

Sol-Gel Coating of Thin Display Glasses - Problems and Remedy

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Abstract. Evaporation cooling is an inevitable but often neglected concomitant effect of sol-gel dip coating and related techniques, which is responsible for occasional coating problems. The phenomenon, however, emerges mostly for thin substrates of less than 1 mm thickness as the heat capacity of the substrate - the main source of heat for the evaporation - is reduced. The cooling of the substrate results in a reduced evaporation rate and an increased humidity in the surroundings of the film, leading to demixing of liquid components and an uncontrolled hydrolysis. The resulting coatings exhibit a hazy and cloudy appearance with crater-like structures in the micron range and consequently, functional properties such as the electrical conductivity of ATO coatings (antimony-doped tin oxide, $\text{SnO}_2\text{:Sb}$) are unsatisfactory. Among a variety of measures to overcome this cooling problem, a moderate heating of the coating liquid to only 25°C was found to be the method of choice to obtain high quality sol-gel thin films on substrates with a thickness down to 0.4 mm as required for display applications. This slight modification of the dip coating processing helps to reduce the susceptibility of the wet film to humidity and to improve the coating quality and the reproducibility in general - both on thin and thick substrates.

Keywords: dip coating, thin films, antimony doped tin oxide, hydrolysis

1. Introduction

Recent developments in flat panel display technologies are demanding thinner substrates for tailored functional coatings like transparent electrodes in order to reduce the weight and increase the performance of devices [1]. Today most displays are already based on glass substrates with a thickness of 0.7 mm, but the trend is for a further decrease in thickness down to only 0.4 mm or even less. Similarly, the requirements on functional coatings are ever-growing and hence more sophisticated tailored materials and deposition techniques have to be developed.

In search of future deposition techniques, sol-gel dip coating is considered a powerful alternative to deposition from the vapour phase and a combination with other deposition techniques combining the benefits of each is also imaginable [2]. Some properties of dip coated films such as the thickness uniformity on large areas and the smoothness for example are unequalled. Furthermore, the low deposition cost and the high flexibility in the processing are further advantages of this technique compared to common PVD processes [3]. But the coating of thin substrates by dip coating turns out to be more difficult than expected as coating liquids that perform well on thick substrates often fail and result in a poor coating quality. Though dip coating is one of the most frequently used wet coating techniques

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and there is already a basic understanding of its fundamental processes [4], such difficulties have not been reported so far, possibly because they are rarely noticed when thicker substrates are used.

This paper reports investigations on this cooling phenomenon and presents an effective remedy to obtain coatings of high quality on thin display glasses [5].

2. Experimental

Sol-gel coatings of antimony doped tin oxide ($\text{SnO}_2\text{:Sb}$, ATO) were prepared from a 0.2 M solution of SnCl_2 in ethanol with a doping level of 5 mol% SbCl_3 and 0.4 M DAA (diacetone alcohol) as a stabilising agent, that was refluxed for 2 h and filtered before use (0.2 μm). Coatings were deposited by the dip coating technique at 4 mm/s on different borosilicate glass substrates with a size of $7 \times 10 \text{ cm}^2$ (AF45 - Schott-DESAG, 0.4 mm/1.1 mm; 1737 - Corning, 0.7 mm; Borofloat 33 - Jenaer Glas, 3.3 mm) at constant ambient conditions of $(20 \pm 1)^\circ\text{C}$ and $(40 \pm 2)\%$ RH followed by a heat treatment at 550°C for 15 min in air. The coatings were characterised with regards to their thickness by means of a surface profiler after chemical etching (Tencor P10), their optical haze (Haze-Gard, BYK-Gardner) and their sheet resistance using a linear four-point technique. Scanning electron microscopy (SEM) images of the coatings were taken at 10 keV after deposition of a thin Au layer.

The temperature evolution during dip coating from pure solvents was monitored using IR thermographical images (Thermovision 470, AGEMA).

