rho V_2}{M} \left[1 - exp\left(-\frac{\pi N_0 k'^2 M^2 t^2}{\rho^2} \right) \right]$$
(3.30)

Replacing the velocity, V_2 , by the related rate constant, k'', we have

$$j = zFk'' \left[1 - exp\left(-\frac{\pi N_0 k'^2 M^2 t^2}{\rho^2} \right) \right]$$
(3.31)

If progressive nucleation is considered, the following expression is obtained:

$$j = zFk'' \left[1 - exp\left(-\frac{\pi M^2 k'^2 J t^3}{3\rho^2} \right) \right]$$
(3.32)

which requires an initial variation of current against time as t^3 , and then an asymptotic value of j of zFk''.

3.3 Adsorption model

The Langmuir model of adsorption is well known and has been extensively used in describing adsorption kinetics of monolayers in electrocrystallization. Several authors [Bar85], [Rang73] have developed the multilayer formalism for the adsorption process. The layer - overlayer adsorption is the process in which the *n*th layer is formed on the (n-1)th layer. Therefore, on a differential element $d\Theta_{n-1}$, of the (n-1)th layer coverage which occurs in the same time interval between τ and $\tau + d\tau$, the *n*th layer will start adsorbing at time τ and at a later time *t* its contribution to the *n*th layer coverage $\Theta_n(t)$ would be

$$f_n(t-\tau)d\Theta_{n-1}(\tau) \tag{3.33}$$

where $f_n(t - \tau)$ is the fraction of an unit area, which would have been covered at time t if adsorption had started at an earlier time τ . By summing all contributions from times zero through t, one obtains the nth layer coverage as

$$\Theta_n(t) = \int_0^t f_n(t-\tau) d\Theta_{n-1}(\tau)$$
(3.34)

where $f_n(t-\tau) = \psi_n [1 - exp(-\chi_n(t-\tau))]$, $\psi_n = \vec{k}_n/\chi_n$ and $\chi_n = \vec{k}_n + \overleftarrow{k_n}$; $\overrightarrow{k_n}$ and $\overleftarrow{k_n}$ are the respective adsorption and desorption rates for the *n*th layer. For simplicity it is assumed that all subsequent layers have identical adsorption and desorption rates. From Eqn. 3.34 it follows that:

$$\frac{d\Theta_n}{dt} = \psi_n \chi_n \int_0^t exp\left[-\chi_n(t-\tau)\right] \left(\frac{d\Theta_{n-1}}{dt}\right)_\tau d\tau$$
(3.35)

The nth layer current:

$$i_n(t) = \psi_n \chi_n \int_0^t exp \left[-\chi_n(t-\tau) \right] i_{n-1}(\tau) d\tau$$
(3.36)

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The overall current ${\cal I}$ and charge Q are:

$$I = \sum_{n=1}^{\infty} i_n$$

$$Q = q_m \sum_{n=1}^{\infty} \Theta_n$$
(3.37)

The use of Laplace transform and further simplifications lead to

$$\overline{I}(p) = q_m \left[1 + \frac{\psi_2 \chi_2}{p + \chi_2 - \psi_2 \chi_2} \right] \frac{\psi_1 \chi_1}{p + \chi_1}$$
(3.38)

and

$$\overline{Q}(p) = q_m \psi_1 \left[\frac{1}{p} - \frac{1}{p + \chi_1} \right] \left[1 - \frac{\psi_2 \chi_2}{p + \chi_2} \right]^{-1}$$
(3.39)

in the Laplace variable p. Transforming back to the time variable, we obtain I(t) and Q(t) as

$$I(t) = q_m \psi_1 \chi_1 exp(-\chi_1 t) + q_m \frac{\psi_2 \chi_2 \psi_1 \chi_1}{\chi_1 - \overleftarrow{k_2}} \left[exp(-\overleftarrow{k_2} t) - exp(-\chi_1 t) \right]$$
(3.40)

and

$$Q(t) = q_m \psi_1 \left[1 - exp(-\chi_1 t) \right] + q_m \frac{\psi_2 \chi_2 \psi_1 \chi_1}{\chi_1 - k_2} \left[\frac{1 - exp(\overleftarrow{k_2} t)}{\overleftarrow{k_2}} - \frac{1 - exp(-\chi_1 t)}{\chi_1} \right]$$
(3.41)
Chapter 4

Diffraction line-broadening analysis

The development of this research field began when Scherrer [Sch18] understood that small crystallites cause broadening of diffraction lines. However, more than a quarter of a century elapsed before a more complex and exact theory of line broadening was formulated by Stokes and Wilson [Sto44]. They included the lattice strain as another source of broadening. Phenomenological line-broadening theory of plastically deformed metals and alloys has been developed by [War50], [War59]. It identifies two main types of broadening: the size and strain components. The former depends on the size of coherent domains (or incoherently diffracting domains in a sense that they diffract incoherently to one another), which is not limited to the grains but may include effects of stacking and twin faults and subgrain structures (small-angle boundaries, for instance); and the latter is caused by any lattice imperfection (dislocations and different point defects). The theory is general and was successfully applied to other materials, including oxides and polymers. However, the parameters obtained need a careful assessment of their physical validity and correlation to the particular structural features of the material under study. With a careful application, it was possible to obtain much more information, such as column-length distribution function, the behaviour of strain as a function of the averaging distance in domains, etc. However, they also have very serious drawbacks: in cases of large line overlapping, or weak structural broadening, the Stokes deconvolution method cannot be applied without severe errors. This is why the integral-breadth fitting methods became attractive again. After Langford [Lan78] introduced a Voigt function in the field of x-ray powder

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diffraction, it was quickly adopted in the Rietveld analysis along with its approximations. It proved to be satisfactory and flexible enough for most purposes when angle dependence of parameters is modeled properly. Alternatively, although the Stokes method has put severe limitations on the analysis, the Warren-Averbach method of separation of size-strain broadening has remained the least constrained method for analyzing diffraction line-broadening. Both size-broadened and strain-broadened line- profiles are modeled with a Voigt function and distance-averaged strain follows the Gauss distribution [Bal93], [Bal95].

4.1 Diffraction line-broadening

Both instrument and specimen broaden the diffraction lines, and the observed line profile is a convolution [Tau73] :

$$h(x) = g(x) \otimes f(x) + background \tag{4.1}$$

Wavelength distribution and geometrical aberrations are usually treated as characteristic of the particular instrument (instrumental profile):

$$g(x) = \varsigma(x) \otimes \gamma(x) \tag{4.2}$$

where ς describes the wavelength-distribution profile and γ is the geometrical-aberration profile. To obtain microstructural parameters of the specimen, the physically (specimen) broadened profile f must be extracted from the observed profile h. The origins of specimen broadening are numerous. Generally, any lattice imperfection will cause additional diffraction-line broadening. Therefore, dislocations, vacancies, interstitials, substitutional, and similar defects lead to lattice strain. If a crystal is broken into smaller incoherently diffracting domains by dislocation arrays (small-angle boundaries), stacking faults, twins, large-angle boundaries (grains), or any other extended imperfections, then domain size-broadening occurs.

4.2 Extraction of physically broadened line profile

The choice of the method to obtain the parameters of pure physically broadened line profiles is of utmost importance for the subsequent line-broadening analysis. Basically, the methods used can be divided in two groups: (i) deconvolution approach where the physically broadened line profile is unfolded from the observed profile using the previously determined instrumental profile; (ii) convolution approach where, contrary to the former, the observed profile is built according to Eq. 4.1 and adjusted to the observed pattern through a least-squares fitting. However, we have a knowledge of h and g, but not of f. Therefore, both the general type and parameters of f are assumed, which introduces a bias in the method. Here it is required that at least the unknown physically broadened diffraction profile f be approximated with some analytical function. In the past, the two commonly used functions were Gauss

$$I(x) = I(0)exp\left(-\pi \frac{x^2}{\beta_G^2}\right)$$
(4.3)

and Lorentz

$$I(x) = I(0)\frac{1}{\frac{\beta_{Lor}^2}{\pi^2} + x^2}$$
(4.4)

From the convolution integral Eq. 4.1, it follows that for Lorentz profiles

$$\beta_{hLor} = \beta_{gLor} + \beta_{fLor} \tag{4.5}$$

and for Gauss profiles

$$\beta_{hG}^2 = \beta_{qG}^2 + \beta_{fG}^2 \tag{4.6}$$

where $\beta = \beta(2\cos\theta_0)/\lambda$ describes the integral breadth in units of space. However, the observed x-ray diffraction line profiles cannot be well represented neither with a simple Lorentz nor with a Gauss function [You82]. Experience shows that the Voigt function, or its approximations,

pseudo-Voigt [Wer74] and Pearson-VII [Hal77] fit very well the observed peak profiles in both xray and neutron-diffraction cases. The Voigt function is usually represented following Langford [Lan78]:

$$I(x) = I(0) \left(\frac{\beta}{\beta_{Lor}}\right) Re\left[erfi\left(\frac{\pi^{1/2}x}{\beta_G} + i\varepsilon\right)\right]$$
(4.7)

where $\varepsilon = \beta_{Lor}/(\pi^{1/2}\beta_G)$. Here, the complex error function is defined as

$$erfi(z) = exp(-z^2)erfc(-iz)$$
(4.8)

and erfc denotes the complementary error function.

Integral breadth of the Voigt function is expressed through its constituent integral breadths (Schoening 1965):

$$\beta = \beta_G \frac{exp(-\varepsilon^2)}{erfc(\varepsilon)} \tag{4.9}$$

Halder and Wagner [Hal66] showed that the following parabolic expression is a satisfactory approximation:

$$\beta^2 = \beta_{Lor}\beta + \beta_G^2 \tag{4.10}$$

Because convolution of two Voigt functions is also a Voigt function, integral breadths are easily separable conforming to Eq. 4.5 and 4.6 .

4.3 Size broadening

Scherrer (1918) gave a basic definition of the "apparent" domain size:

$$\langle D \rangle_v = \frac{K\lambda}{\beta_S(2\theta)cos\theta}$$
(4.11)

The constant K depends on crystallite shape [Wil62], but generally is close to unity. Clearly, size broadening is independent of the reflection order, that is, independent of diffraction angle. This measure of domain size is a volume-weighted quantity.

Warren and Averbach [War50] derived another definition of domain size: the surface-weighted average. The Warren-Averbach method originally was developed for plastically deformed metals, but since its introduction it found successful applications to many other materials. Each domain is represented by columns of cells along the \mathbf{a}_3 direction normal to the diffracting planes (00*l*). All variables here are expressed as functions of column length $L = n |\mathbf{a}_3|$, which is assumed to be positive, being a distance in real space between a pair of cells along direction of \mathbf{a}_3 . The size coefficient then reads as follows

$$A_{S}(L) = \int_{L}^{\infty} \left(1 - \frac{L}{L'}\right) p_{v}(L') dL' = \frac{1}{\langle D \rangle_{s}} \int_{L}^{\infty} \left(L' - L\right) p_{s}(L') dL'$$
(4.12)

with the column-length distribution function

$$p_v(L) = \frac{L}{\langle D \rangle_s} p_s(L) \tag{4.13}$$

Here, the average surface-weighted domain size and the surface-weighted and volume-weighted column-length distribution functions are

$$\left(\frac{dA_S(L)}{dL}\right)_{L \to 0} = -\frac{1}{\langle D \rangle_s} \tag{4.14}$$

$$p_s(L) \ltimes \frac{d^2 A_S(L)}{dL^2} \tag{4.15}$$

$$p_v(L) \ltimes \frac{d^2 A_S(L)}{dL^2} L$$

For a Voigt size-broadened profile, the size coefficient is given as a Fourier transform of Eq. 4.7:

$$A_S(L) = exp(-2L\beta_{LorS} - \pi L^2 \beta_{GS}^2)$$

$$(4.16)$$

By differentiating it twice, we obtain

$$\frac{d^2 A_S(L)}{dL^2} = \left[\left(2\pi L \beta_{GS}^2 + 2\beta_{LorS} \right)^2 - 2\pi \beta_{GS}^2 \right] A_S(L)$$
(4.17)

If the column-length distribution functions are known, it is possible to evaluate mean values of respective distributions:

$$< D >_{s,v} = \frac{\int_0^\infty L p_{s,v}(L) dL}{\int_0^\infty p_{s,v}(L) dL}$$
 (4.18)

Integrals of this type can be evaluated analytically [Pru86]. By solving the integral and for surface-weighted and volume-weighted domain size it follows that

$$\langle D \rangle_s = \frac{1}{2\beta_{LorS}} \tag{4.19}$$

$$< D >_v = \frac{exp(\varepsilon_S^2)}{\beta_{GS}} erfc(\varepsilon_S) = \frac{1}{\beta_S}$$

The same value of $\langle D \rangle_s$ is found from Eq. 4.14 and $\langle D \rangle_v$ is consistent with the Scherrer equation Eq. 4.11 .

4.4 Strain broadening

Stokes and Wilson [Sto44] defined an "apparent" strain as

$$\xi = \beta_D(2\theta) \cot\theta \tag{4.20}$$

The maximum (upper-limit) strain is derived as

$$\mu = \frac{\Delta d}{d} = \frac{\xi}{4} = \frac{\beta_D(2\theta)}{4tan\theta} \tag{4.21}$$

$$\mu = \frac{\beta_D}{2s}$$

where $s = 2sin\theta/\lambda$. Subscript *D* denotes distortion-related parameter. Langford et al. [Lan78] objected that the strain μ has a doubtful meaning because it takes only the maximum value; there is no strain distribution that would be expected in a real material. [Sto44] has also defined a root-mean-square (RMS) value of strain μ_{RMS} on the assumption of a Gauss strain distribution, which differs from μ by a constant factor only: $\mu_{RMS} = (2/\pi)^{1/2}\mu$. From Eq. 4.21 it is clear that strain broadening is angle dependent, hence it will depend on the reflection order. The RMS strain was not used extensively in the integral-breadth methods, but was adopted later in the Fourier Warren-Averbach approach. Note that these two RMS values of strain are equal only in the case of a Gaussian strain distribution, as explained below. If *L* is the undistorted distance, and distortion changes distance by ΔL , the component of strain in the **a**₃ direction (orthogonal to reflecting planes) averaged over cell-separation distance *L* can be defined as $\in (L) = \Delta(L)/L$. It defines the distortion coefficients of the physically broadened line profile:

$$A_D(L,s) = \langle exp(2\pi i s L \in (L)) \rangle$$

$$(4.22)$$

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To obtain the strain component, it is necessary to approximate the exponential term. For not too large L the following approximation is useful:

$$< exp(2\pi isL \in (L)) > \approx exp(-2\pi^2 s^2 L^2 < \in^2 (L) >)$$
 (4.23)

This relationship is exact if the strains $\in (L)$ are distributed around the mean value according to the Gauss error function for all L values. In general it is valid up to the terms in $\in^3 (L)$ because it is expected that the strain distribution is symmetrical [Sto44]. In the case of the pure-Gauss strain broadening ($\beta_{DLor} = 0$), the MSS is independent of L

$$<\in^2>^{1/2} = \left(\frac{2}{\pi}\right)^{1/2}\mu$$
 (4.24)

There is no obvious connection between RMSS and μ if the strain-broadened line profile contains a Lorentz component. However, in the case of the pure-Lorentz strain-broadened line profile, with Eq. 4.21, which is assumed regardless of the particular line-profile function it follows that the two measures of strain are related:

$$\mu = (\pi^2/2)Ls \ll_{Lor}^2 (L) >$$
(4.25)

In the general case, the maximum strain is determined from the integral breadth of a Voigt function:

$$2\mu s = \beta_{GD} exp(-\varepsilon_{GD}^2)/erfc(\varepsilon_D)$$
(4.26)

it follows that

$$\frac{\mu}{\langle \epsilon_V^2 (L) \rangle^{1/2}} = \left(\frac{\pi}{2}\right)^{1/2} \frac{exp(-\epsilon_D^2)}{erfc(\epsilon_D)} \frac{1}{\left(1 + \frac{2\epsilon_D^2}{\beta_{LorDL}}\right)^{1/2}}$$
(4.27)

where V denotes Voigt function.

4.5 Separation of size and strain broadening

From the preceeding paragraphs, it is evident that size broadening is angle independent, whereas strain broadening depends on diffracting angle. This is a basis for their separation. In preceding paragraphs, consequences of both size-broadened and strain-broadened Voigt profile were discussed. A convolution of two Voigt functions, being a physically broadened profile, is also a Voigt function. The size and strain (distortion) integral breadths of Lorentz and Gauss parts are combined simply:

$$\beta_{Lor} = \beta_{LorS} + \beta_{LorD}(s) \tag{4.28}$$

$$\beta_G^2 = \beta_{GS}^2 + \beta_{GD}^2(s) \tag{4.29}$$

These relations assume that the size component does not depend on s, whereas the strain component does depend on s. The actual s dependence is determined by the strain model chosen. Currently, there are two possible models:

(i) Stokes and Wilson [Sto44] definition of "apparent" strain requires that both β_{LorD} and β_{GD} be linear functions of s. This approach is built into all simplified integral-breadth methods and introduced in the multiple-line Voigt method by:

$$\beta_{Lor} = \beta_{LorS} + \beta_{LorD} \frac{s}{s_0} \tag{4.30}$$

$$\beta_G^2 = \beta_{GS}^2 + \beta_{GD}^2 \frac{s^2}{s_0^2} \tag{4.31}$$

Here, β_{LorD}/s_0 and β_{GD}^2/s_0^2 are constant for the pattern and taken conveniently for the first peak.

