

# DIFFUSION AT THE INTERFACE BETWEEN Ag DOPED SiO<sub>2</sub> LAYERS AND THE GLASS SUBSTRATE

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*Silica layers containing silver were prepared by the sol-gel method and deposited on the Float glass substrate. Heat treatment at different temperatures (60 and 550°C) and time periods (1 to 6 hours) followed afterwards. Silica layer texture without any particles was observed by electron microscopy. Silver, sodium, tin and silicon concentration profiles on "tin" side of Float glass substrates and in the deposited layers were evaluated by the help of Secondary Neutral Mass Spectrometry and discussed with respect to diffusion process taking place at the interface of the system substrate-layer. The concentration profiles of Ag and Na confirmed exchange diffusion mechanism at 550°C by which silver moves quickly from the surface layer into glass substrate.*

## INTRODUCTION

Silver doped silica sol-gel layers find the application possibility in many areas, e.g. catalysis, sensors, batteries or by the preparation of photosensitive or antibacterial glasses. [1] - [11]. These application fields require high quality of products. Hence, characterization and description of all the processes and influencing parameters are needed to properly control the final product properties. Beside the composition, atomic structure and microstructure, also the interaction of these layers with the substrate may also influence the properties of the layers. This effect can be expected because system layer-substrate is submitted to high temperature treatment used as the final step of layers formation. As glass substrates some glasses are frequently used composition of which is identical or near the common flat glasses. In such case interdiffusion at the layer-substrate interface can be expected in samples treated at higher temperatures [12]. As a result, composition and properties of the thin layer applied on the surface of those substrates can be changed especially due to diffusion of alkali ions from the substrate.

It is the aim of the work to extend information on diffusion interaction between thin sol-gel SiO<sub>2</sub> layers containing silver and Float glass substrate. The interaction can involve diffusion of some ions, which are present both in the substrate and in the layer deposited. Therefore, concentration profiles of moveable elements at the interface were measured and discussed.

## EXPERIMENTAL

### Sol preparation

Silica layers doped with silver particles were prepared via the sol-gel method. Tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTS) and aminopropyltriethoxysilane (ATEOS) were used as precursors, ethanol (EtOH) and water as solvents and nitric acid as a catalyst. ATEOS contains amino groups that form stable silver amino-complexes and thus ensures uniform distribution of silver particles in a sol. Glycidic groups, present in GPTS, are easily oxidizable and allow silver ion reduction to neutral particles at lower temperature. The preparation procedure is illustrated in the Figure 1.

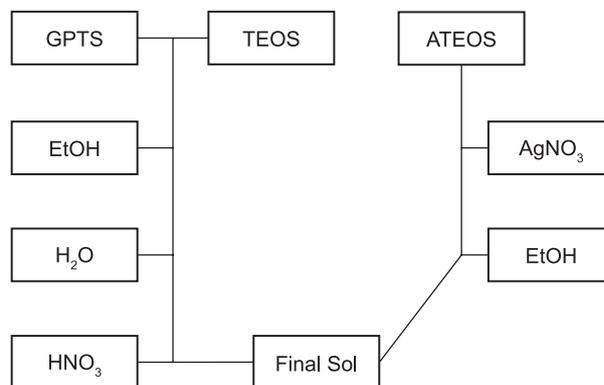


Figure 1. Scheme of sol preparation.

GPTS, TEOS, water and nitric acid (HNO<sub>3</sub>) were mixed for about 1 hour (left part of Figure 1). In parallel, silver nitrate (AgNO<sub>3</sub>) was dissolved in ATEOS and ethanol and stirred for 1 hour as well. Both solutions were mixed together afterwards and stirred for 30 minutes. Layers of the highest optical quality were obtained by use of following molar ratio: TEOS : GPTS : ATEOS : H<sub>2</sub>O : EtOH : HNO<sub>3</sub> : AgNO<sub>3</sub> 1 : 3 : 0.7 : 25 : 45 : 5 : 0.3. More detailed description of the procedure was presented previously [13].

#### The substrate and preparation of layers

Layers were deposited on microscopic glass slides by the dip-coating process. The glass slides were prepared by the Float technology. Chemical composition of a thin surface layer on “tin” and “air” side of the substrates was determined by the XRF analysis. The results indicate practically the same content of all compounds on both sides of the substrates except 0.68 wt.% Sn content on the “tin” side.

The slides were cleaned by a detergent, rinsed out by distilled water and ethanol and dried before layer deposition. The substrates were immersed into the sol for 60 s and pulled up at the rate of 1mm/s. The coated substrates were dried at 60°C for 30 minutes in an oven and than treated in air atmosphere at the low temperature of 60°C for 6 hours and at the temperature of 550°C for 1, 2, 4 and 6 hours. Yellow colored layers were obtained after the heat-treatment independently of the heating temperature.

## RESULTS AND DISCUSSION

### Electron Microscopy

Two kinds of coated glasses were prepared for electron microscopy observations: coated glasses heated at 60°C for 6 hours and at 550°C again for 6 hours. Surface structure of two layers which were prepared by the low and high temperature treatment was observed by the electron microscopy (Hitachi S-4700) (Figures 2 and 3).