3. Results and Discussion

3.1. Evaporation Cooling During Dip Coating

Dip coating of thin substrates ($< 1.0 \text{ mm}$) occasionally results in coatings with a hazy and cloudy appearance which is shown for an $\text{SnO}_2\text{:Sb}$ coating in Fig. 1(a). As a consequence of this inhomogeneous morphology, functional properties such as the electrical conductivity are unsatisfying as well. This phenomenon is occurring during the film drying especially at the lower border of the substrate, but a study of the origins of these effects is complicated by the fact that the haze is not observed for all coating liquids, but rather depends on the type of precursor, the solvent and particularly on the additives used. In addition, also the atmospheric conditions seem

to play an important role, namely the temperature and the relative humidity.

There is evidence that the problems with coating of thin substrates are mainly due to a temperature drop caused by evaporation-induced cooling during the drying of the wet film. This was elucidated by means of IR thermographical images by monitoring the substrate temperature during dip coating from pure solvents. Figure 2 shows the temperature evolution for different substrate thicknesses ranging from 0.4 to 3.3 mm measured in the middle of the substrate taking the beginning of the withdrawal as the starting point ($t = 0 \text{ s}$). The temperature for the thickest substrate (3.3 mm) drops only slightly down to a minimum temperature of 19°C , but then takes several minutes to come back to the ambient temperature. For thinner substrates the minimum temperature that is reached during the evaporation is decreasing down to a value of only 13°C for the 0.4 mm thick substrate. Moreover, the substrate temperature in this case recovers after only 2 min. For later discussion it should be mentioned that the minimum temperature could even be lower than depicted in Fig. 2 because of the delayed beginning of the temperature acquisition. Minimum values below 8°C were detected especially in the lower part of the coating where the coating liquid accumulates (see also Fig. 1(a)).

An influence on the degree of evaporation cooling also comes from the solvents (Fig. 3) via the evaporation rate and the heat of evaporation ΔH_{vap} . Ethanol, which is one of the most frequently used solvents in dip coating for its fast drying, correspondingly shows the strongest cooling effect in this series of alcohols. With increasing molecular weight of the alcohol the temperature drop is less drastic as the evaporation rate is lower and the heat consumption is expanded over a longer period so that there is more time for a heat exchange with the environment.

The cooling of the substrate results in a slower evaporation of the liquid components of the wet film and simultaneously the relative humidity in the next environment of the film is increased. This leads to an intensified hydrolysis of the sol-gel films as they stay wet for a longer time and the water activity in the atmosphere is higher. The substrate temperature can even fall below the dew point of water which is approx. 7°C for ambient conditions of 20°C and 40% RH. This is the case at the lower end of the substrate where the solvent accumulates during the withdrawal and the formation of droplets can really be observed here. Moreover, the temperature drop also leads to a