(ii) Warren definition of mean-square strain requires that the Lorentz and Gauss distortion integral breadths depend differently on s [Bal93] and the same relations read

$$\beta_{Lor} = \beta_{LorS} + \beta_{LorD} \frac{s^2}{s_0^2} \tag{4.32}$$

$$\beta_G^2 = \beta_{GS}^2 + \beta_{GD}^2 \frac{s^2}{s_0^2} \tag{4.33}$$

Here, β_{LorD}/s_0^2 and β_{GD}^2/s_0^2 are constant for the pattern and the "apparent" strain is not independent of the diffraction angle because β_{LorD} and β_{GD} dependent differently on s.

Chapter 5

Basic concepts of experimental techniques

In this chapter a short overview of the theoretical aspects of the techniques used in this work is given.

5.1 Linear sweep voltammetry

The complete electrochemical behaviour of a system can be obtained through a serious of steps to different potentials with recording of the current-time curves. However, the accumulation and analysis of these data can be tedious especially when a stationary electrode is used. Also, it is not easy to recognize the presence of different species (i.e., to observe waves) from the recorded i-t curves along, and potentials steps that are very closely spaced are needed for the derivation of well-resolved i-E curves. More information can be gained in a single experiment by sweeping the potential with time and recording the i-E curves directly. Usually the potential is varied linearly with time with sweep rates ν ranging from 10 mV/s to about 1000 V/s with conventional electrodes. A typical LSV response curve for the anthracene system is shown in Figure 5.1 (b). If the scan starts at a potential well positive of $E^{0'}$ for the reduction, only nonfaradaic currents flow for a while. When the electrode potential reaches the vicinity

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of $E^{0'}$ the reduction begins and current starts to flow. As the potential continues to grow more negative, the surface concentration of anthracene must drop; hence the flux to the surface (and the current) increases. As the potential moves past $E^{0'}$, the surface concentration drops nearly to zero, mass transfer of anthracene to the surface reaches a maximum rate at the potential E_p^c (see Fig. 5.1), and then it declines as the depletion effect sets in. The observation is therefore a peaked current-potential curve like that depicted.



Figure 5.1: (a) Linear potential sweep or ramp starting at E_i . (b) Resulting i - E curve, E_p^c -represents the potential corresponding to the peak current of the cathodical reaction [Bard01].

5.2 Cyclic voltammetry

To receive the preliminary information about a new system the cyclic voltammetry (CV) is nearly always the technique of first choice. The cyclic voltammetry can be applied for a study of all electrochemical reactions without limitations. With the help of this method, it is possible to get information about the type of reactions observed in the system and the potentials at which they occur. CV is also frequently used for measurements of the diffusion coefficients. At the same time this technique is unfortunately not the best one to obtain quantitative data about electrochemical nucleation processes.

Briefly, this method can be introduced as a reversal technique, which involves sweeping the

electrode potential between two limits at a known sweep rate. At the beginning the working electrode is held at some potential, E_i , where no electrode reactions occur. During measurement the potential is swept linearly at a rate ν between two limiting potentials E_1 and E_2 , So, at any time t the potential is:

$$0 < t < \tau \qquad E(t) = E_i - \nu t$$
$$t > \tau \qquad E(t) = E_i - 2\nu\tau + \nu\tau \quad (5.1)$$

where τ is the time required for the scan in one direction. The same sweep rate is normally chosen for the forward and reverse sweep. Its typical value lies in the range from several mVs⁻¹ to several Vs⁻¹. The corresponding current is recorded as a function of the varying potential. A theoretical cyclic voltammogram for a reversible system is shown in Fig. 5.2.



Figure 5.2: Cyclic potential sweep voltammetry [Bard01]. a) potential sweep during cyclic voltammetric measurement; E_i is initial value, E_1 and E_2 are two limiting values. b) a typical cyclic voltammogram of a reversible reaction; letters a and c are referred to anodic and cathodic process, E_P and I_P are potential and current peak.

For the cathodic scan (applied potential is decreasing) the current has a negative sign, for the anodic scan (applied potential is increasing) the current has a positive sign. To obtain the exact form of the cyclic voltammogram it is necessary to solve the Ficks second Law for O and R with the appropriate boundary conditions. Lets consider a reversible reduction of a species O

$$O + ne^- \leftrightarrow R$$
 (5.2)

which takes place at a planar electrode and assume that a solution initially contains only O species. According to the Ficks first Law the current density is proportional to the concentration gradient of O at the electrode:

$$I = -nFD_0 \left(\frac{\partial c_0}{\partial x}\right)_{x=0}$$
(5.3)

where F is the Faraday constant, D_0 is the diffusion coefficient of O, c_0 is the concentration of O and x is distance from the electrode surface. This equation is valid if all other mechanisms of mass transport (such as migration and convection) can be neglected. In other words it means that diffusion is the sole mode of the mass transport. In diluted and unstirred solutions at constant temperature this can be taken as a good approximation [Bard01]. If these conditions are fulfilled, then the cyclic voltammogram is a result of the solution of the Fick's second Law:

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial x^2}$$

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial x^2}$$
(5.4)

with the following boundary conditions:

$$t = 0, x \ge 0$$
 $c_0 = c_0^{\infty}$ and $c_R = 0,$ **a**)
 $t \ge 0, \quad x \to \infty$ $c_0 = c_0^{\infty}$ and $c_R = 0,$ **b**)

$$t > 0, \quad x = 0 \qquad \begin{cases} D_0 \left(\frac{\partial c_0}{\partial x}\right) = -D_R \left(\frac{\partial c_R}{\partial x}\right) & \mathbf{c} \\ \left(\frac{c_0}{c_R}\right)_{x=0} = \exp\left\{\frac{nF}{RT} \left(E - E^0\right) & \mathbf{d} \right) \end{cases}$$
(5.5)

where E^0 is the equilibrium potential under standard conditions, c and D are concentration and diffusion coefficient of the species O and R, respectively, other parameters have their usual meaning (Eqn. 5.3). The first three conditions, 5.5 a-c, are quite general, whereas the last one, 5.5 d, holds only for a reversible reaction (reaction, for which the electron transfer is so fast that for any change in electrode potential Nernstian equilibrium is always maintained). For the totally reversible reaction $E_p^c - E_p^a = 57.0/n$ mV. The solution of this problem is quite difficult and details can be found, for example, in [Bard01].

5.3 Chronoamperometry

Chronoamperometry is a technique, which consists basically in applying some constant potential to the working electrode and recording the current-time response. This is a very useful technique for obtaining initial information about nucleation and growth in a studied system. From the current-transient curve such quantities of the system as a diffusion coefficient and amount of charge for deposition can be determined.

5.3.1 Principle of chronoamperometry.

Consider again a reversible reaction, Eq. 5.2. At the beginning of the transient experiment the potential of the working electrode is held at E_i , Fig. 5.3 (a). At t=0 the potential



Figure 5.3: The chronoamperometric experiment. a) the potential-time profile applied during the experiment, E_i is initial value and E_1 is the potential where no reduction of O occurs or some other potential of interest; b) the corresponding response of the current due to the changes of the potential [Dog04].

is instantaneously changed to a new value E1, Fig. 5.3 a), and corresponding current-time response is recorded. An example of the current response is shown in Fig. 5.3 b).

5.3.2 Solution of the diffusion equation.

In order to determine the exact form of current-time dependence it is again necessary to solve Fick's second Law (Eq. 5.4) under the following boundary conditions:

$$t = 0, \quad x \ge 0: \qquad c_0 = c_0^{\infty}, \qquad a)$$

$$t \ge 0, \quad x \to \infty: \qquad c_0 = c_0^\infty, \qquad b)$$

$$t > 0, \quad x = 0: \qquad c_0 = 0.$$
 (5.6)

For details of solution of this problem see [Bard01]. For a planar electrode the current density is given by the Cottrell equation:

$$|I| = \frac{nF\sqrt{D_0}c_0^\infty}{\sqrt{\pi t}} \tag{5.7}$$

For diffusion controlled process it can be noticed that the current falls as $t^{-1/2}$. This feature is frequently used as a test for this type of process and from the slop of I vs. $t^{-1/2}$ the diffusion coefficient D_0 can be calculated.

5.4 Impedance spectroscopy

The technique where the cell or electrode impedance is plotted vs. frequency is called electrochemical impedance spectroscopy (EIS). In a general sense, an electrochemical cell can be considered simply as an impedance to a small sinusoidal excitation; hence we ought to be able to represent its performance by an equivalent circuit of resistors and capacitors that pass current with the same amplitude and phase angle that the real cell does under a given excitation. A frequently used circuit, called the Randies equivalent circuit, is shown in Figure 5.4. The parallel elements are introduced because the total current through the working interface is the sum of distinct contributions from the faradaic process, i_f , and double-layer charging, i_c . The double- layer capacitance is nearly a pure capacitance; hence it is represented in the equivalent

circuit by the element C_d . The faradaic process cannot be represented by simple linear circuit elements like, R and C, whose values are independent of frequency. It must be considered as a general impedance, Z_f . Of course, all of the current must pass through the solution resistance; therefore R_{Ω} is inserted as a series element to represent this effect in the equivalent circuit. It is important to understand that equivalent circuits drawn for electrochemical cells are not unique. Moreover, only in the simplest cases can one identify individual circuit elements with processes that occur in the electrochemical cell. This is especially true for equivalent circuits that represent more complicated processes, such as, coupled homogeneous reactions or the behavior of adsorbed intermediates. In fact even the simple $R_{\Omega}C_d$ circuit in the absence of a faradaic process at low electrolyte concentration shows frequency dispersion (i.e., variation of R_{Ω} and C_d with frequency). The variation of the impedance with frequency is often of interest and can be displayed in different ways. In a Bode plot Fig. 5.5, $\log |\mathbf{Z}|$ and phase angle are both plotted against $log(\omega)$. At short times the current consists of a large nonfaradaic component due to charging of the double-layer capacitance. The nonfaradic current decays exponentially with time constant $R_{\Omega}C_d$, where R_{Ω} is an uncompensated resistance and C_d is the double layer capacitance)

$$|I| = \frac{E}{R_{\Omega}} e^{-t/R_{\Omega}C_d}$$
(5.8)

Thus, the time constant $R_{\Omega}C_d$ will determine the shortest time required to conduct the chronoamperometric experiment. Therefore, measurements should be performed for times which are much larger than $R_{\Omega}C_d$. After passing the time equal to $R_{\Omega}C_d$, the double layer capacitance is charged by 63% and one can easily estimate the time needed for double layer charging [Bard01]. At long time, however, the natural convection comes into effect and diffusion in that case is not the only mode of the mass transport. Hence, the typical time range of chronoamperometric measurements lies normally in the range from 0.001 to 10 s. However, there are a number of additional instrumental and experimental limitations [Bard01]. For example, current and voltage characteristics of a potentiostate can limit the current maximum and time resolution (potentiostatic limitations).



Figure 5.4: Equivalent circuit of an electrochemical cell.



Figure 5.5: Bode plots [Bard01]: above - the variation of the logarithm of impedance with the logarithm of frequency; at the bottom of the figure the dependence of the phase angle on the log frequency is presented.

5.5 X-ray diffractometry

X-ray diffractometry is a technique in crystallography in which the pattern produced by the diffraction of X-rays through the closely spaced lattice of atoms in a crystal is recorded and then analyzed to reveal the nature of that lattice. This generally leads to an understanding of the material and molecular structure of a substance. The spacing in the crystal lattice can be determined using Bragg's law. Bragg's Law (Fig. 5.6) refers to the simple equation:

$$\lambda n = 2dsin\theta \tag{5.9}$$

derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to



Figure 5.6: Deriving Bragg's Law using the reflection geometry and applying trigonometry. The lower beam must travel the extra distance (AB + BC) to continue traveling parallel and adjacent to the top beam.

explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence [Bre13]. The variable d is the distance between atomic layers in a crystal, and the variable lambda λ is the wavelength of the incident X-ray beam; n is an integer. Diffractometer is a measuring instrument for analyzing the structure of a usually crystalline substance from the scattering pattern produced when a beam of radiation or particles (as X rays or neutrons) strikes it. The electrons that surround the atoms, rather than the atomic nuclei themselves, are the entities which physically interact with the incoming X-ray photons. This technique is widely used in chemistry and biochemistry to determine the structures of an immense variety of molecules, including inorganic compounds, DNA and proteins.



5.6 Atomic force microscopy

Figure 5.7: AFM diagram.

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope. The AFM was invented by Binnig, Quate and Gerber [Bin86], and is one of the foremost tools for the observation of matter at the nanoscale.

The AFM (Fig. 5.7) consists of a cantilever (probe) with a sharp tip at its end that is used to scan the specimen surface. The probe is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into close proximity of a sample surface, the Van der Waals force between the tip and the sample leads to a deflection of the cantilever according to Hooke's law. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. However a laser detection system can be expensive and bulky; an alternative method in determining cantilever deflection is by using piezoresistive AFM probes. These probes are fabricated with piezoresistive elements that act as a strain gage. Using a Wheatstone bridge, strain in the AFM probe due to deflection can be measured, but this method is not as sensitive as laser deflection. If the tip were scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Generally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. The resulting map of s(x,y) represents the topography of the sample. Over the years additional modes of operation have been developed for the AFM. The primary modes of operation are contact mode, non-contact mode, and dynamic contact mode. In the contact mode operation, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. In the non-contact mode, the cantilever is externally oscillated at or close to its resonance frequency. The oscillation is modified by the tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. Because most samples develop a liquid meniscus layer, keeping the probe tip close enough to the sample for these inter-atomic forces to become detectable while preventing the tip from sticking to the surface presents a major hurdle for non-contact mode in ambient conditions. In dynamic contact mode, the cantilever is oscillated such that it comes in contact with the sample with each cycle, and then enough force is applied to detach the tip from the sample.

Schemes for non-contact and dynamic contact mode operation include frequency modulation and the more common amplitude modulation. In frequency modulation, changes in the oscillation frequency provide information about a sample's characteristics. In amplitude modulation (better known as intermittent contact, semi-contact, or tapping mode), changes in the oscillation amplitude yield topographic information about the sample. Additionally, changes in the phase of oscillation under tapping mode can be used to discriminate between different types of materials on the surface. The AFM has several advantages over the scanning electron microscope (SEM). The AFM can produce images of materials as small as 1nm, while the SEM is limited to around 100nm. Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms.

5.6.1 Nanoindentation

Nanoindentation is a new method for characterization of material mechanical properties on a very small scale. Features less than 100 nm across and thin films less than 5 nm thick can be evaluated. Test methods include indentation for comparative and quantitative hardness measurements and scratching for evaluation of wear resistance and thin film adhesion. Experimentally, proximal probe tips such as the atomic force microscope, are used both to perform the indentations and to image the sample surface afterwards. The force acting on the tip is measured as a function of the indentation depth, and this relationship allows mechanical properties, such as hardness and Young's modulus, to be determined. The indenter is generally made from diamond and has an axisymmetric or pyramidal geometry with a small radius of curvature at the apex, since the indenter blunts with continued operation.

5.7 Transmission electron microscopy

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What you can see with a light microscope is limited by the wavelength of light. TEMs use electrons as light source and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope. The ray of electrons is produced by a pin-shaped cathode heated up by current, see Fig. 5.8. The electrons are vacuumed up by a high voltage at the anode. The acceleration voltage is between 50 and 150 kV. The higher it is, the shorter are the electron waves and the higher is the power of resolution. But this factor is hardly ever limiting. The power of resolution of electron microscopy is usually restrained by the quality of the lens-systems and



Figure 5.8: TEM diagram.

especially by the technique with which the preparation has been achieved. Modern gadgets have powers of resolution that range from 0.2 - 0.3 nm. The useful resolution is therefore around 300,000 x.

The accelerated ray of electrons passes a drill-hole at the bottom of the anode. Its following way is analogous to that of a ray of light in a light microscope. The lens-systems consist of electronic coils generating an electromagnetic field. The ray is first focused by a condenser. It then passes through the object, where it is partially deflected. The degree of deflection depends on the electron density of the object. The greater the mass of the atoms, the greater is the degree of deflection. Biological objects have only weak contrasts since they consist mainly of atoms with low atomic numbers (C, H, N, O). Consequently it is necessary to treat the preparations with special contrast enhancing chemicals (heavy metals) to get at least some contrast. Additionally they are not to be thicker than 100 nm, because the temperature is raising due to electron absorption. This again can lead to destruction of the preparation. It is generally impossible to examine living objects.

After passing the object the scattered electrons are collected by an objective. Thereby an

5.8. SCANNING ELECTRON MICROSCOPY

image is formed, that is subsequently enlarged by an additional lens-system (called projective with electron microscopes). The thus formed image is made visible on a fluorescent screen or it is documented on photographic material. Photos taken with electron microscopes are always black and white. The degree of darkness corresponds to the electron density (= differences in atom masses) of the candled preparation. It is possible to see objects to the order of a few angstrom (10^{-10} m) . For example, studies of small details in the cell or different materials down to near atomic levels can be provided. The possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research.

5.8 Scanning electron microscopy



Figure 5.9: SEM diagram.

The scanning electron microscope is a surface electron microscope, see Fig. 5.9. It can handle larger specimens which require very little preparation. Electrons are released from a heated filament. They are drawn into a beam and accelerated by high voltages applied to the source electrodes. The beam is focused as the electrons pass through the magnetic condenser and focusing lenses. It is scanned in a raster pattern on the surface of the specimen by varying the current in the magnetic deflection coils. As the primary electron beam strikes the surface of the specimen four kinds of emission take place: (a) secondary electrons from the surface atoms, (b) back scattered primary electrons, (c) x-rays coming from the surface atoms struck by the electrons, and (d) some visible radiation caused by cathodoluminescence. Magnification in the SEM can be understood in the following way: a certain sized raster pattern is formed on the surface of the specimen as the primary electron beam is scanned back and forth. Another similar raster pattern is formed on the face of the cathode ray tube (picture tube) as its electron beam is scanned back and forth. The size of the raster pattern on the cathode ray tube is fixed by the size of the tube. The size of the raster pattern formed on the specimen can be varied by changing the current in the deflection coils. The magnification of the scanning electron microscope is the cathode ray tube scan width divided by the width of the scan on the specimen surface. Thus the magnification is increased by making the probe scan width smaller.