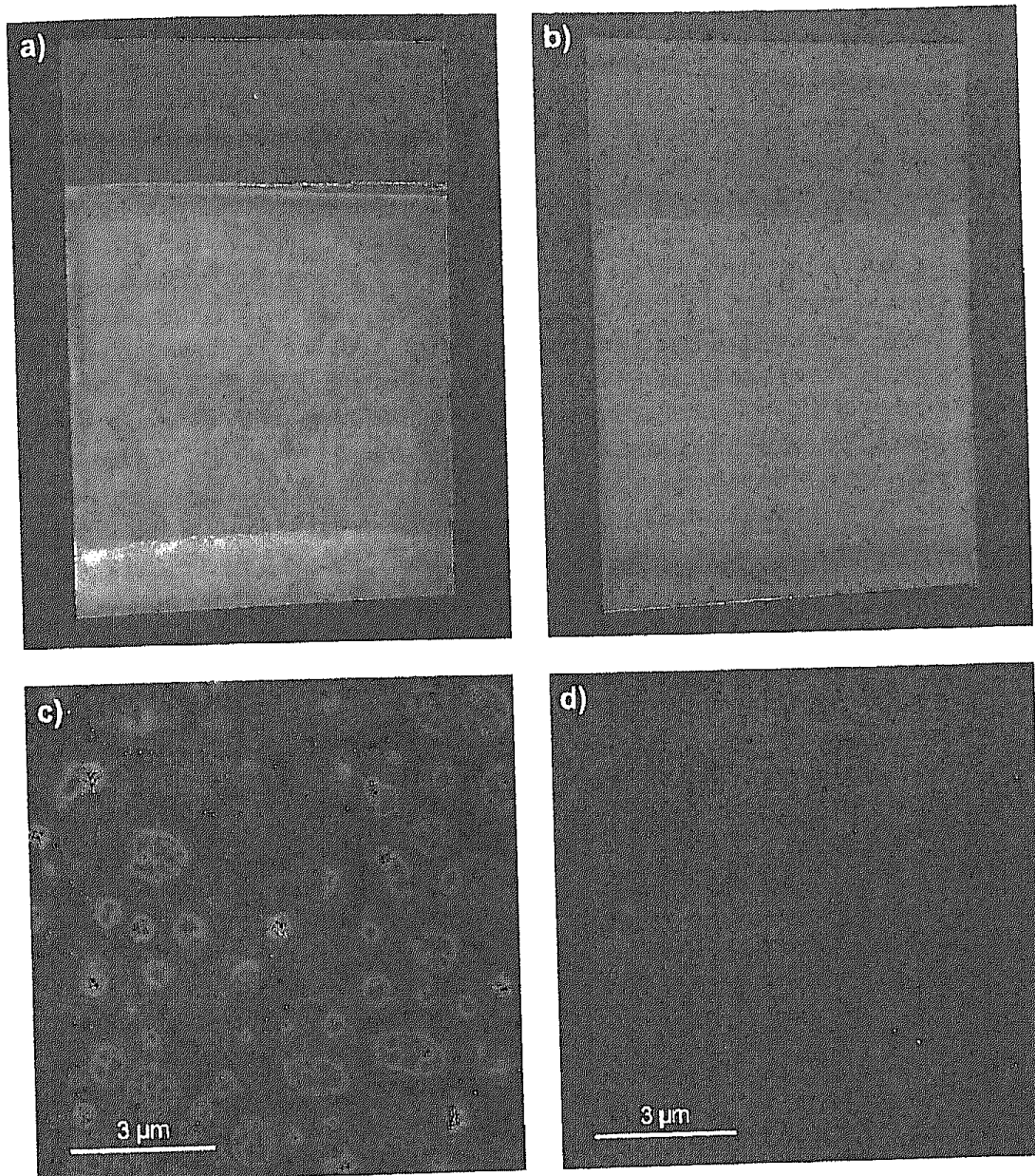


Figure 1. Photographs of (a) a hazy, cloudy sol-gel ATO coating (≈ 50 nm) on a 0.4 mm thick 1737 substrate (7×10 cm²) coated under conventional conditions at room temperature (20°C) and (b) a clear, homogeneous coating deposited at a solution temperature of 25°C. Below the corresponding SEM images are given in (c) and (d).

preferential evaporation of the more volatile components leaving back high-boiling point additives like the diacetone alcohol favouring a demixing of the components. Both effects - the uncontrolled hydrolysis and the demixing - lead to a very rough and inhomogeneous coating surface as it is shown in Fig. 1(c).

3.2. Approaches to Reduce the Substrate Cooling

Based on the knowledge of the parameters that determine cooling on evaporation several measures can be proposed to alleviate the substrate cooling during dip coating, namely

- (a) a lower amount of evaporating solvent,
- (b) a lower evaporation rate or heat of evaporation,
- (c) an external heat supply,
- (d) an "internal" heat supply.

The most intuitive measure is the lowering of the amount of evaporating solvent either by an increase of the solid content or by depositing thinner liquid films. But both measures influence the coating properties and restrict the range of coating thicknesses that can be deposited. The same applies to the lowering of the evaporation rate or the heat of evaporation ΔH_{vap} by changing the solvents and additives. Though it is

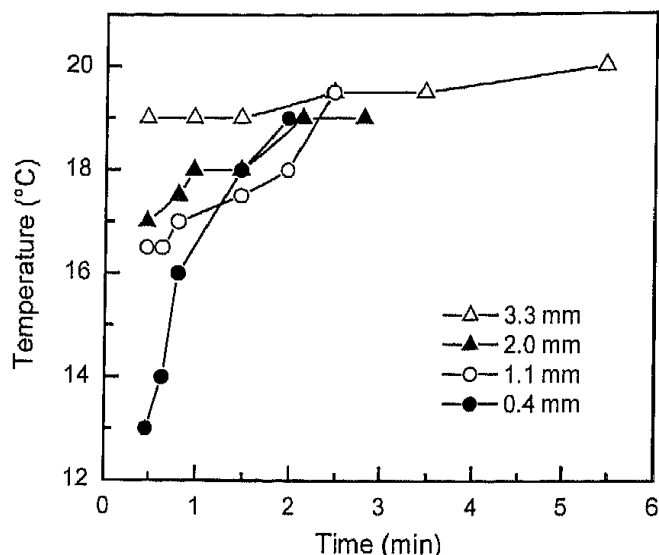


Figure 2. Temperature evolution of the substrate during dip coating from ethanol for different substrate thicknesses (monitored by IR thermography).

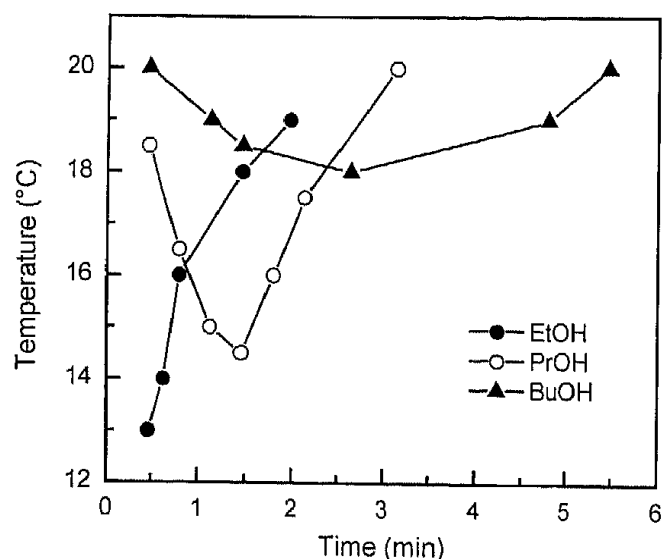


Figure 3. Temperature evolution of a 0.4 mm thick 1737 substrate during dip coating from different solvents (monitored by IR thermography).

quite effective to expand the heat consumption over a longer period (see also Fig. 3), the longer drying time may become a processing problem. Moreover, solvents with a lower evaporation rate are typically long-chained compounds which also influence the properties of the coatings especially by increasing the porosity.

A more technical approach is the implementation of an external heating source to supply the heat of evaporation. This can be accomplished by a simple IR heater that is placed over the coating liquid to heat the substrate during withdrawal, but this requires elaborate processing methods as such a heating is a se-

vere interference in the most sensitive stage of film formation.

The most elegant method, however, is to provide the system with enough "internal" heat to compensate that required for evaporation. At first view, it seems this could easily be realised by an increase of the ambient temperature to increase the heat capacity of the substrate and of the solution. But this does not really help as the temperature drop compared to the ambient temperature would be similar and thus the problems would be comparable. For a technical application, however, a noticeable increase of the ambient temperature is not practicable and often not tolerable.