5.9 Microindentation

The term microhardness test usually refers to static indentations made with loads not exceeding 9.8 N. The indenter is either the Vickers diamond pyramid or the Knoop elongated diamond pyramid. The procedure for testing is very similar to that of the standard Vickers hardness test, except that it is done on a microscopic scale with higher precision instruments. The surface being tested generally requires a metallographic finish; the smaller the load used, the higher the surface finish required. Precision microscopes are used to measure the indentations; these usually have a magnification of around $\times 500$ and measure to an accuracy of +0.5 micrometres. Also with the same observer differences of +0.2 micrometres can usually be resolved. It should, however, be added that considerable care and experience are necessary to obtain this accuracy.

The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load of 9.8 to 980 N as shown in Fig. 5.10. The full



Figure 5.10: The diagram of hardness measurement. Above - the indentation process; at the bottom - the imprint of the indenter on the investigated sample.

load is normally applied for 10 to 15 seconds. The advantages of the Vickers hardness test are that extremely accurate readings can be taken, and just one type of indenter is used for all types of metals and surface treatments. Although thoroughly adaptable and very precise for testing the softest and hardest of materials, under varying loads, the Vickers machine is a floor standing unit that is more expensive than the Brinell or Rockwell machines.

Chapter 6

Electrodeposition of nanostructured metals

In this Chapter the principles of the electrodeposition of gold and gold alloys from non-toxic electrolyte by means of direct and pulsed techniques are described. The influence of chemical and physical parameters on the nanostructure of the deposit is investigated.

6.1 Preparation of the electrolyte

For many decades cyanide containing baths for gold and gold alloys electrodeposition were used. On the one hand, the $Au(CN)_2$ and $Au(CN)_4$ complexes are very stable, cyanide salts are very cheap and the gold preparation process is well known [Li97]. On the other hand, cyanide is very poisonous even at a very low concentration. A number of attempts to produce gold electrolytes from thiomalat, mercaptoethanol, iodide, hydroxide, phosphate [Aby03] thiosulfate [Nob94], sulphite [Nat03] were made [Osa97], [Gre03]. The disadvantages of these electrolytes are: instability, toxicity and water sensitivity [Sim00]. A stable and non-toxic electrolyte for gold electrodeposition using a 3-mercapto-1-propanesulfonic acid sodium salt (MPS) [Yev07] is prepared according to the following reactions:

1.
$$HAuCl_4 \xrightarrow{Base} Au(OH)_3$$

2.
$$Au(OH)_3 + 4HS - R \rightarrow [Au(S - R)_4]^- + 3H_2O + H^+$$

3. $[Au(S-R)_4]^- \xrightarrow{time \text{ or } \Delta T} [Au(S-R)_2]^- + R - S - S - R$

where

$$R = -(CH_2)_3 - SO_3Na$$

The reaction of tetrachlorogold-(III) acid with ammonium hydroxide leads to gold-(III) hydroxide (1), which reduces to the colourless gold (I) thiol containing complex by interacting with MPS [Hol85] (2). The resulting solution (3) is colorless and exhibits long time stability. The electrolyte consists of 5 g L⁻¹ H[AuCl₄], 10.5 g L⁻¹ MPS, 160 mL (50% NH₄OH). The pH was adjusted to 10.

6.2 Electrodeposition of gold by direct current



Figure 6.1: Typical X-ray diffraction pattern of the deposited gold sample. Red lines represent characteristic 2-Theta positions for pure gold.

The gold samples were electrodeposited form the pure electrolyte at different temperatures and different current densities. A cell with an anode consisting of high acid resistant stainless steel of low iron content and a copper cathode was used. Copper as cathode material was used because it is isostructural with gold with a nearly identical lattice constant what allow to avoid surface cracks and to minimize microstrain in the deposit. To investigate the stability of the electrolyte the current density was increased from 5 mA cm⁻² to 40 mA cm⁻². No changes in the condition of the electrolyte was observed. It was concluded after a lot of experiments that the same bath can be used for the electroleposition of several samples in the different ranges of temperatures. The temperature was changed from 298 K up to 363 K after that the evaporation of water from the electrolyte was observed. In Fig. 6.1 typical X-ray diffraction pattern of the deposited gold sample is shown. The red lines represent characteristic 2-Theta positions for the pure gold. The characteristics for gold were taken from international JCPDS database. It should be mentioned that during gold electrodeposition by direct current the gold crystallites have sizes about 70 nm, as can be observed in Fig.6.2.



Figure 6.2: TEM of the gold sample electrodeposited by direct current.

6.3 Pulsed electrodeposition of gold

The pulsed electrodeposition technique (PED) is a versatile method for the preparation of nanostructured metals and alloys [Pui86], [Boc67]. The formation of nanostructured materials by electrodeposition comprises the nearly instantaneous formation of a large number of nuclei and the comparatively slow growth of the deposited nuclei. The control of both processes is possible by the variation of pulse parameters (j_p : average current density, t_{on} : duration of pulses, t_{off} : duration between two pulses), by the variation of the bath temperature and by the electrolyte composition (e.g. additives, grain refiners, brighteners). According to the



Figure 6.3: Dependence of the crystallite size on the bath temperature and the average current density. It is evident from the picture that the crystallite size of gold decreases with increasing the temperature of the bath and with increasing the current density. Pulse duration $t_{on}=1$ ms, duration between two pulses $t_{off}=20$ ms.

theory of nucleation [Kash00] size and number of nuclei depend on the overvoltage. A high nucleation density on the electrode surface can be achieved by a high overvoltage. This high overvoltage can only be maintained for a few milliseconds because the metal ion concentration in the vicinity of the cathode decreases and therefore the process would become diffusion-controlled [Bud96]. During the t_{off} -time the metal ions diffuse from the bulk electrolyte to the



Figure 6.4: Bright (left) and dark (right) field TEMs of gold sample deposited at t_{on} : 1 ms and t_{off} : 20 ms, T = 348 K, $j_p = 50$ mA cm⁻² from the electrolyte without any additives. The crystallites of about 20 nm can be observed.

cathode and compensate the metal ion depletion. Also during the t_{off} -time, due to exchange current processes, Ostwald ripening sets in that means that the larger crystallites, which are energetically more preferred, grow at the expense of the smaller crystallites. This process can be impeded by surface active substances (grain refiners) as additives to the electrolyte. All PED experiments are made with the following pulse parameters: t_{on} : 1 ms and t_{off} : 20 ms. The dependence of the crystallite size on the bath temperature and current density is investigated (see Fig. 6.3) changing the bath temperature from 298 K to 348 K and the current density from 10 mA $\rm cm^{-2}$ to 100 mA $\rm cm^{-2}$. The crystallite size decreases both with increasing bath temperature and with increasing current density, see Fig. 6.3. In Fig. 6.4 TEMs of gold sample deposited at t_{on} : 1 ms and t_{off} : 20 ms, T = 348 K, $j_p = 50$ mA cm⁻² from the electrolyte without any additives are shown. The crystallites' sizes of about 20 nm can be observed. Upon a temperature change from 298 to 348 K the crystallite size changes from 28 to 16 nm, whereas an increase of the current density from 5 to 100 mA $\rm cm^{-2}$ causes a decrease in crystallite size by a factor of 1.5. This behavior is also reported by K. Lin and R. Weil [Lin86]. The sulfur atoms act as grain refiner by covering the fresh deposited gold nuclei and prevent further crystallite growth, probably by interaction of the free electron pairs of the sulfur atoms with the metal surface [Osa97]. In support of this assumption the Energy Dispersive X-ray analysis (EDX) shows the presence of sulfur in the deposited gold sample (Fig. 6.5).



Figure 6.5: EDX picture of pulsed electrodeposited gold .

6.4 Investigation of the influence of grain refiners

j_p / mA cm ⁻²	crystallite size / nm					
	additive free	benzoic acid	Na saccharin	nicotinic acid	tartaric acid	NaAsO ₂
10	28	22	25	23	25	10
30	22	26	28	28	27	10
50	21	28	30	31	30	8
100	21	37	39	37	35	7

Figure 6.6: Dependence of the crystallite size on the current density in the presence of different additives (benzoic acid, sodium saccharin, nicotinic acid, tartaric acid, $NaAsO_2$) at room temperature. The concentrations are given in the text. The experimental uncertainty in the crystallite size is between 3 and 7 nm, depending on the size.

The influence of the organic and inorganic grain refiners on the nanostructure of gold is investigated. As standard organic additives we have chosen tartaric acid ($c=0.5 \text{ g L}^{-1}$), benzoic acid ($c=0.5 \text{ g L}^{-1}$), nicotinic acid ($c=0.5 \text{ g L}^{-1}$) and Na- saccharin ($c=2.5 \text{ g L}^{-1}$) but none of them brought about the expected result. As shown in Fig. 6.6, instead of a decrease of the crystallites size, the reverse effect is observed - the crystallites size increases with increasing current density. A possible explanation of this behavior could be that the free electron pairs of the additives react with thiol species in the electrolyte which leads to a release of gold ions. This accelerates the Ostwald ripening and causes the growth of larger gold crystallites.



Figure 6.7: Linear sweep voltammetric measurements. Influence of different additives on the potential required for the cathodic reaction (additive-free filled squares, NaAsO₂ (c=0.5 g L⁻¹) empty circles, nicotinic acid (c= 0.5 g L⁻¹) empty stars, tartaric acid (c= 0.5 g L⁻¹) empty squares). The measurements start at positive potentials and move into negative direction where gold deposition occurs. The inset enlarges the measurements in the potential range [+250;-400] mV.

As inorganic additive NaAsO₂ is added in an amount of 0.5 g L^{-1} : just this small amount decreases the crystallite size down to 10 nm. Probably, the nanocrystals in this way are protected against Ostwald ripening by the adsorption of the arsenic compound. It was also shown by [Din92] that arsenic additives in a phosphate bath for gold electrodeposition decrease the crystallite size and therefore increase the hardness of the deposits. In order to investigate the influence of grain refiners on the potential required for the cathodic reaction a serias of cathodic linear sweep voltammetric (LSV) measurements is made in an additive-free electrolyte and in a bath with additives. The polarization measurements are carried out using a potentiostat EGG Instruments Model 6310 in a standard three electrodes cell. We use a platinum counter electrode and Hg/HgSO₄-reference electrode (the presented potentials are quoted in the present contribution, however, with respect to the NHE). The linear sweep voltammograms (LSV) are recorded with a scan rate of 100 mV s⁻¹ at room temperature. It should be mentioned that such a high scan rate was enough to observe the influence of additives on the shape of the polarization curve. The LSV curves are recorded at 100 mV s⁻¹ between E = 0.6 V and E = -1.5 V in the negative cathodic direction where the gold electrodeposition occurs (see Fig.6.7). To initiate the deposition of gold atoms on the surface of the electrode a sufficiently negative potential is required. If the surface of the cathode is partially blocked by sulfur or arsenic containing substances the deposition becomes more difficult and therefore a larger overpotential is needed. A change of the minimum potential required for gold deposition is observed depending on the type of additives. In Fig. 6.7 it is shown that the arsenic containing electrolyte causes the largest potential whereas the nicotinic acid containing bath the smallest, even smaller than the additive-free electrolyte. As was mentioned above



Figure 6.8: Dependence of gold crystalline size from MPS concentration in electrolyte and current density. Deposition parameters: $t_{on} = 1 \text{ ms}$, $t_{off} = 20 \text{ ms}$, T = 348 K. Empty circles, filled circles and filled stars represent data obtained during gold electrodeposition Asfrom the pure electrolyte with $c(\text{MPS})=10.48 \text{ g L}^{-1}$, $c(\text{MPS})=20.96 \text{ g L}^{-1}$, $c(\text{MPS})=31.44 \text{ g L}^{-1}$, respectively.

nicotinic acid and tartaric acid react with the gold-thiol complex; some gold ions become free and therefore a less negative potential is required for the cathodic reaction. Dependence of the gold crystallites size on MPS concentration in the electrolyte and on the current density



Figure 6.9: Comparison of X-ray diffractograms of gold samples deposited under different conditions: black line represent the diffractogram of gold deposited from pure bath at room temperature $(j_p=50 \text{ mA cm}^{-2})$; blue line describes the diffractogram of gold deposited by the next conditions $(j_p=50 \text{ mA cm}^{-2}, \text{ T}=348 \text{ K})$; red line corresponds to the diffractogram of gold deposited from the bath with NaAsO₂ as additive $(j_p=50 \text{ mA cm}^{-2}, \text{ T}=348 \text{ K})$.

is investigated and the results are presented in Fig. 6.8. All the deposition experiments were made with the following parameters: $t_{on} = 1 \text{ ms}$, $t_{off} = 20 \text{ ms}$, T = 348 K and recorded at current densities of 10, 20, 50 and 100 mA cm⁻². To investigate the influence of MPS on the gold crystallite size during pulse electrodeposition three electrolytes with different concentration of MPS were prepared, especially in the initially prepared electrolyte the concentration of MPS was $c = 10.48 \text{ g L}^{-1}$. For the preparation of the electrolytes for the next investigations the concentration of MPS was doubled and tripled. As followes from Fig. 6.8 increasing the concentration of MPS in the bath it is possible to decrease the crystallite size of the gold deposit. This observation allows us to make a conclusion about the "grain refining" property of MPS. Probably some compounds of MPS, namely sulfur, attach the gold crystallites and prevent their subsequent growth. In Fig. 6.9 the comparison of X-ray diffractograms of gold samples deposited under different conditions are shown. The black line represents the diffractogram of gold deposited from pure bath at room temperature $(j_p=50 \text{ mA cm}^{-2})$; the blue line describes the diffractogram of gold deposited by the next conditions $(j_p=50 \text{ mA cm}^{-2}, \text{T}=348 \text{ K})$; the red line corresponds to the diffractogram of gold deposited from the bath with NaAsO₂ as additive $(j_p=50 \text{ mA cm}^{-2}, \text{T}=348 \text{ K})$. It can be observed how the diffraction line profile changes depending on the deposition conditions.

6.5 Effectiveness of the electrolyte



Figure 6.10: Dependence of the mass of deposited gold on the time of the experiment.

The effectiveness of the pure electrolyte with the following pulse parameters: $t_{on} = 1$ ms, $t_{off}=20$ ms, j_p of 50 mA cm⁻², was investigated at room temperature. The total amount of gold in the electrolyte was 68 mg. During the first hour of PED we observed a rapid increase of the deposition rate: in 10, 20 and 40 minutes 10, 18 and 30 mg of gold metal is deposited, respectively (Fig. 6.10). This rate decreased during the next two hours; no change in the deposition rate is observed and the total mass of the deposited nanocrystalline gold was 40 mg. The effectiveness of the electrolyte at room temperature is 70%. During the (galavanostatically operated) experiment the voltage between the cathode and the anode was measured, which increased to -3.2 V. This magnitude is high enough to initiate a side reaction - hydrogen evolution. Hydrogen evolution on the cathode could possibly decrease the current
efficiency, and probably for this reason the effectiveness of the electrolyte reaches only 70%. The bath exhibits long time stability (some months) and can be used for gold electrodeposition experiments.

6.6 Surface morphology of n-gold



Figure 6.11: REM of the surface of a glassy carbon electrode after 30 min of gold deposition by pulse techniques ($j_p = 50 \text{ mA cm}^{-2}$, $t_{on} = 1 \text{ ms}$, $t_{off} = 20 \text{ ms}$, T = 298 K).

The morphology of gold deposited on glassy carbon electrodes by pulse techniques was investigated by SEM and is presented in Fig. 6.11 . A large surface area can be observed because of the small crystallite size and dendritic growth, what can be used in biomedical applications. Gold is a very popular material because of its specific physical properties, namely high biocompatibility and high resistance to the corrosion. Biofunctionalisation of electrodes with enzymes are important for analytical and preparative applications [Nuz97],[Zim00]. Some electroenzymatic measurements with electrodeposited nanocrystalline gold surfaces were performed and an increase of the enzyme activity by the factor 2 was observed [Gaj].

6.7 Pulsed electrodeposition of gold alloys

Nanoscaled gold alloys with silver, palladium, copper and platinum are deposited from our electrolyte with $j_p = 50 \text{ mA cm}^{-2}$, $t_{on} = 1 \text{ ms}$, $t_{off} = 20 \text{ ms}$ at room temperature. The alloy composition was controlled by the metal-ion concentration in the bath. As metal source we used AgNO₃, PdCl₂, CuSO₄*5H₂O and Pt(NO₃)₂ in different amounts (see Fig. 6.12). The

metal salts	concentration	crystallite size	Au content in
	/ g*L-1	/ nm	alloy
	_		/%
AgNO ₃	3,75	30	34
AgNO ₃	2,5	35	79
AgNO ₃	3,35	28	89
PdCl ₂	0,7	12	70
NaAsO ₂	0,5		
PdCl ₂	0,5	9	88
NaAsO ₂	0,5		
$Pt(NO_3)_2$	1,5	28	67
Pt(NO ₃) ₂	0,5	30	86
CuSO ₄ *5H ₂ O	0,5	20	71
CuSO ₄ *5H ₂ O	1,5	28	92

Figure 6.12: Bath compositions for gold alloys deposition and the resulting crystallite sizes.

alloy composition of the resulting deposits was calculated from the respective lattice constants which are determined by X-ray diffraction (Fig.6.13) according to the equation:



Figure 6.13: X-ray diffraction patterns of different gold alloys. The shift of the peak positions of Bragg's (111) patterns can be observed depending on the alloy composition.

$$a = \frac{\sqrt{h^2 + k^2 + l^2}}{2sin\theta}\lambda\tag{6.1}$$

where a - lattice constant for the cubic system, h, k, l - Miller indices; λ - the wave length; 2 θ - corresponding peak position of Bragg reflexes.

The results are compared with the literature data and show a good agreement [Shu69]. The metal percentage in the deposit is determined by using Vegard's law. Vegard's law is an approximate empirical rule which says that a linear relation exists, at constant temperature, between the crystal lattice constant of an alloy and the concentrations of the constituent elements. In Fig. 6.14 the results obtained from a calibration curve "lattice constant versus the gold content" are presented. It can be observed that by changing the concentration of Ag, Pd, Pt and Cu salts in the electrolyte the alloys with different concentrations of above mentioned metals can be prepared. Furthermore, it was experimentally shown that the crystallites' sizes of the alloys vary in the nanoscale range (up to 50 nm) depending on the concentrations of Me salts. It was also shown, that the deposits with high Au content (> 80%) have smooth shining surfaces, whereas, the deposits with low Au content (< 80%) represent rough surfaces and



Figure 6.14:

Determination of the composition of binary gold alloys by X-ray diffraction. On the left hand ordinate axis the lattice constants for pure silver, platinum, palladium and copper metals are given (from top to bottom), respectively. On the right hand ordinate axis the lattice constant for pure gold is displayed. From a comparison of the measured lattice constants of the alloys with the linear interpolations (straight lines in the figure) the binary alloys composition have been determined. The experimental uncertainty in the lattice constants is below ± 0.05 .

have bigger crystallite sizes. As was concluded in previous sections MPS acts as grain refiner during the electrodeposition. Changing the composition of the electrolyte by the addition of Me salts, probably, some sulfur compounds cannot interact with gold crystallites and, therefore, the crystallites' sizes of the alloys increase. With increasing concentration of Me salts in the bath the number of the defects appearing during the electrodeposition also increases what leads to the increase of the surface roughness.

Chapter 7

Kinetics of gold electrocrystallization

Electrochemical technique is a powerful tool to investigate in situ electrocrystallization processes [Kash00], [Mil02]. The basics of phase formation and growth during the early stages of electrocrystallization on a foreign substrate are now fairly well understood [Bud96]. The growth of each individual nucleus is determined by the rate of incorporation of new atoms, i.e. ion transfer and/or diffusion. It is well known that the current due to the initial growth of a nucleus depends on its geometry. Different models based on the different geometrical forms namely hemispheroids [Aby82], [Eme04], [Aby02], paraboloids [Aby04], spherical caps [Aby86], right circular cones [Aby02], are minutely described in the literature. After the initial growth the overlap of growing centers takes place. In the case of charge-transfer control the growth initiates the overlap of the growing nuclei, however, in the case of diffusion control the covering of the diffusion zones should be considered [Sch99]. The Avrami formalism [Avr40] generally used in the case of two-dimensional growth cannot be applied directly to the threedimensional growth as the distribution of the deposit in the direction perpendicular to the surface is not random in space. However, the statistical approach can be applied at any level above the surface provided that growth in the direction parallel to the substrate is delayed with respect to the initial nucleation process and is well described for hemispheroids [Aby82] and right circular cones [Arm65]. Furthermore, side reactions such as hydrogen evolution [And81], [Aby91] and/or concurrent adsorption process [Bos81], [Bar85] must be considered describing the early stages of the electrocrystallization.

In this chapter the kinetics of electrocrystallization of nanostructured gold on the glassy carbon electrodes are investigated. The experimental results of current transients recorded during gold electrodeposition are shown and predictions about the nucleation nature of gold are made. The fits of experimental results with existing theoretical equations are made and possible reasons for the inconsistency between experimental results and theoretical predictions are discussed.

7.1 Determination of the deposition potential



Figure 7.1: Cyclic voltammetry diagram of the glassy carbon electrode in the investigated electrolyte (first scan).

For the determination of the deposition potential of gold from the electrolyte discussed in Chapter 6 a set of potentiostatically controlled measurements was performed. A three electrode cell was used and all the experiments were performed at room temperature. The working electrode was the front part of a glassy carbon disc with a surface area of $S_{el} = 0.07 \text{ cm}^2$ polished to mirror bright finish. The choice of glassy carbon allows to examine the nanostructure and microstructure of the deposit when the substrate has no preferred texture. The counter electrode was a platinum plate with a surface area 2 cm² and the reference electrode was a standard calomel electrode. In this chapter in chronoamperometric measurements the cathodic current is defined as positive quantity. To determine the range of potentials where the gold deposition takes place cyclic voltammetry measurements are performed. The measurement was started at the potential 0.5 V and moved in the negative cathodic direction then swept in the positive potentials direction.

In Fig. 7.1 one can observe a peak in the potential range [-1; -1.5 V] vs. SCE, which probably corresponds to the gold deposition. A small current was recorded at the potentials more positive than -1 V vs. SCE. It was probably caused by the reduction of traces of oxygen in the solution. The current increased abruptly as potential became more negative than -1 V vs. SCE. Two potential regions were clearly seen. At more positive potentials, a current peak appeared on the cyclic voltammetry; in other words, the current initially increased with potential, formed a maximum and then decreased forming a minimum. In a second potential range, the current increased abruptly as the potential became more negative, this corresponds to the gold deposition simultaneously with the hydrogen evolution. Hydrogen gas bubbles on the surface were clearly observed at about -1.5 V vs. SCE. To determine whether the CV peak observed during gold deposition process is particularly related to the hydrogen evolution reaction LSV measurements were performed in the solutions of different pH. If the hydrogen



Figure 7.2: Linear sweep voltammetric measurements of the glassy carbon working electrode in the solutions with different pH, scan rate 20 mV s⁻¹. By decreasing the pH of the electrolyte the concentration of hydrogen in the solution increase and, therefore, causes the increase of the peak current.

evolution reaction contributes significantly to this process the peak height should be larger at lower pH (higher concentration of H^+). In Fig. 7.2 LSV measurements in the electrolyte for gold deposition are performed. The pH of the solution was changed by adding citric acid in different amount to the starting electrolyte with pH=11. In Fig. 7.2 the increase of the current by decrease of the solution's pH can be clearly observed. Summarizing all information it is obvious that the peak observed on CV in the potential region [-1100; -1500] mV vs. SCE is associated with gold deposition process with concurrent hydrogen evolution reaction.

7.2 Chronoamperometric measurements

As followed from the previous section gold electrodeposition takes place at the potentials more negative than -1V vs. SCE. Fig.7.3 and Fig.7.4 illustrate a set of the current-time transients obtained in the electrolyte at the potentials more negative than -1 V vs. SCE (for the explanation of the chronoamperometric technique see Chapter 5). It should be admitted



Figure 7.3: Current-time transients registered in the potential range [-1150 mV; -1260 mV] vs. SCE.

that the current-time transient recorded at the potential -1150 mV vs. SCE does not bring



Figure 7.4: Current-time transients registered in the potential range [-1270 mV; -1400 mV] vs. SCE.

much information about the deposition process, moreover, no deposit has been observed on the surface of the electrode. For all the transients recorded at more negative potentials it is possible to determine three characteristic regions. The initial current decrease, observed by all curves, could be caused by different processes: a) a double layer charging current; b) a direct deposition of metal into the lattice without nucleation; and c) other side reactions, such as hydrogen evolution [And81]. After an induction time, the nucleation process starts and gold crystals grow. This leads to an increase of the current with time as result of the increase of the electroactive surface area. The third part of the current is strongly dependent on the potential applied. At more positive potentials the current increases slowly and does not reach the maximum what corresponds to the nucleation and growth, whereas, at more negative potentials, the current reaches a maximum and then decrease to the steady state. Therefore, further information about the mechanism of gold electrocrystallization should be obtained.

7.3 Mechanism of gold deposition

The current minimum, observed at the beginning of the current transients (Fig. 7.3 - 7.4) increases moving towards more negative potentials. The time, corresponding to the current minimum, extends to a few seconds, depending on the potential applied. These observations show that the process occurring during the current decrease is strongly depended on the potential. As was mentioned above the initial current decrease can be due to different reactions, very often due to the charging of the electrical double layer. Otherwise, normally it is a really short time of about some ms. In order to receive more information about the double layer charging time electrochemical impedance measurements were performed. A three electrode cell was used, the same way as for chronoamperometric measurements. The frequency was changed from 100 kHz down to 10 mHz. Using the Bode-Plot (the explanation see in Chapter 5, Fig. 5.5) the resistivity of the electrolyte was measured. In Fig. 7.5 the Bode-Plot according to the experimental data is shown. At short times the current consists of a large nonfaradaic component due to the charging of the double-layer capacitance. The nonfaradaic current decays exponentially with a time constant $R_{\Omega}C_d$ according to the equation 5.8, as is explaned in Chapter 5. From Fig.7.5 the values for the double layer capacity and the uncompensated resistance were determined and amount to of $C_d = 34 \ \mu F$, $R_{\Omega} = 177.8$ Ohm. Therefore, the time corresponding to the electrochemical double layer charging was calculated to be 6 ms. Comparing this time with the time of the initial falling parts of the currents in Fig. 7.3-7.4 it becomes clear that some processes other than double layer charging cause the initial decrease of the currents. As will be shown in the next section gold domains have been observed after 3 s of the deposition time. These observations mean that the gold deposition process starts before the time corresponding to the current minimum is reached. The initial current minimum corresponds principally to a direct gold deposition without nucleation. This could be possible via an adsorption of the gold complex followed by the electron transfer. As was reported by [Gnan67], [Eise78] gold electrodeposition from cyanide solution occurs due to the adsorption of gold-cyanide complex followed by charge transfer reaction at more positive potentials or directly through charge transfer at more negative potentials. It is assumed that the gold electrodeposition from our mercapto- containing electrolyte can have a similar



Figure 7.5: Impedance measurements in the investigated electrolyte. The double layer capacity and the uncompensated resistance can be determined and correspond to the values of $C_d = 34 \ \mu F$, $R_{\Omega} = 177.8$ Ohm.

behaviour. Therefore, at more positive potentials the deposition occurs via the adsorption of the gold-mercapto complex followed by the electron transfer:

$$Au (S - R)_{2}^{-} + H^{+} \iff AuS - R_{ads} + HS - R$$

$$AuS - R_{ads} + H^{+} + e^{-} \Rightarrow Au + HS - R$$

$$(7.1)$$

At more negative potentials gold deposition can occur by direct charge transfer:

$$Au \left(S - R\right)_{2}^{-} + 2H^{+} + e^{-} \Longrightarrow Au + 2HS - R \tag{7.2}$$

where R presents $-(CH_2)_3 - SO_3Na$. The reasonable question is how to determine "more positive" and "more negative" potentials? The answer was given by [Gnan67]. In some of the elementary reactions, charges may not cross the total double layer. If the observed value of the charge transfer coefficient, α , deviates substantially from 0.5 [Bard01] then the actual charge transfer occurs across only a fraction of the Helmholz double layer. Therefore, the "more positive" and "more negative" potentials can be determined calculating the charge transfer coefficients in the defined potential range. In the case of large overpotentials, higher than 100

7.3. MECHANISM OF GOLD DEPOSITION

mV [Atk95], the Tafel equation can be written as

$$\eta = \frac{2.3RT}{\alpha nF} log j_0 - \frac{2.3RT}{\alpha nF} log j$$
(7.3)

where η is the overpotential, j_0 - exchange current density, α - charge transfer coefficient, other letters have their usual meaning. The equation 7.3 corresponds to

$$\eta = a - b * \log j \tag{7.4}$$

"a" and "b" are characteristic constants of the electrode system. A plot of electrode potential versus the logarithm of current density is called the "Tafel plot" and the resulting straight line the "Tafel line". "b" is the "Tafel slope" that provides information about the mechanism of the reaction, and "a" provides information about the rate constant of the reaction. In Fig. 7.6



Figure 7.6: Tafel plot constructed on the basis of the initial current minimum shown in Fig. 7.4 for gold electrodeposition.

Tafel plots constructed on the basis of the initial current minimum are shown. Two linear regions with two different slopes are observed. Tafel slopes are 1.101 ± 0.00006 V dec⁻¹ in potential range from -1200 to -1340 mV vs. SCE and 0.421 ± 0.00021 V dec⁻¹ at potentials between -1350 to -1400 vs. SCE, respectively. The corresponding charge transfer coefficients are calculated using the equations 7.3 and 7.4. The values of α are calculated to be 0.05 and 0.15 for the potential ranges from -1200 to -1340 mV vs. SCE and from -1350 to -1400 mV vs. SCE, respectively.

Therefore, the potential range from -1200 mV to -1340 mV vs. SCE corresponds to "more positive" one and the gold deposition mechanism probably occurs via the adsorption of gold complex followed by the electron transfer according to the reaction 7.1; at "more negative" potentials in the potential region from -1350 to -1400 mV vs. SCE the deposition, probably, occurs by direct charge transfer due to the reaction 7.2.

7.4 Determination of nucleation behaviour.

To investigate whether the nucleation of gold is potential and time dependent the surfaces of the electrodes were investigated with SEM after gold deposition at different potentials or at constant potential but different times. In Fig. 7.7 the micrographs of glassy carbon surfaces after a) 3 s, b) 8 s, c) 16 s of gold deposition at the potential -1350 mV vs. SCE are shown. One can observe the new gold domains forming during the whole time of chronoamperometric experiment. The domains have also different sizes what is evidence of progressive behaviour of the nucleation process. Furthermore, in Fig. 7.7 (d) it can be clearly seen that the gold crystallites have mixed conic, cubic and spherical forms. It is generally known that the crystal form depends strongly on the particular experiment conditions and on the presence of additives. Different crystallographic faces could have different growth velocities depending on the surface energy such that the growth forms differ significantly from the equilibrium ones. A most general rule says that faces having a higher growth rate disappear from the growing crystal and the growth forms contain simple, closely packed crystallographic faces that spread with lower velocities [Cle90]. Slow-growing orientations are those which form facets at equilibrium. Some impurities segregate to the surface where they can alter the surface free energy and thus the equilibrium shape. As was mentioned in Chapter 6 the presence of sulfur in the deposit was observed using the X-ray energy dispersive analysis. It is already reported by several authors that sulfur and mercapto compounds adsorb preferably on Au(111) surfaces [Got01], Sob05], Dub92. In this case other faces will grow faster and determine the crystal form. Furthermore, Au(111) was found to be the preferred texture according to the analysis of X-ray diffraction patterns of the deposit. These theoretical considerations combined with experimental observations can explain the mixed conic and cubic crystal forms, shown in Fig.

7.7. It was also concluded that because of the incorporation of sulfur atoms into the gold deposit its crystallites do not exceed 100 nm, the sulfur atoms adsorb on the active sites of gold crystallites and prevent their subsequent growth. In Fig. 7.8 the morphology of



Figure 7.7: SEM of the glassy carbon surfaces after a) 3 s, b) 8 s, c) 16 s of gold deposition at the potential -1350 mV vs. SCE; d) the magnification of c), shows different forms of gold crystallites.

the working glassy-carbon electrodes after 30 s of gold deposition at different potentials is shown. As evident from the micrographs the gold domains have different sizes depending on the deposition potential. In Fig. 7.8 a) the domains exceeds 1 μ , furthermore, it can be seen that the domains join and form bigger grains in expense of smaller ones. Increasing the overpotential which is requirable for gold crystallization the sizes of the domains decrease (Fig. 7.8 a) - d)). This phenomenon confirms the theory of nucleation [Kash00],[Bard01], [Mil02] and the electrochemical version of Kelvin equation which says that a high nucleation density can be achieved by applying a high overvoltage. At high overpotentials a lot of gold nuclei form simultaneously, the energy is enough to form a lot of individual domains with smaller sizes. In Fig. 7.9 the micrographs of the surface of the glassy carbon electrode after



Figure 7.8: SEM of the glassy carbon surfaces after 30 s of gold deposition at the potentials a) -1300 mV, b) -1350 mV, c) -1400 mV and d) -1450 mV vs. SCE.

30 s of gold deposition at -1350 mV vs. SCE are shown. The growth of gold domains at the expense of smaller ones can be observed. Fig. 7.10 shows the normalized current transients for the electrodeposition of gold on a glassy carbon electrode. The theoretical curves, corresponding to three-dimensional instantaneous (Eq.3.23) and progressive (Eq. 3.24) nucleation are compared with the experimental data. It can be seen that the theoretical curves describe the experimental data relatively well before the current maximum is reached. From Fig. 7.10 it can be concluded that the rising part of the normalised currents represents progressive behaviour. The experimental data obtained at the potentials from -1.35 V down to -1.4 V vs. SCE deviate considerably from the theoretical curves after the current maximum. However, it is difficult to determine the nucleation and growth type only by current transient comparison prior to nuclei overlapping. Not better coincidence of the experimental data with theoretical curves of 2-D instantaneous (Eq. 3.21) and 2-D progressive (Eq. 3.22) nucleation and growth was observed. The theoretically calculated curves for 2-dimensional nucleation and



Figure 7.9: SEM of the glassy carbon surfaces after 30 s of gold deposition at -1350 mV vs. SCE. The growth of the gold domains at the expense of small ones can be observed.



Figure 7.10: Non-dimensional plots of transients, recorded at the potentials (a) -1.25 V, (b) -1.27 V, (c) -1.4 V, (d) -1.5 V vs. SCE together with theoretical curves for 2-D instantaneous (blue curves) and progressive (red curves) nucleation and growth.