In this regard, a self-evident measure could also be found in the heating of the substrate before coating, which should give the substrate enough heat for evaporation. During immersion, however, the substrate would lose part of its heat to the coating liquid and a reproducible coating would hence be difficult to realize, especially in the course of a multiple deposition process where the temperature of the coating liquid would rise steadily.

Instead, preference was given to a similar method based on the heating of the coating liquid keeping the ambient temperature at 20°C, which proved highly efficient to overcome the mentioned problems.

3.3. Heating of the Coating Liquid

The idea behind heating the coating liquid is to heat the substrate during immersion rather than exploiting an effect from the heated solution itself. Compared to the conventional dip coating hence only a temperature controlled vessel and a defined immersion time of the substrate in order to ensure a temperature equalisation are required. The added heat content of the substrate compensates the heat required for the evaporation of the volatile components of the wet film and thus prevents a significant cooling of the substrate below the ambient temperature. As a consequence, the drying is faster and film formation proceeds unaffected as indicated by the much smoother appearance of the obtained coating shown in Fig. 1(b) and (d).

This beneficial effect is even more clearly seen in Fig. 4 that shows both the haze, reflecting the surface morphology, and the sheet resistance of an ATO coating as a function of the temperature of the coating liquid. For this 0.4 mm thick substrate, a liquid temperature of only 25°C is sufficient to drastically improve the coating quality. While at room temperature (20°C) the

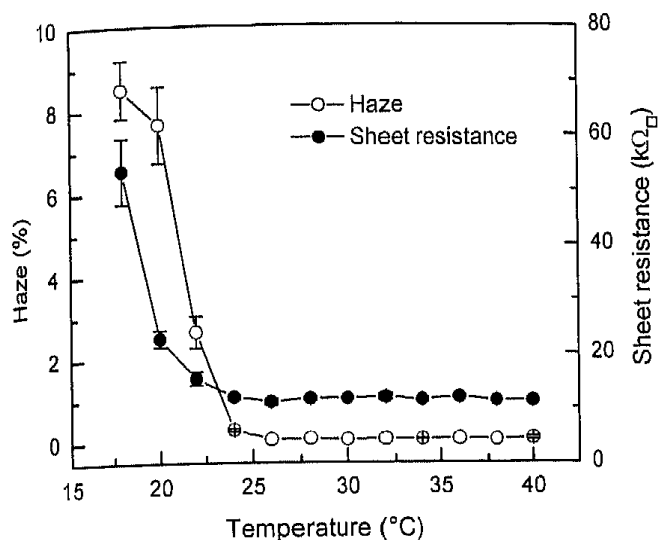


Figure 4. Haze and sheet resistance of sol-gel ATO coatings (≈ 40 nm) on a 0.4 mm thick substrate as a function of the temperature of the coating liquid.

coatings are rather hazy with values around 8% and consequently the macroscopic sheet resistance is high, both values decrease significantly at a liquid temperature higher than 24°C to reach values of $< 0.1\%$ for the haze and ≈ 12 kΩ□ for the sheet resistance. A further increase in the liquid temperature thus is not only unnecessary but rather counterproductive as it increases the evaporation rate of the liquid in the container.

4. Conclusion

Evaporation cooling is an inevitable concomitant effect of film drying in sol-gel dip coating and related wet

coating techniques. However, coating problems, which typically show up as a hazy and cloudy appearance of the coating, mainly emerge with thin substrates as their heat capacity is too low to compensate for the heat consumed by the evaporation. The resulting temperature drop lowers the evaporation rate while the relative humidity in the surroundings of the film is increased and, as a consequence, the hydrolysis is intensified and a demixing of liquid components is favoured. A flexible remedy for this problem is found in the heating of the coating liquid to a moderate temperature of 25°C that gives high quality sol-gel thin films on thin substrates with a thickness down to 0.4 mm, an important prerequisite to an application in display industry. This slight modification of dip coating also helps to reduce the susceptibility of the wet film to humidity and to improve the coating quality and the reproducibility in general.

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