Figure 7.11: Non-dimensional plots of the transients, recorded at the potentials (a) -1.35 V, (b) -1.36 V, (c) -1.37 V, (d) -1.38 V, (e) -1.39 V, (f) -1.4 V vs. SCE together with the theoretical curves for 3-D instantaneous (blue curves) and progressive (red curves) nucleation and growth.

growth do not coincide with experimental results at all. At the potential E = -1.4 V vs. SCE the rising parts of the current can be relatively well described by both 2 - D instantaneous and 3 - D progressive nucleation and crystal growth. Possible 2-D and 3-D nucleation behaviour at the same deposition potential is also reported by [Hwa00] during the electropolymerization of aniline on highly oriented pyrolytic graphite. The probable reason of such a big deviation of experimental results from the theoretically calculated ones after the current maximum is reached (see Fig. 7.10 and Fig. 7.11) is the concurrent hydrogen evolution reaction, which can change the shape of the current-time transients . This side reaction can start direct after the potential is applied, in this case the rising parts of the currents should be distorted by the contribution of hydrogen. It is also possible that initially the gold complexes which are located close to the cathode move through the electrolyte very fast and form the nuclei. After that, during the movement of gold ions to the cathode, hydrogen evolution takes place on the surface

of the working electrode [Dep03]. It can be seen from Fig. 7.10 that due to the analysis of the experimental data using 3 -D nucleation and growth models the experimental curves show progressive behaviour at the whole range of measured potentials. Small deviations from the theoretically calculated curves for 3-D progressive nucleation were observed at the potentials -1.39 V and -1.4 V vs. SCE. Nevertheless, hydrogen bubbles were observed distinctly on the surface of the cathode at such negative potentials. Coming to the analysis of Fig. 7.11 it can be clearly seen that the nucleation changes from progressive at more positive potentials (-1.25 V and - 1.27 V vs. SCE) to instantaneous at more negative potentials (-1.4 V and -1.5 V vs. SCE). The change of the 3-D nucleation behaviour due to the deposition potential was also reported by [Dep03], [Dep04] during the electrodeposition of gold from cyanide solution. They have registered progressive behaviour of nucleation at the deposition potential -1.45 V vs. SCE changing to instantaneous coming to the potential -1.7 V. It was also reported that the nucleation strongly on the surface composition of the electrode [Vri01].

7.5 Measurements with RDE



Figure 7.12: Dependence of the shape of LSV curves on the rotation rate at the scan rate of 20 mV s⁻¹.

7.5. MEASUREMENTS WITH RDE

The current-time transients, presented in the previous sections are difficult to analyse because such processes as diffusion and charge transfer affect their shapes. To investigate the influence of the diffusion and charge transfer on the shapes of the current transients the measurements with a rotating disc electrode (RDE) (Metrohm 628-100, area 0.87 cm²) were performed. For data recording the potentiostat/galvanostat Model 282 (Princeton Applyid Research) was used. A set of LSV curves obtained in the electrolyte for gold deposition is shown in Fig. 7.12. The curves were recorded at the scan rate of 20 mV s⁻¹. The shape of the voltammetric curves allows to conclude that increasing the rotation rate of the electrode the deposition potential of gold is shifted towards more positive potentials. Acquired data were tested according to the Levich equation [Bard01] which predicts the current observed at a rotating disk electrode. A deviation of plot of j vs. $\omega^{1/2}$ from a straight line intersecting the origin suggest that a kinetic limitation is involved in the electron-transfer reaction. This equation takes into account both



Figure 7.13: Chronoamperometric measurements of a glassy carbon rotating disc electrode with the rotation rate of 2000 rpm in the electrolyte for gold deposition at different deposition potentials.

the rate of diffusion across the stagnant layer and the sigmoidal wave observed in rotated disk voltammetry:

$$j_d = (0.620)nFAD^{2/3}\omega^{1/2}v^{-1/6}c \tag{7.5}$$

where ω is the angular rotation rate of the electrode (radians s⁻¹) and v is the kinematic viscosity of the solution (cm² s⁻¹). The kinetic limitations can be determined using the

Koutecky-Levich equation [Bard01]:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{l,c}} = \frac{1}{i_K} + \frac{1}{(0.620)nFAD^{2/3}\omega^{1/2}v^{-1/6}c}$$
(7.6)

Here, i_K represents the current in the absence of any mass-transfer effects, that is, the current that would flow under the kinetic limitation if the mass transfer were efficient enough to keep the concentration at the electrode surface equal to the bulk value, regardless of the electrode reaction. Clearly, $i/\omega^{1/2}c$ is a constant only when i_K is very large. Otherwise, a plot of i vs. $\omega^{1/2}$ will be curved and tend toward the limit $i = i_K$ as $\omega^{1/2} \to \infty$.

A plot of $1/i \ vs. \ 1/\omega^{1/2}$ should be linear and can be extrapolated to $\omega^{-1/2} = 0$ to yield $1/i_K$. determination of i_K at different potentials then allows the determination of the kinetic parameters i_0 and α according to the equation:

$$i_K = i_0 exp(-\alpha \frac{F}{RT}\eta) \tag{7.7}$$

where F is the Faraday constant [C mol⁻¹], R is the gas constant [J K⁻¹mol⁻¹], T - the temperature of the electrolyte [K], i_0 represents the exchange current [A], α is the charge transfer coefficient and η is the overpotential [V]. Plots of j against $w^{1/2}$ for curves recorded



Figure 7.14: Plots of j against $w^{1/2}$ constructed at the scan rate of 20 mV s⁻¹.

at 20 mV s⁻¹ are shown in Fig. 7.14. One can conclude that the process remains under diffusion control in the potential range -0.4 V to -1.2 V, with the kinetic contribution increasing



Figure 7.15: Dependence of the shape of LSV curves on the rotation rate at the scan rate of 20 mV s⁻¹. The figure shows that increasing the rotation rate of the working electrode the cathodic curves move toward more positive potentials. The inset describes the LSV curves in the whole range of the measurement.

when moving towards more negative potentials. Otherwise, it is difficult to analyse such data using Eqs. 7.5, 7.6, 7.7. Small data statistics is caused by the technical limitations of the RDE Metrohm 628-100, especially the possibility to make measurements only with 5 different rotation rates. In Fig. 7.13 a set of experimental chronoamperometric measurements recorded at 2000 rpm is shown, where, probably, the diffusion does not play a significant role . The current increases very fast and reaches a steady state value. It is obvious that curves presented in Figs. 7.3, 7.4 and 7.13 differ significantly in their forms and therefore the nature of gold electrocrystallization is described by different types of nucleation and/or by different processes which control the deposition of gold.

To obtain data with good statistics the RDE Model 616 Princeton Applied Research ($S_{el} = 1 \text{ cm}^{-2}$) was used. The electrode allows to perform measurements in the range from 1 up to 9000 rpm with a step of 1 rpm. In Fig. 7.15 a set of LSV measurements on a glassy carbon electrode with different rotation rates are presented. The measurements were made with the



Figure 7.16: Plots of j against $w^{1/2}$ constructed at the scan rate of 20 mV s⁻¹.

scan rate of 20 mV s⁻¹, furthermore, it was also observed that the shapes and current of LSV curves do not differ sufficiently changing the scan rate from 5 mV s⁻¹ to 50 mV s⁻¹. The inset in Fig. 7.15 shows that with increasing rotation rate of the working electrode the cathodic curves move toward more positive potentials. In Fig. 7.16 the plots of j against $w^{1/2}$ recorded



Figure 7.17: Plots of j^{-1} against $w^{-1/2}$ constructed at a scan rate of 20 mV s⁻¹.

at a scan rate of 20 mV s⁻¹ are presented. A linear dependence between j and $w^{1/2}$ in the potential range from -0.4 V to -1.2 V can be observed. At more negative potentials the data do not show a linear dependence that indicates a non diffusion nature of the electrochemical

processes. The recorded data were analyzed in terms of the Eq. 7.6. In Fig. 7.17 plots of j^{-1} against $w^{-1/2}$ recorded at the scan rate of 20 mV s⁻¹ are presented. The data exhibit good linearity what allows to determine the kinetic current density. Extrapolating to $\omega^{-1/2} = 0$ it is possible to yield $1/i_K$. The magnitudes for j_K obtained from Fig. 7.17 are presented

E vs. SCE / V	-0.4	-0.6	-0.8	-1.0	-1.2
$ j_K / \text{ mA cm}^{-2}$	0.95	1.35	1.85	2.63	20

Table 7.1: Kinetic current densities calculated on the basis of Fig.7.17.



Figure 7.18: Plots of j against $w^{1/2}$ constructed at the scan rate of 20 mV s⁻¹.

in Table 7.1. The kinetic current density increases moving towards more negative potentials. Otherwise, at the potential -1.2 vs. SCE, the value obtained for the kinetic current density seems to be very high and improbable. For this reason the value of the kinetic current density obtained at the potential -1.2 V was not used for subsequent data analysis. According to the Eq.7.7 it is possible to determine kinetic parameters such as exchange current density j_0 and charge transfer coefficient α by plotting lnj_K vs. η . In Fig. 7.18 the dependence of lnj_K on different overpotentials is presented and a linear behaviour of the data can be observed. The linear fit of the data was performed and the kinetic parameters $j_0 = 0.29 \pm 0.02$ mA cm⁻² and $\alpha = 0.042 \pm 0.0006$ were determined. The charge transfer coefficient is in a good agreement with the value obtained in one of the previous sections ($\alpha = 0.05$).

7.6 Approximations of current-time transients

7.6.1 Adsorption

In the previous parts of this chapter general aspects of gold deposition mechanism have been considered. The complete understanding of this process, however, requires an additional analysis of the deposition kinetics. Kinetic parameters of gold electrodeposition can be evaluated using current transients results of the chronoamperometric measurements. Generally, with the help of different theoretical models, which can be applied for a description of the currenttime response, it is possible to classify such quantities and processes as diffusion coefficient, adsorption kinetics, nucleation, growth rates, surface alloying etc. On the other hand, the deposition process can be rather complex, when certain parameters have a strong influence on the deposition: the type and crystallographic orientation of the substrate, deposit- substrate interaction, electrolyte, temperature. Several general models for a description of current transients can be found in the literature [Arm66], [Aby86], [Sch99]. Qualitatively the theoretical descriptions are based on the following assumptions. At the beginning a nucleation proceeds with a constant rate and at certain locations on the electrode surface on the active sites. The number of active sites might change with time, and two types of nucleation are normally considered: instantaneous and progressive. The rate determining step plays a significant role in the theoretical description of the deposition kinetics. Such a step can be a rate of the incorporation of adatoms in the growing centers and/or rate of the mass transport /diffusion.

On the basis of the analysis used by [Dog04], [Bar85], [Var92] it was assumed that in the case of gold electrodeposition on glassy-carbon electrodes more than one process could be involved. The process at short times can be related to the deposition of a certain number of Au layers on glassy carbon influenced by strong interactions due to a certain number of surface defects of a glassy carbon electrode [Bud96]. This kind of incorporation of gold into the working electrode without nucleation will be further called adsorption. [Bar85] developed a kinetic model of multilayer adsorption during electrochemical phase formation along the same lines as the multilayer model of nucleation and growth in electrocrystallization. The kinetic adsorption model (see Chapter 3, Eq. 3.40) predicts an exponential decrease of the current due to the decrease of the concentration of adsorbed species, the gold-mercapto complex in the context of this work. Assuming that the desorption rate $\overleftarrow{k} = 0$, the current density can be described as

$$j_{ads} = q_{ads}k_{ads}exp(-k_{ads}t) \tag{7.8}$$

The simulated curves due to the Eq. 7.8 are presented in Fig. 7.19. It is known that the



Figure 7.19: Calculated current transients for the adsorption process due to Eq. 7.8 with different parameters. Solid line corresponds to the curve simulated with the following parameters: $q_{ads} = 0.001 \text{ C cm}^{-2}$, $k_{ads} = 1 \text{ s}^{-1}$, dotted line describes the curve simulated with the following parameters: $q_{ads} = 0.005 \text{ C cm}^{-2}$, $k_{ads} = 0.3 \text{ s}^{-1}$.

initial decrease of the current transients observed during the gold electrodeposition can be related to the direct deposition of adatoms without nucleation [Li96]. As can be observed in Fig. 7.3 and 7.4 the time of the current decay depends strongly on the potential applied. The origin of the substrate differs significantly in structure from gold. Therefore, gold adatoms



Figure 7.20: Total charge transferred due to gold deposition on a glassy-carbon electrode at different potentials.



Figure 7.21: Fit of the experimental data recorded at -1250 mV vs. SCE with Eq. 7.8.

are looking for energetically favorable places on glassy-carbon, especially for defects (kinks, cracks etc.). It is obvious from the thermodynamical point of view that applying a bigger overpotential the minimum energetic barrier necessary for direct gold incorporation into the defects on the surface of the working electrode will be overpassed faster. Nevertheless, it was determined (see Fig. 7.20) that after 3 s of gold deposition at the potential -1350 mV the charge transferred to the electrode amounts to $q = 2.9 \text{ mC cm}^{-2}$. This value corresponds approximatly to the charge which is required for the deposition of more then ten compact monolayers (~ 204 μ C cm⁻² per monolayer [Li96]); it means that the gold deposition process

starts before t_{min} is reached. In Fig. 7.21 the approximation of the initial falling part of the current-time transient recorded at the potential -1250 mV with the Eq. 7.8 is presented. The parameters obtained from the fit are $k_{ads}=0.54 \text{ s}^{-1}$ and $q_{ads}=1.34 \text{ mC cm}^{-2}$; their magnitudes are in a good agreement with experimentally calculated values for charge transferred during the adsorption process.

7.6.2 Charge-transfer

Coming to the analysis of the rising parts of the current transients it should be mentioned that the nucleation and crystal growth can be controlled by direct charge transfer reactions and/or by diffusion. In a simple case of charge transfer control under potentiostatic condition instantaneous nucleation and two-dimensional (2-D) cylindrical growth density is described by [Li96]:

$$j_{ch} = \frac{2zF\pi h M N_0 k_{2D}^{\prime 2} t}{\rho} exp\left(-\frac{\pi M^2 N_0 k_{2D}^{\prime 2} t^2}{\rho^2}\right)$$
(7.9)

and for 2D progressive nucleation

$$j_{ch} = \frac{2zF\pi hMJ_{2D}k_{2D}^{\prime 2}t^2}{\rho}exp\left(-\frac{\pi M^2J_{2D}k_{2D}^{\prime 2}t^3}{3\rho^2}\right)$$
(7.10)

where k'_{2D} is the lateral growth rate constant (mol cm⁻² s⁻¹), h is the layer height (cm), N_0 the total number of active centres (cm⁻²), J_{2D} the nucleation rate (nuclei cm⁻² s⁻¹), M the atomic weight (g mol⁻¹) and ρ the density (g cm⁻³) of the deposit. The fits of the experimental current transients recorded at -1390 mV vs. SCE with the Eq. 7.9 are shown in Fig. 7.22 and with Eq.7.10 in Fig. 7.23. It can be seen that theoretical equations do not describe the data adequately: for these mechanisms (Eq. 7.9 - 7.10) the observed current initially increases and then decreases to zero when the surface is completely covered by the two-dimensional crystals. For three-dimensional instantaneous nucleation and growth of right-circular cones, current is given by Eq. 3.31 and for 3-D progressive by Eq. 3.32 (see Chapter 3) [Arm65],



Figure 7.22: Fit of the experimental current transient recorded at -1390 mV vs. SCE with Eq. 7.9; empty circles represent the experimental data, solid lines represent the theoretical fits.



Figure 7.23: Fit of the experimental current transient recorded at -1390 mV vs. SCE with Eq. 7.10; the black line represents the experimental data, solid line represents the theoretical fit.

[Aby80]. In Fig. 7.24 the current time transients calculated for the nucleation of gold due to the charge-transfer-controlled reactions according to Eq. 3.31 and Eq. 3.32 are presented. Solid lines correspond to the case of instantaneous nucleation with the following parameters: a) $k'^2N_0 = 0.0001 \text{ mol}^2 \text{ cm}^{-4} \text{ s}^{-2}$, $k'' = 1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; b) $k'^2N_0 = 0.00015 \text{ mol}^2 \text{ cm}^{-4} \text{ s}^{-2}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; b) $k'^2N_0 = 0.00015 \text{ mol}^2 \text{ cm}^{-4} \text{ s}^{-2}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; b) $k'^2J = 0.0001 \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}$, $k'' = 1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; d) $k'^2J = 0.00015 \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; d)

In Fig. 7.25 the fits of the experimental current transients recorded at -1390 mV (left) and



Figure 7.24: Calculated current time transients for the nucleation of gold due to the three dimension charge transfer controlled reactions (Eq. 3.31 and Eq. 3.32). Solid lines correspond to the case of instantaneous nucleation with the following parameters: a) $k'^2 N_0 = 0.0001 \text{ mol}^2 \text{ cm}^{-4} \text{ s}^{-2}$, $k'' = 1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; b) $k'^2 N_0 = 0.00015 \text{ mol}^2 \text{ cm}^{-4} \text{ s}^{-2}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. Dotted lines describe progressive nucleation of gold with the following parameters: c) $k'^2 J_{ch} = 0.0001 \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}$, $k'' = 1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; d) $k'^2 J_{ch} = 0.00015 \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; d) $k'^2 J_{ch} = 0.00015 \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$; d) $k'^2 J_{ch} = 0.00015 \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}$, $k'' = 1.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$.



Figure 7.25: Fits of the experimental current transient recorded at -1390 mV (left) and -1230 mV (right) vs. SCE with the Eq. 3.31 due to 3-D instantaneous nucleation and growth of right circular cones; empty circles represent the experimental data, solid lines describe the theoretical fits.

-1230 mV (right) vs. SCE with the Eq. 3.31 due to 3-D progressive nucleation and growth of right circular cones are presented; empty circles represent the experimental data, solid lines - theoretical fit. The fit to the transient recorded at -1390 mV shows lack of conformability with the experimental data. Nevertheless, it can be seen that the theoretical fit describes experimental data recorded at -1230 mV vs. SCE relatively well in the rising part of the current transient but underestimates the data in the part of the current maximum. The kinetic parameters obtained from the fit to the data recorded at -1230 mV vs. SCE have the following values $k'' = 1 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$, $k'^2 N_0 = 2.46 \times 10^{-7} mol^2 \text{ cm}^{-4} \text{ s}^{-2}$. In Fig. 7.26 the experimental current transients recorded at -1390 mV (left) and -1230 mV (right) vs. SCE fitted with the Eq. 3.32 due to 3-D progressive nucleation and the growth of right circular cones are shown. Empty circles represent the experimental data, solid lines - theoretical fits. It can be seen that the rising part of the transients can be described by both threedimensional models depending on the potential of the deposition. At more positive potentials the transients can be described by instantaneous nucleation and three-dimensional growth and at more negative potentials the nucleation seems to have progressive behaviour. Nevertheless, the kinetic parameters obtained from the fits are the following: $k^{2}J_{ch} = 1.9 \times 10^{-6} \text{ mol}^2 \text{ cm}^{-6}$ s^{-3} , $k'' = 2.48 \times 10^{-13}$ mol cm⁻² s⁻¹ for the transient recorded at the potential -1390 mV; $k'^2 J_{ch} = 2.7 \times 10^{-7} \text{ mol}^2 \text{ cm}^{-6} \text{ s}^{-3}, \ k'' = 1.1 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$ for the experimental data recorded at -1230 mVvs. SCE.

It was reported by [Cre92] and [Li96] that two dimensional phase formation can be followed by three dimensional crystal growth. To check this assumption the experimental current transient recorded at -1390 mV vs. SCE was fitted with theoretical equation describing two dimensional progressive growth of cylinders and three dimensional progressive growth of right circular cones:

$$j = \frac{2zF\pi hMJ_{2D}k_{2D}^{\prime 2}t^2}{\rho}exp\left(-\frac{\pi M^2J_{2D}k_{2D}^{\prime 2}t^3}{3\rho^2}\right) + zFk_{3D}^{\prime\prime}\left[1 - exp\left(-\frac{\pi M^2k_{3D}^{\prime 2}J_{3D}t^3}{3\rho^2}\right)\right]$$
(7.11)

Nevertheless, the theoretical fit according to the combination of Eq. 7.10 and Eq. 3.32 does



Figure 7.26: Fits of the experimental current transients recorded at -1390 mV (on the left) and -1230 mV (on the right) vs. SCE with the Eq. 3.32 due to 3-D progressive nucleation and growth of right circular cones; empty circles- experimental data, solid lines - theoretical fits.

not present suitable results and desirable coincidence, as followed from Fig. 7.27. The rising part of the current transient is really well described, in the region of current maximum experimental and theoretical data coincide, but after the current maximum region theoretical and experimental curves disperse.

As was mentioned above the side reaction such as hydrogen evolution can modify the shape



Figure 7.27: Fit of experimental current transient recorded at -1350 mV vs SCE with Eq. 7.11; empty circles describe the experimental data, solid line corresponds to the theoretical fit.

of transient, furthermore, very likely diffusion controlled processes influence the transients, therefore it is difficult to evaluate truthful kinetic parameters.

In Fig. 7.13 a set of experimentally recorded current transients using RDE is shown. It was also predicted in Section 7.5 that at 2000 rpm diffusion does not influent sufficiently the gold deposition process. The analysis of the kinetics of gold electrodeposition is possible due to the analysis of current transients recorded at RDE at 2000 rpm. In Fig. 7.28 the approximations



Figure 7.28: Fits of experimental current transients recorded at -1700 mV and at -1800 mV vs. SCE with Eq. 3.31 (due to three dimensional instantaneous) and Eq. 3.32 (due to three dimensional progressive) nucleation and growth of right circular cones; empty circles- experimental data, black lines - theoretical fits with Eq.3.31, red lines represent theoretical fits according to Eq.3.32 .

of experimental current transients recorded at the potentials -1700 mV and at -1800 mV vs. SCE at rotating disc electrode are shown. The fits to the experimental data with theoretical equations for three dimensional instantaneous (Eq. 3.31) and three dimensional progressive (Eq. 3.32) nucleation and growth of right circular cones are performed. In Fig. 7.28 empty circles describe experimental data, black solid lines - theoretical fits due to Eq.3.31, red solid lines represent theoretical fits according to Eq.3.32 . Kinetic parameters obtained from the fits for the data recorded at -1700 mV and -1800 mV vs. SCE are presented in Table 7.2. It should be mentioned that only charge transfer processes occur in the electrolyte during the experiments with rotating disc electrode at 2000 rpm, and, therefore, only charge transfer theoretical models for nucleation and growth can be applied to fit the corresponding data.

nucleation type	$-1700~\mathrm{mV}$ vs. SCE	$-1800~\mathrm{mV}$ vs. SCE
instantaneous	$k'' = 5 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$	$k'' = 5.16 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$
	$k'^2 N_0 = 6.1 \times 10^{-8} \text{ mol}^2 \text{ cm}^{-4} \text{s}^{-2}$	$k'^2 N_0 = 6.1 \times 10^{-8} \text{ mol}^2 \text{ cm}^{-4} \text{s}^{-2}$
	$k'' = 5.07 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$	$k'' = 5.15 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$
progressive	$k'^2 J = 4.5 \times 10^{-8} \text{ mol}^2 \text{ cm}^{-6} \text{s}^{-3}$	$k'^2 J = 4.5 \times 10^{-8} \text{ mol}^2 \text{ cm}^{-6} \text{s}^{-3}$

Table 7.2: Kinetic parameters obtained from the fits (Fig.7.28).

Therefore, the disagreement between experimental data and theoretically calculated curves can be explained by side reactions which take place parallel to the gold deposition process. Namely, gold nuclei grow slowly in comparison with theoretical predictions that confirms assumption about the side reaction - hydrogen evolution.

7.6.3 Diffusion



Figure 7.29: Calculated current-time transients for the nucleation of gold due to the nucleation and diffusion controlled growth (Eq. 3.19, 3.20), $D = 14 \times 10^{-6}$ cm² s⁻¹, $c = 14.7 \times 10^{-6}$ mol cm⁻³, k = 0.06. Solid lines correspond to the case of instantaneous nucleation with the following parameters: a) $N_0 = 1 \times 10^4$, b) $N_0 = 2 \times 10^4$. Dotted lines describe progressive nucleation of gold with the following parameters: c) $J = 1 \times 10^4$ cm⁻² s⁻¹, d) $J = 2 \times 10^4$ cm⁻² s⁻¹.

The theoretical prediction for the current density of progressive nucleation in the case of overlap of nucleation exclusion zones is derived by [Sch99] and is described by Eq. 3.20. In Fig. 7.29 the calculated current-time transients for the nucleation and growth of gold due to the diffusion controlled processes are shown. The simulations are made due to Eq. 3.19 (instantaneous



Figure 7.30: Fits to the data recorded at -1390 mV vs. SCE. Empty circles represent experimental data, solid line - theoretical fit of the experimental data with Eq. 3.20.

nucleation and diffusion controlled growth) and Eq. 3.20 (progressive nucleation and diffusion controlled growth) with the following parameters: $D = 14 \times 10^{-6}$ cm² s⁻¹, $c = 14.7 \times 10^{-6}$ mol cm⁻³, k = 0.06. Solid lines correspond to the case of instantaneous nucleation with the following parameters: a) $N_0 = 1 \times 10^4$, b) $N_0 = 2 \times 10^4$. Dotted lines describe progressive nucleation of gold with the parameters: c) $J = 1 \times 10^4$ cm⁻² s⁻¹, d) $J = 2 \times 10^4$ cm⁻² s⁻¹. In Fig. 7.30 the theoretical fits to the data recorded at -1390 mV vs. SCE with Eq. 3.20 are shown. Empty circles represent the experimental data, solid lines - the theoretical approximations. After a few seconds (depending on the potential) progressive nucleation and three-dimensional growth of diffusion zones probably takes place and the red line (Fig. 7.30) represents the fit of the experimental data with Eq. 3.20. The kinetic parameters obtained from the fits are: $D = 13.9 \times 10^{-6}$ cm² s⁻¹, $J = 2.8 \times 10^4$ cm⁻² s⁻¹. It can be concluded that after the current maximum is reached the theoretical fit underestimates the experimental data what can be the consequence of some parallel processes which take place during gold deposition.



7.6.4 Determination of the diffusion coefficient

Figure 7.31: Cottrell plot of the current-time transients of gold on glassy carbon recorded at different deposition potentials.

The chronoamperometrical results from the steady-state region of j vs. t can be used to calculate the diffusion coefficients at various overpotentials using the Cottrell equation (Eq. 5.7). As shown in Fig. 7.31 the current is indeed found to be linear with respect to $t^{-1/2}$ for glassy- carbon, as predicted by Cottrell equation. In Tables 7.3, 7.4 the diffusion coefficients calculated from the slope of linear fits to the experimental data recorded at different depositions potentials are presented.

E, mV vs. SCE	-1400	-1390	-1380	-1370	-1360
$D \times 10^{-6}, cm^2 s^{-1}$	$16{\pm}0.1$	$16.1 {\pm} 0.1$	$14.4{\pm}0.5$	$15.1 {\pm} 0.5$	14.9 ± 0.5

Table 7.3: Diffusion coefficients obtained from the linear fits (Fig.7.31).

E, mV vs. SCE	-1330	-1310	-1300	-1290	-1280	-1270
$D \times 10^{-6}, cm^2 s^{-1}$	$6.12{\pm}0.1$	$6.72{\pm}0.1$	$7.18 {\pm} 0.1$	$6.34{\pm}0.1$	$3.30{\pm}0.6$	$3.42{\pm}0.6$

Table 7.4: Diffusion coefficients obtained from the linear fits (Fig.7.31).

For deposition potential range from -1270 to -1330 mV vs. SCE the average diffusion coefficient
was calculated to be $D = 5.51 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and for the potential range from -1350 mV to -1400 mV the average value of diffusion coefficient was estimated to be $D = 15.4 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$. The difference between the diffusivity at low and high overpotentials is not sufficient. The same order of diffusion coefficient was reported by [Sob05] during gold electrocrystallization from thiosulfate-sulfite electrolyte.

7.6.5 Mixed nucleation and growth process

The process of nucleation and growth at the limiting conditions can be controlled by charge transfer at short times or by diffusion at longer times, when the concentration of active species decreases. Probably, if the initial concentration of active species in the electrolyte is very low, the process of new phase formation can be simultaneously controlled by both charge transfer and diffusion processes [Gom04]. Such mixed "charge transfer + diffusion" controlled growth was observed by [Dan02], [Rud06] during the electrodeposition of copper on glassy carbon electrode and by [Gom04] during the electrodeposition of cobalt-molybdenum on vitreous carbon electrode. [Guo06] has shown that during copper electrocrystallization on oxidized ruthenium at long times of chronoamperometric experiments the current decays to a potentialdependent steady-state current that is consistent with mixed "diffusion + charge transfer" control. Moreover, the deviation of crystallites shapes from hemispherical ones can also be the evidence of mixed controlled crystal growth [Guo06]. In Fig. 7.3 and 7.4 the potential dependent steady current can be observed at times longer than 15 s during gold deposition on glassy carbon electrode surface. It is evident from Fig. 7.7 - d) that gold crystallites have different shapes at the same deposition potential. Furthermore, the concentration of gold in the electrolyte is 14.7×10^{-6} mol cm⁻³, what is really a small quantity. Analyzing all above described results and comparing them with the literature it is possible to suppose that gold electrodeposition on a glassy carbon electrode, probably, occurs by mixed "charge transfer + diffusion" controlled nucleation and growth. It was shown in previous sections that none of simple nucleation and growth models can describe experimental results pretty well. The assumption about the side hydrogen evolution reaction was made, but in reality, side reaction should only slightly shift the shape of the current time transients from the



Figure 7.32: Current-time transients recorded at the potentials from -1350 mV to -1400 mV vs. SCE. Symbols represent the experimental data; solid lines - theoretical fits by using of Eq. 7.12.

theoretically calculated ones. In Fig. 7.30 one can clearly observe that in the region after the current maximum the nucleation and growth behaviour can hardly be described by simple model. It was assumed that the electrocrystallization of gold on a glassy carbon electrode occurs by the direct incorporation of the gold ions into the defects of glassy carbon surface followed by 3 dimensional mixed charge transfer + diffusion controlled nucleation and growth. By the combination of equations 7.8, 3.32 and 3.20 one can obtain :

$$j(t) = j_{ads}(t_0) + j_{ch(progr)}(t - t_0) + j_{D(progr)}(t - t_0)$$
(7.12)

In Fig. 7.32 the fits to the experimental data with Eq.7.12 are presented. It can be seen that the theoretical fits describe the experimental data pretty well . In Table 7.5 kinetic parameters obtained from the theoretical fits with Eq.7.12 of the experimental data (Fig.7.32) are presented. Coming to the analysis of the kinetic parameters obtained from the fits it should be admitted that the parameters presented in Table 7.5 seem to have physically realistic magnitudes. However, the charge transfer due to the adsorption process seems to have an overestimated magnitude. The average value of the charge $q_{ads} = 2.55$ mC cm⁻² corresponds

E/mV	k_{ads}/s^{-1}	$q_{ads}/rac{mC}{cm^2}$	$k'' \times 10^{-8} / \frac{mol}{cm^2 s}$	$k^{\prime 2}J_{ch}/rac{mol^2}{cm^6s^3}$	$J_{diff} \times 10^4 / \frac{1}{cm^2 s}$	$D \times 10^{-6} / \frac{cm^2}{s}$
-1350	$0.65{\pm}0.02$	$2.01{\pm}0.01$	$1.39{\pm}0.05$	$1.10{\pm}0.05$	$1.45 {\pm} 0.1$	$13.5 {\pm} 0.3$
-1360	$0.4{\pm}0.02$	$2.53{\pm}0.02$	$1.39{\pm}0.05$	$1.00{\pm}0.05$	$1.80{\pm}0.1$	13.2 ± 0.2
-1370	$0.64{\pm}0.02$	$2.46{\pm}0.02$	$1.42{\pm}0.05$	$1.39{\pm}0.03$	$2.43{\pm}0.1$	$13.8 {\pm} 0.4$
-1380	$0.7{\pm}0.03$	$2.58{\pm}0.02$	$1.40{\pm}0.05$	$1.20{\pm}0.07$	$3.14{\pm}0.1$	14.1±0.1
-1390	$0.2{\pm}0.02$	$2.8{\pm}0.02$	$1.35 {\pm} 0.05$	$1.33 {\pm} 0.05$	$3.45{\pm}0.1$	$12.9{\pm}0.4$
-1400	$0.2{\pm}0.02$	$2.9{\pm}0.02$	$1.40{\pm}0.05$	$1.40{\pm}0.03$	$3.50{\pm}0.1$	$14.2{\pm}0.1$

Table 7.5: Kinetic parameters obtained from the theoretical fit with Eq. 7.12 of the experimentaldata from Fig. 7.32.

to the charge which is required for the deposition of more than ten compact gold monolayers [Li96]. It was experimentally calculated how many mol of gold were deposited on glassy carbon electrode during 32 s of chronoamperometric experiment at -1350 mV vs SCE. The cathode was weighted before and after the deposition and the quantity of gold in the deposit was calculated from the difference. The sum of the growth rate constants in different directions $(k'+k'')=2\times10^{-6}$ mol cm⁻² s⁻¹ was obtained. Unfortunately it is not experimentally possible to separate the growth rate constants in lateral and vertical directions. Otherwise, if we assume that $k' \sim 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ then the nuclei will grow faster in the lateral direction and the cones' planes will have larger areas. In Fig. 7.7 - d) the differences in the crystal shapes can be observed what can be the result of mixed nucleation and growth processes. Experimentally, cones with large plane areas are observed that is in agreement with the above made assumption. The diffusion coefficients obtained from the fit have the same order of magnitude as those calculated by means of Cottrell equation (see Tables 7.3 - 7.4) and are in a good agreement with data reported in the literature [Sob05]. It can be seen that the nucleation rate increases when the applied potential increases. Larger overpotential causes faster movement of gold ions and, therefore, faster formation of adatoms and nuclei. Such a behaviour was also reported by [Mil03] during the electrocrystallization of silver on a glassy carbon electrode. Although the experimental data are well described by the Equation 7.12, it is not clear how to take onto account the overlapping of diffusion zones, growing nuclei and probable side processes. Therefore, further investigations in this field are welcomed.

Chapter 8

Characterization and properties of nanostructured metals

The thermal stability of nanocrystalline materials is important from both fundamental and practical viewpoints. It is known that for nanocrystalline pure materials the thermal stability is rather low[Gle89]. For nanocrystalline Cu, Pd, Ni and Ag, abnormal grain growth was reported to occur even at room temperature or at a slightly higher temperatures [Gun92], [Nat97]. While the grain growth was always very inhomogeneous, results of X-ray line width measurements on nanocrystalline Cu also indicated grain growth after prolonged storage at room temperature [Ger94]. Nanocrystalline materials show thermodynamical instability because of the grain boundaries phenomena. Gold and gold alloys are of wide use in dental industry for the production of crowns of teeth and in electronic industry for use in connectors. To improve the mechanical properties (hardness etc.) of coatings and bulk materials nanoscaling in crystallite size should be achieved. But the problem of hardness decrease during the production/utilization process at elevated temperatures causes a decrease of the life time of the material. For this reason the investigations of the temperature stability of gold and gold alloys are very important. In the design of micro/nanodevices, mechanical properties are essential since most of them are known to exhibit a dependence on specimen size [Li03]. Recent developments in science and engineering have advanced the capability to fabricate and control structures on the scale of micro/nanometers. This presents a whole new spectrum of opportunities to build micro/nanoscale structures and devices, and brings problems of material behavior on the micro/nanometer scales into the domain of engineering. A precise characterization of the mechanical properties of these micro/nanostructures is required to use them as structural/functional elements in the micro/nanodevices. The extremely small dimensions of micro/nanostructures impose a tremendous challenge for experimental study of their mechanical properties and reliability. A promising approach for measuring the mechanical properties of nanostructures is direct micro-mechanical indentation and nanoindentation. Nanoindenter/atomic force microscope (AFM) combination provides the eyes, hands and tools for imaging, characterizing, manipulating and machining the nanoscale structures, fulfilling the dream of manufacturing at the nanoscale.

8.1 Thermal stability of nanostructured gold

The stability of the electrodeposited gold nanocrystallites at high temperature conditions is investigated with X-ray diffraction using a position sensitive detector (Braun Inc., Germany). In the angular range covered by the detector we observe the gold (111) and (200) Bragg reflections. The samples deposited from the additive-free MPS bath (sample 1) and from the bath containing NaAsO₂ (sample 2) are heated in air from 298K to 1073 K with a rate of 2 K min⁻¹ (scan duration: 5 min.) In Fig.8.1 the TEM picture of sample 2 is shown.

Every 5 minutes a new diffractogram is recorded during the temperature ramp. In Fig. 8.2 X-ray patterns of gold (111) and (200) Bragg reflections are presented. The width of gold patterns decreases with the temperature increase. The crystallite sizes resulting from the widths are shown in Fig. 8.3. It is evident that sample 1 and sample 2 do not exhibit any grain growth up to 623 K. This indicates a higher thermal stability than samples deposited from a sulphite bath: Cojocaru et al. [Coj] have observed a thermal stability only up to 323 K, whereas Natter at all. previously have observed a thermal stability of gold samples deposited from sulphite bathes up to 423 K [Nat03]. Obviously presented gold samples have such a high thermal stability because of the presence of sulfur or arsenic atoms in the grain boundaries. Very likely the first plateau (see Fig.8.3) is caused by these impurities segregated

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Figure 8.1: TEM picture of a gold sample deposited from the bath with NaAsO₂ (c=0.25 g L^{-1}) as additive before heating.



Figure 8.2: X-ray diffractogramms of gold (111) and (200) Bragg reflections due to the different temperature of sample and different time of observation



Figure 8.3: Measurement of the thermal stability of nanostructured gold. Filled circles, filled stars, and filled triangles represent the heating results for samples deposited from the additive-free MPS electrolyte, a bath with NaAsO₂ (c=0.5 g L⁻¹) and a bath with additional MPS as additive (c=10 g L⁻¹), respectively. The experimental uncertainties in the sizes did not exceed 5 nm.

in the grain boundaries. In Chapter 6 in Fig. 6.5 the energy dispersive X-ray spectrum of sample 1 is shown. It is possible to observe the presence of sulfur in the deposit, however, the quantitative analysis unfortunately is not possible with this technique. These results are in a good accordance with Carotenuto et al. [Caro03]: they concluded that the thermal stability (up to ca. 573 K) of thiol-derivatized gold clusters results from strong bonds of the thiol group with the metal surface. To prove the assumption of the influence of sulfur compounds on the thermal stability of gold nanocrystals the concentration of MPS was doubled (sample 3). The sample was deposited under the same conditions. As expected sample 3 shows a better thermal stability (up to 673 K) than the samples 1 and 2 (see Fig. 8.3). Above 673 K a fast crystallites growth up to 32 nm (sample 1), up to 25 nm (sample 2) and up to 27 nm (sample 3) is observed. Apparently the fast growth is caused by the decomposition of the -SH bonds, which takes place at this temperature. As expected, the different content of sulfur or arsenic in the deposit leads to different crystallite sizes. From the high temperature experiments we conclude that sulfur or arsenic containing additives decrease the gold crystallite size during

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the electroplating process by segregating in the grain boundaries and therefore increase the thermal stability of deposited gold.

8.2 Thermal stability of nanostructured gold alloys



Figure 8.4: TEM measurements of nanostructured gold-silver alloy.

Gold-silver (60:40) and gold-palladium (70:30) alloys are electrodeposited by pulse technique $(t_{on} = 1 \ ms, t_{off} = 20 \ ms, j_p = 50 \ mA \ cm^{-2})$ at room temperature. On Fig. 8.4 and Fig. 8.5 one can observe transmission electron micrographs of alloys before the heating. Both pictures show that the crystallite size of gold-silver and gold-palladium alloys does not exceed 20 - 25 nm. EDX analysis shows the presence of sulfur in both samples (Fig. 8.6 and Fig. 8.7). These observations allow to connect the small crystallite size of gold-silver and gold-palladium alloys with the presence of sulfur in the deposit and to conclude that sulfur components act as grain refiners during the electrodeposition of gold alloys from mercapto- containing electrolyte. To determinate the thermal stability of gold alloys the samples were heated from room temperature up to 873 K with a rate of 2 K min⁻¹ using a high temperature X-ray



Figure 8.5: TEM measurements of nanostructured gold-palladium alloy.



Figure 8.6: EDX measurements of nanostructured gold-silver alloy.

diffractometer.

No change in the shape of diffraction patterns of gold-silver alloy is observed up to the temperature of 600 K. Gold-palladium alloy has thermal stability up to 700 K. After the above mentioned temperatures a rapid crystallite growth up to 50 nm is observed. Gold-palladium alloy represent the highest thermal stability, probably, because of the smallest radius of Pd atoms (0.137 nm) in comparison with Au (r = 0.146 nm) and Ag (r = 0.144 nm). Detailed



Figure 8.7: EDX measurements of nanostructured gold-palladium alloy.

analysis of this prediction will be presented in the next section.

8.3 Kinetics models of grain growth

At high temperatures the crystallites grow during a relatively short period of time and then the crystallite size does not change essentially any more with time. The theoretical basis for understanding of isothermal grain growth was proposed by Burke and Turnbull [Bur52]. They deduced the grain growth from the movement of grain boundaries and assumed atom transport across the boundaries under a pressure due to surface curvature. A brief discussion of the models can be found in [Nat00]. The comparison between three theoretical models of grain growth kinetics is given below.

1. The generalized parabolic grain-growth model proposed by Burke and Turnbull [Bur52]. They assumed that in an ideal system after an annealing time t crystallite size increases with a temperature dependent constant $g_1 = n * a_1$ and a crystallite growth can be described by the differential equation:

$$\frac{dD(t)}{dt} = \frac{a_1}{D(t)} \tag{8.1}$$

Where D is the average grain diameter, for $D(t) = D_0$ for t = 0, the solution of the differential

equation is

$$D(t)^n - D_0^n = g_1 t (8.2)$$

The empirical grain-growth exponent, n, varies between values of 2 and 4.

2. The grain-growth model with impediment. Grey and Higgins [Gre73] took into account the experimental observation of a limiting grain size. In this model, as a result of crystallite growth, the driving pressure vanishes at a certain stage and Eq. 8.1 should be supplemented by a growth-retarding term b_2 :

$$\frac{dD(t)}{dt} = \frac{a_2}{D(t)} - b_2 \tag{8.3}$$

With the initial grain size D_0 , the solution of Eq. 8.3 is

$$\frac{D_0 - D(t)}{b_2} + \frac{a_2}{b_2^2} ln\left(\frac{a_2 - b_2 D_0}{a_2 - b_2 D(t)}\right) = t$$
(8.4)

At $t \to \infty$ the grains do not grow anymore, i.e.

$$\frac{dD(t)}{dt} = 0$$

hence

$$D_{\infty} = \frac{a_2}{b_2}$$

and Eq. 8.4 can be expressed as

$$g_2 t = \frac{D_0 - D(t)}{D\infty} + \ln\left(\frac{D_\infty - D_0}{D_\infty - D(t)}\right)$$
(8.5)

With

$$g_2 = \frac{b_2^2}{a_2} = \frac{a_2}{D_{\infty}^2}$$

3. Grain-growth model with size-dependent impediment. Michels at al. [Mich99] suggested that the retarding constant should be a function of the grain size in grain-growth processes of nanocrystalline metals. They assumed that in the process of grain growth when the grain-boundary volume fraction decreases the impurities in the grain boundaries are more enriched:

$$\frac{dD(t)}{dt} = \frac{a_3}{D(t)} - b_3 D(t)$$
(8.6)

With the same initial conditions as above, the solution of this differential equation is

$$D(t) = \sqrt{\frac{a_3}{b_3} + (D_0^2 - \frac{a_3}{b_3})exp(-2b_3t)}$$
(8.7)

Using

$$D_{\infty} = \sqrt{\frac{a_3}{b_3}}$$

this can be expressed as

$$D(t) = \sqrt{D_{\infty}^2 - (D_{\infty}^2 - D_0^2)exp(-g_3 t)}$$
(8.8)

With the rate constant

$$g_3 = 2b_3 = \frac{2a_3}{D_{\infty}^2}$$

This equation is the grain-growth model with size-dependent impediment. The time depending constant g_3 contains the information about the retarding constant. The temperature dependent rate constants g_1, g_2, g_3 contain the information about the grain boundary mobility $M_{boundary}$, which is described through the self-diffusion coefficient D_s

$$M_{boundary} = \frac{D_s}{k_B T} \tag{8.9}$$

The diffusivity follows the Arrhenius law with the activation energy Q, but according to Eq. 8.9 the mobility and kinetic rate constants g_1, g_2, g_3 exhibit an additional T^{-1} dependence such as:

$$TgD_{\infty}^2 \propto exp\left(\frac{-Q}{RT}\right)$$
 (8.10)

Hence, the activation energies of the grain boundary self-diffusion processes can be obtained from the slope of a plot $ln(TgD_{\infty}^2)$ versus T^{-1} [Nat00].

8.3.1 Growth kinetics of nanostructured gold

The growth kinetics of nanostructure gold is investigated using high-temperature X-ray diffraction [Yev06]. Gold sample with initial size of 16 nm deposited from the bath with NaAsO₂ $(c = 0.25 \ gL^{-1})$ as additive was heated from room temperature up to 873 K with a rate of



Figure 8.8: Measurement of the thermal stability and microstrain of nanostructured gold. The experimental uncertainties in the sizes does not exceed 5 nm.



Figure 8.9: Temperature and time evolution of the volume-weighted average crystallite diameters of gold. The lines represent fits with different kinetic grain-growth models; the dashed lines represent fits with the generalized parabolic grain-growth model, the dotted lines are the results of fits with the growth model with impediment and the solid lines show the fit results using the grain growth model with size-dependent impediment.

 2 K min^{-1} . Initially gold has a microstrain 0.35% (Fig. 8.8). After heating nano-gold up to 873K this parameter decreases to 0.01%. To observe the growth kinetics of gold nanocrystallites, fits to the experimental data are performed. Fig. 8.9 shows the comparison between measured data and the theoretically calculated ones based on the kinetic models offered by Burke [Bur52], Gray and Higgins [Gre73] and Michels [Mich99]. The dashed lines represent the fits with the generalized parabolic grain-growth model (Eq. 8.2), the dotted lines are the results of the fits with the growth model with impediment (Eq. 8.5) and the solid lines shows the fit results using the grain growth model with size-dependent impediment (Eq. 8.8). As follows from the Fig. 8.9 not all applied models achieve a good agreement with the experimental data. Especially the generalized parabolic growth model and the growth model with impediment cannot be brought into agreement with the experimental data and yield unrealistic and unphysical parameters. In contrast to nanocrystalline iron which had been prepared without any grain refiners [Nat00] the gold samples have impurities such as sulfur and arsenic and therefore only the model which takes into account the impurities in the grain boundaries can describe the experimental data. However, the growth model with size dependent impediment describes the experimental data very well. From the evaluation of the temperature dependence of the rate constants obtained for the last mentioned theoretical model it is possible to determine the activation energy of the grain growth of nano-gold. We have made extended Arrhenius evaluations using the model with the retarding term proportional to the size. According to the equation 8.10 the experimental value of activation energy of 29.5 kJ mol^{-1} for nano-gold crystallite growth can be calculated from the Arrhenius plot (Fig. 8.10). The linear correlation coefficient of the experimental data is -0.991. The grain boundary selfdiffusion coefficient of poly-crystalline gold in the temperature range of 640K - 717K obeys the Arrhenius law with an activation energy of 84.9 kJ mol⁻¹ [Land90], that is more than two times higher than the experimentally received value of activation energy of nano-gold grain growth. The disagreement between the experimental results and the literature ones can be related to the difference in the grain boundary structure between nanostructured and coarse grained materials and therefore to the difference in the grain boundary self-diffusion.



Figure 8.10: Temperature dependence of the temperature dependent rate constants in extended Arrhenius representations for nano-gold sample.

8.3.2 Growth kinetics of nanostructured gold alloys



Figure 8.11: Dependence of the AuAg alloy and Au crystallite size and microstrain on the annealing temperature.

The gold-silver alloy (60:40) and the gold-palladium (70:30) alloy are galvanostatically electrodeposited by pulse technique ($t_{on} = 1 \ ms, t_{off} = 20 \ ms, j_p = 50 \ mA \ cm^{-2}$) at room temperature and were heated from room temperature up to 873 K with a rate of 2 K min⁻¹



Figure 8.12: Dependence of the AuPd alloy and Au crystallite size and microstrain on the annealing temperature.

using high temperature X-ray diffraction. The gold-silver sample showed thermal stability up to approximately 600 K (Fig. 8.11). The microstrain decreases during the heating from the value of 0.45%, corresponding to the sample measured at room temperature, down to 0.001%and after that the crystallite growth sets in. The gold-palladium alloy shows higher thermal stability than the pure gold and the gold-silver alloy. In Fig. 8.12 it is shown that the goldpalladium crystallites as well as the gold sample and the gold-silver alloy start to grow after the the microstrain has decreased from 0.65 % down to 0.001%. The decrease in the microstrain during the annealing at high temperatures can be explained. Upon subsequent annealing, the defects appearing during the electrodeposition will be annihilated at various sinks such as dislocations, jogs, and grain boundaries. As was mentioned in the previous sections Pd atoms have the smallest radius (in comparison with Au and Ag). Therefore, the AuPd alloy should have the highest value of strain compared with the nanocrystalline pure gold sample and the AuAg alloy. After annealing the samples the crystallite growth starts after the microstrain decreases, therefore, the AuPd alloy represents the highest thermal stability. To investigate the growth mechanism we measure a series of isotherms at temperatures where a rapid crystallite growth is observed.

The X-ray patterns were recorded in reflection $(\theta - 2\theta)$ mode, at the following temperatures:



Figure 8.13: Dependance of the AuAg alloy crystallite size and microstrain on the annealing temperature.



Figure 8.14: Dependance of the AuPd alloy crystallite size and microstrain on the annealing temperature.



Figure 8.15: Temperature dependence of the temperature dependent rate constants in extended Arrhenius representations for the nanostructured gold, the gold-silver and the gold-palladium samples.

573, 623, 673, 723 and 743 K in the case of the gold-silver alloy and at 573, 623, 673, 723 and 773 K in the case of the gold-palladium alloy. The resulting volume-weighted average diameters of the gold-silver alloy are displayed in Figure 8.13 and of the gold-palladium alloy in Figure 8.14; at high temperatures they show a fast increase in the grain size value at long times, which exhibits a pronounced temperature dependence. At lower temperatures, only a moderate and comparatively smooth grain growth can be observed, which stops after a short period of time. The isothermal measurements were recorded every 60 sec. The annealing time during heating the sample to the fixed temperature is calculated to be 21 sec. This is a very short time in comparison with the time of the whole measurement and therefore no corrections to the time of isotherms data are applied. As the fits with the generalized parabolic graingrowth model and the growth model with impediment do not yield acceptable results we have made extended Arrhenius evaluations using the model with the retarding term proportional to the size. The activation energies for the gold-silver alloy and the gold-palladium alloy samples are determined from the Arrhenius plot. The quantitative data for thr gold-silver alloy and for the gold-palladium alloy are Ea= $28.7 \text{ kJ}^*\text{mol}^{-1}$ and Ea= $71.5 \text{ kJ}^*\text{mol}^{-1}$, respectively. Kim

and Flanagan [Kim67] observed the value of 202.6 kJ*mol⁻¹ for the self-diffusion activation energy of Au-30%Pd alloy after the annealing for two hours at the temperatures above 573 K. Since they observed some impurities in the alloys the formation of an immobile vacancyimpurity complex is suggested. Therefore the self-diffusion activation energy is the sum of the vacancy migration energy and its binding energy to the impurity. If Pd is added to Au the probability of finding vacancies next to Pd atoms may be very much reduced, and this would result in an increase in the activation energy of self-diffusion on alloying with Pd. Van Liempt [Lie32] also predicted an increase in activation energies for self-diffusion as Pd concentration increases alloying with Au. The literature predicts also higher value of self-diffusion activation energy for Au-40%Ag. Radelaar [Rad68] calculated the activation energy of gold-silver alloy to be 166.9 kJ*mol⁻¹ at the temperatures higher than 573 K. The activation energies for self-diffusion calculated in this work are much smaller than the magnitudes described in the literature. One of the possible reasons can be the difference in grain boundaries structure between nanocrystalline and coarse grain materials what was also observed by several authors [Buk04], [Sch98].

8.4 Surface analysis of nanostructured gold

For mechanical analysis gold was galvanostatically deposited on a copper disc electrodes with the following parameters : $t_{on} = 1ms$, $t_{off} = 20 ms$, T = 343 K, $j_p = 50 mA cm^{-2}$. The copper cathode was polished with emery paper using the diamond DP-spray $(1 \ \mu m)$ from Struers and washed with distill water. In Fig. 8.16 the electron micrograph of the gold deposited on a copper electrode by pulse technique is shown. It can be seen that the surface is rather smooth and can be analyzed with such techniques as AFM and nanoindentation. Otherwise, in Fig. 8.17 an electron micrograph of the gold deposited on a glassy carbon electrode by pulse technique is presented. One can observe the cauliflower surface structure with dendritic growth. In Fig. 8.18 electron micrograph of the surface of a rotation disc glassy carbon electrode after 10 s of gold deposition at E = -1.5 V vs. SCE and T = 298 K is shown. As can be concluded from Figs. 8.17 and 8.18 samples of gold deposited on a glassy carbon surface do not have a really smooth surface, furthermore, it is shown that the morphology of

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Figure 8.16: SEM of the gold deposited on a micrometer sized polished copper electrode. Deposition parameters $t_{on} = 1$ ms, $t_{off} = 20$ ms, $j_p = 50$ mA cm⁻², T = 343 K.



Figure 8.17: SEM of the surface of the glassy carbon electrode after 30 min of gold deposition by pulse technique ($j_p = 50 \text{ mA cm}^{-2}$, $t_{on} = 1 \text{ ms}$, $t_{off} = 20 \text{ ms}$, T = 298 K)..



Figure 8.18: SEM of the surface of the rotation disc glassy carbon electrode after 10 s of gold deposition at E = -1.5 V vs. SCE and T = 298 K.

the deposited gold is strongly depended on the substrate structure.

8.4.1 Roughness analysis

For roughness analysis a Veeco Dimension 3100 Atomic Force Microscope with closed loop scanner and 10 nm diameter Si tip was used. The gold sample deposited on a polished copper cathode by pulse techniques was investigated. In Fig. 8.19 the changes in the topography, the phase and the amplitude are presented. In can be clearly seen that the gold sample has a very smooth surface. As evident from Fig. 8.19 the phase and the amplitude stay homogeneous on the surface area of $50 \times 50 \ \mu m$ and the surface roughness does not exceed 50 nm. In Fig. 8.20 a three-dimensional picture of the investigated gold surface is presented. The cauliflower like gold growth with nanoscaled grain size can be observed. According to the experimental results (Fig. 8.19) mean roughness on the surface $50 \times 50 \ \mu m$ is calculated according to the following equation

$$R_a = \frac{1}{L} \int_0^L |f(x)| dx$$
 (8.11)

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(8.12)

where L is the length of the roughness curve. The root mean square roughness is calculated according to the formula

 $RMS = \sqrt{\frac{\sum (z_i - z_a)^2}{n}}$

Figure 8.19: Atomic force micrographs of the nanostructured gold sample; on the left side the topography of the surface is shown, in the middle the phase analysis is presented, and on the right side the change of the amplitude is shown.

where $n = 512 \times 512$ number of points. The values of $RMS = 13.462 \ nm$ and $R_a = 10.401 \ nm$ were calculated.



Figure 8.20: Three-dimensional gold surface pictures.

8.4.2 Microindentation

The gold sample deposited on a polished copper electrode was analyzed by LEICA VMHT Mot instrument with a diamond indenter, in the form of a square-based pyramid with an angle of 136° between the opposite faces was used. The Vickers hardness HV was calculated due to the Eq. 8.13 and is the test force divided by the sloping (i.e. surface) area of the indenter up to a depth where it has the same cross-sectional area as the residual indent. The full load was applied for 10 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load were measured using a microscope and their averages were calculated. The Vickers hardness is calculated according to the equation:

$$HV = \frac{2Fsin\frac{136^{\circ}}{2}}{d^2} \approx 1.84 \left(\frac{F}{d^2}\right) \tag{8.13}$$

Where F - applied test force, d - arithmetic mean of the two diagonal lengths d_1 and d_2 . The Vickers hardness is the quotient obtained by dividing the load by the square mm area of indentation. In Table 8.1 the microhardness experimental measurements results are presented. The measurements were made at three different test forces: 9.8 mN, 49 mN and 98.1 mN. For better statistics 12 measurements at every test force were performed. It can be seen that the variation in the obtained results is rather large and it strongly depends on the applied force. The average hardness values obtained for the forces of 9.8 mN, 49 mN and 98.1 mN are 72.3 HV, 102.8 HV and 101.95 HV, respectively. Such a variation can, probably, be the result of different depths made by the indenter. It was reported by several authors that the hardness of the gold films depends on their thickness in contrast to the hardness of massive materials of the same composition [Byk04]. They have examined that the hardness of the gold metallic films increases by a factor of 2.3-6.4 relative to the hardness of massive material. One should admit that by using such forces as 49 mN and 98.1 mN the probability of the substrate influence on the indentation results increases. Nevertheless, the literature results for massive gold metal amount to 20-30 HV and for massive copper metal - 49 HV [Wise64]. Such a disagreement of experimental results with literature ones can also be explained by the theory of Petch-Hall [Hal51], [Pet53] which says:

Force/mN	Hardness/HV	Force/mN	Hardness/HV	Force/mN	Hardness/HV
9.8	66.9	49	110	98.1	109
	64.4		106		119
	60.1		114		108
	88.4		96		96
	81.7		94		96
	70.8		89		108
	65.8		98		114
	69.5		104		114
	69.6		107		126
	68.2		110		124
	80.4		97		107
	72.6		109		117

Table 8.1: Experimental results of microhardness measurements of the nanostructured gold sample with gold layer thickness $5\mu m$.

- the shear force on grain boundary increases with grain size.

- grain boundaries are better able to support the shear stress for smaller grain size, therefore, dislocation motion is more effectively blocked for smaller grain sizes

- yield stress should increase with decreasing grain size.

The crystallite size of gold sample which was used for micro-indentation measurements was estimated to be 30 nm. Therefore, obtained results are in good agreement with theory.

8.4.3 Nanoindentation

A Hysitron Triboscope nanoindenter in conjunction with a Veeco Dimension 3100 AFM was used to perform imaging and nanoindentation. The indenter tip (d = 500 nm) was used to image and locate a gold surface and then indent it with the same tip. The indentation impression was also imaged with the same tip. This post-test *in situ* imaging capability provides the ability to verify that the test was performed in the anticipated location, which maximize the ability of data and aids in explanation of unexpected test results. Hardness and elastic modulus were calculated from load-displacement data obtained by nanoindentation using a three-sided pyramidal diamond (Berkovich) indenter tip. The nanoindenter monitors and records the load and displacement of the indenter during indentation with a force resolution of about 1 nN and displacement resolution of about 0.2 nm. A typical indentation experiment consists of four sequential steps: approaching the surface, loading to peak load, holding the indenter at peak load for 5 s and finally unloading completely. Fig. 8.21 shows the representative AFM images of the indents. In Fig. 8.22 the indentation load-displacement curves of the indent are presented. The peak nanoindentation depth was controlled to be less than 300 nm, which is about 5% of the film thickness. Therefore, the substrate affect on measurement of the hardness and elastic modulus of the film can be ignored [Li02], [Bhu03].



Figure 8.21: AFM images of the indents on a 5 μ m thick gold film.

The inset in Fig. 8.22 shows schematic illustration of indentation load-displacement data representing important measured parameters. From load/unload curve important parameters



Figure 8.22: The representative nanoindentation load-displacement curves; the inset shows schematic illustration of indentation load-displacement data showing important measured parameters [Oli92].

such as elastic unloading stiffness, hardness and elastic modulus can be calculated according to the following equations:

$$S = \frac{dP}{dh} \tag{8.14}$$

$$H = \frac{P_{max}}{A} \tag{8.15}$$

$$E = \frac{\sqrt{\pi}}{2\sqrt{A}}S\tag{8.16}$$

where S is elastic stiffness, P and P_{max} are applied force and maximal applied forces, H is the hardness, A is the contact area or the indenter shape function and E is the elastic modulus. An increase in indentation depth as a function of time at different constant peak indentation forces were found in Fig. 8.22. This is, probably, because the gold film is soft and dislocations moved beneath the indenter tip during the indentation holding segment, which contributed to the increasement in indentation depth [Bhu03]. The indentation impression was measured immediately after the indentation test using the same tip. In Fig. 8.23 the hardness and elastic modulus values are plotted as the functions of the displacement. As evident the

hardness and the elastic modulus reach very fast the stable values and do not depend on the contact depth. The average hardness of the nanostructured gold sample was calculated to be $H_{average} = 2.26 \pm 0.04 \ GP$ and the reduced modulus has a value of $H_R = 85.1 \pm 0.2 \ GP$. The gold film exhibits higher hardness if compare with the literature results. It was reported by [Can04] that gold singe crystal represents hardness $0.77 \pm 0.05 \ GPa$. [Kra00] investigated the



Figure 8.23: The hardness and the elastic modulus values plotted as the functions of the contact depth.

properties of single crystalline gold islands by means of nanoindentation. The value of elastic modulus in [111] direction of the gold grains was reported to be (50 ± 16) *GPa* and the hardness was calculated to have the value of 80 ± 27 *MPa*. Nanomechanical characterization of gold nanowires has been carried out by [Li05]. They have measured the hardness $(1.73\pm0.3 \ GPa)$ and elastic modulus $(109\pm10 \ GPa)$ of the unreleased gold wires by nanoindentation technique. Another nanoindentation results for gold wire mechanical analysis report the hardness value of 1.4 ± 0.1 *GPa* [Sha04]. A value of 2.1 ± 0.3 *GPa* for the hardness of gold film and 119 ± 10 *GPa* for the elastic modulus is reported in the literature [Li05]. As evident the nanostructured gold which has been characterized in this work exhibits higher value for the hardness than the bulk gold single crystal and even than gold nanowire. It is believed that the higher hardness and high elastic modulus results from the nanoscale grains [Bhu03]. The difference between the measured hardness and elastic modulus between gold film and the nanowires [Li05] may be due to the indentation elastic/plastic deformation zone on the wire becoming larger than the wire width, thereby resulting in larger projected area and consequently small hardness and elastic modulus values.

Chapter 9

Conclusion and outlook

In the presented work new and interesting results concerning the electrocrystallization and characterization of nanostructured materials, namely gold and binary gold alloys are presented.

A stable electrolyte, free of cyanides and sulphites, is prepared for gold electroplating. Au⁺ is stabilized by complex formation with 3-mercapto-1-propanesulfonic acid sodium salt. Nanoscaling has been achieved by pulsed current electrodeposition, nevertheless, by direct current plating the crystallites sizes of gold samples do not exceed 100 nm.

Changing different physical and chemical deposition parameters such as the temperature of the electrolyte, the concentration of additives or current parameters it is possible to control the crystallite size and, therefore, the properties of the materials. Some additives act as grain refiners by the attachment to the growing nuclei cluster and the prevention of their subsequent growth. It is experimentally shown that variation of deposition parameters such as current density and the temperature of the electrolyte causes deviations of gold crystallite sizes, namely the crystallites decrease from 26 nm down to 16 nm by increase of above mentioned parameters. It is shown that sulfur or arsenic containing additives decrease the gold crystallite size in the electroplating process down to 7 nm attaching to gold surfaces and preventing subsequent gold growth. None of organic additives brought about suitable results, probably, because of strong interactions with organic components of the electrolyte.

Nanocrystalline binary gold alloys with silver, palladium, platinum and copper are electode-

posited by pulse technique. The crystallite size is controlled by the proper choice of pulse technique, the temperature, current density and the concentration of Me salts.

The kinetics of electrocrystallization of nanostructured gold on a glassy carbon electrode from mercapto- containing electrolyte are investigated using electrochemical potentiostatic techniques and SEM. The nucleation behaviour of gold at different potentials is determined, it is shown that the nucleation can be described by 3D progressive model. During the gold deposition process the side reaction, especially hydrogen evolution takes place in the whole range of the deposition potentials and, therefore, causes the deviation of the current-time curves from theoretically predicted ones. It is experimentally shown that changing the applied potential it is possible to control the size of gold domains. Probable gold deposition mechanism is presented; it is assumed that the deposition process can occur through the adsorption of the gold complex followed by charge transfer at more positive potentials and through direct charge transfer at more negative potentials. The fits of experimental results with proposed theoretical equation due to the combination of charge transfer and diffusion control of nucleation and growth are made; some kinetic parameters such as exchange current density, nucleation rates, growth constants, diffusion coefficient were determined and possible reasons for the inconsistency between the experimental results and the theoretical predictions are discussed.

Electrodeposited nanocrystalline gold, the gold-silver and the gold-palladium alloys are investigated by in-situ high temperature X-ray diffraction in the angular range covered the gold (111) and (200) Bragg reflections. The samples showed thermal stability up to 700 K. It is experimentally shown that the crystallites start to grow after the microstrain disappears from the heated samples. It is concluded that the presence of sulfur atoms in the deposit causes the nanostructure of the samples. The activation energies for the gold, the gold-silver and the gold-palladium alloys are determined using extended Arrhenius representations and have the following values: $E_{a(Au)}=29.5$ kJ mol⁻¹, $E_{a(Au-Ag)}=28.7$ kJ mol⁻¹ and $E_{a(Au-Pd)}=71.5$ kJ mol⁻¹. The activation energies for self-diffusion calculated in this work are much lower than the magnitudes described in the literature. One of the possible reasons can be the difference in grain boundaries structure between nanocrystalline and coarse grain materials.

Surface structure of the nanocrystalline gold sample deposited on a polished copper electrode

is investigated by means of SEM and AFM. The cauliflower surface structure and, therefore, the big surface/volume ratio of the deposited gold makes it attractive for miniaturized biomedical applications. According to the surface analysis the root mean square roughness and mean roughness are determined and have the values of 13.462 nm and 10.401 nm, respectively. Applying the microindentation and nanoindentation analysis the values for hardness $H_{average} =$ $2.26 \pm 0.04 \ GPa$ and reduced modulus $H_R=85.1\pm0.2 \ GP$ are obtained. The magnitudes received by using both techniques are higher than those obtained from the literature. This disagreement can be a consequence of the difference in crystallite sizes and grain boundaries of the investigated materials. Grain boundaries are better able to support the shear stress for smaller grain size, therefore, dislocation motion is more effectively blocked for smaller grain sizes and, therefore, the hardness of nanostructured materials increases.

The possibility to create materials with adjusted properties attracts attention of scientists and is always of current importance. Gold and gold alloys are of wide use in dental industry for the production of crowns of tooth and in electronic industry for use in connectors. To improve the mechanical properties (hardness etc.) of coatings and bulk materials nanoscaling in crystallite size should be achieved. For this reason the investigations of the crystallization processes and physical properties of gold and gold alloys are very important and should be further performed.

Appendix A

Abbreviations

AFM - atomic force microscopy

- SEM scanning electron microscopy
- XRD X-ray diffractometry
- MPS 3-mercapto-1-propanesulfonic acid sodium salt
- TEM transmission electron microscopy
- DC direct current
- PED pulsed electrodeposition
- LSV linear sweep voltammetry
- CV cyclic voltammetry
- EIS electrochemical impedance spectroscopy
- EDX energy dispersive X-ray analysis
- NHE normal hydrogen electrode
- SCE saturated calomel electrode
- 2-D two dimension
- 3-D three dimension
- HV the Vickers hardness number

Appendix B

Publications and conference presentations

B.1 Publications

O. Yevtushenko, H. Natter und R. Hempelmann, Proc. Int. Conf. Surfaces, Coatings and Nanostructured Materials, (nanoSMat 2005), Aveiro, O-162-O-164 (2005), ISBN 973-713-065O. Electrodeposition and characterization of nanostructured gold and gold alloys

O. Yevtushenko, H. Natter und R. Hempelmann, J. Thin Solid Films, **515** No. 1, 353-356 (2006). Grain-growth kinetics of nanostructured gold

O. Yevtushenko, H. Natter und R. Hempelmann, J. Solid State Electrochem., **11** No. 2, 138-143 (2007). Influence of bath composition and deposition parameters on nanostructure and thermal stability of gold

B.2 Conference presentations

B.2.1 Oral presentations

O. Yevtushenko, H. Natter, R. Hempelmann, *Electrodeposition and characterisation of nanostructured gold and gold alloys*, International Conference on Surfaces, Coatings and Nanostructured Materials (nanoSMat2005), 7-9 September 2005, Aveiro, Portugal

O. Yevtushenko, H. Natter, R. Hempelmann, *Electrocrystallization and thermal stability of nanocrystalline gold alloys*, GDCh-Jahrestagung, 11-14 September 2005, Düsseldorf

B.2.2 Poster presentations

O. Yevtushenko, H. Natter, R. Hempelmann, *Electrodeposition of nanocrystalline gold by pulse techniques*, Hauptversammlung 2005 der Deutschen Bunsengesellschaft fur Physikalische Chemie, 5-7 May 2005, Frankfurt

J. Gajdzik, O. Yevtushenko, H. Natter, G.W. Kohring, F. Friedrich, R. Hempelmann, *Biomodification of gold electrodes for electroenzymatic applications*, Hauptversammlung 2006 der DeutschenBunsengesellschaft, 25-27 May 2006, Erlangen

J. Gajdzik, O. Yevtushenko, H. Natter, G.W. Kohring, F. Giffhorn, R. Hempelmann, *Biofunctionalisation of smooth and nanocrystalline gold electrodes with SDH*, 11th Int. Conf. Electroanalysis, 11-15 June 2006, Bordeaux, France

O. Yevtushenko, H. Natter, R. Hempelmann, *Electrocrystallization and properties of nanostructured gold*, ISE Annual Meeting, 27.08-01.09 2006, Edinburgh, Scotland

Appendix C

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