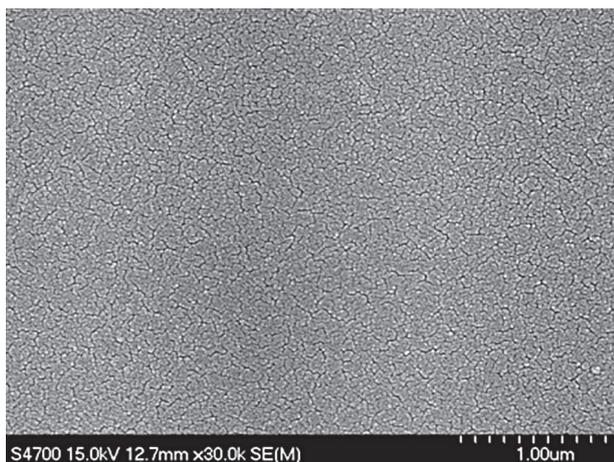


Figure 2. Samples dried at 60°C for 6 hours (tin side).

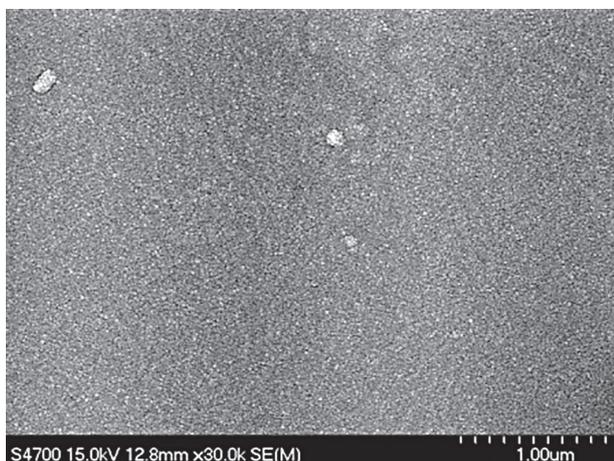
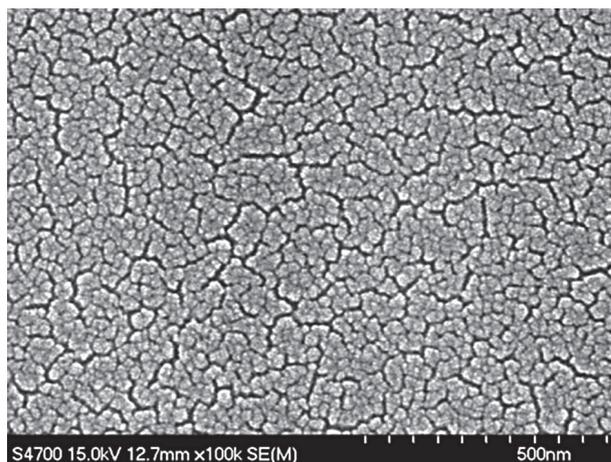
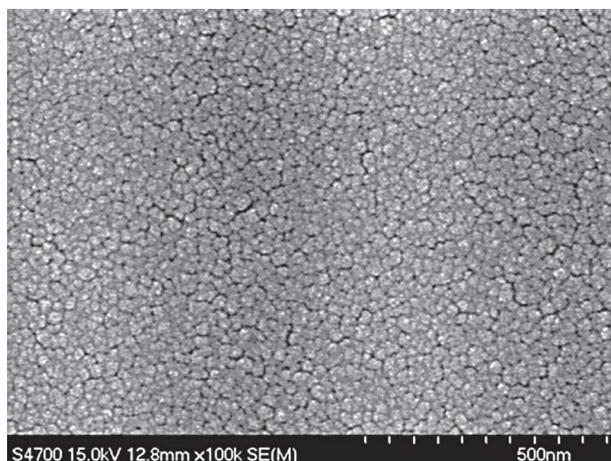


Figure 3. Samples treated at 550°C for 6 hours (tin side).



Apparently, slightly cracked surface was observed under the microscope with an EDS analyzer and no isolated particles were determined. The cracks partially disappeared due to sintering process if the layer was prepared by the treatment at 550°C.

### Secondary Neutral Mass Spectroscopy

Secondary Neutral Mass Spectroscopy (SNMS) was used to determine concentration profiles of some elements in the region near the layer-substrate interface. These measurements were performed by the help of the INA3 device of Leybold AG. Concentration profiles of silica,  $^{107}\text{Ag}$ ,  $^{109}\text{Ag}$ ,  $^{116}\text{Sn}$ ,  $^{118}\text{Sn}$  and  $^{120}\text{Sn}$  were measured and evaluated. Concentration changes (signal intensity) of different elements (Si, Ag and Sn) in samples depths are shown in the following figures (Figures 4-8). Concentration profiles of silver and silicon in the sol-gel layer and on “tin” surface of the substrate are presented on Figure 4. The layer was prepared by long time (6 h) drying at 60°C. The concentration profiles represent practically initial Si distribution in the layer and in the substrate and initial Ag distribution in the layer because the profiles are not disturbed by diffusion

with respect to low temperature treatment. The breaks in initial concentrations profiles can be considered as the boundary between the substrate and the deposited layer. Silver signal in glass substrate represents only a “background” noise of silver; it means there is zero silver concentration in the substrate. As it is seen, silver is uniformly distributed in the entire sol-gel layer. Small difference of Si signal in the layer and glass substrate has been observed as well. The reason is different silica

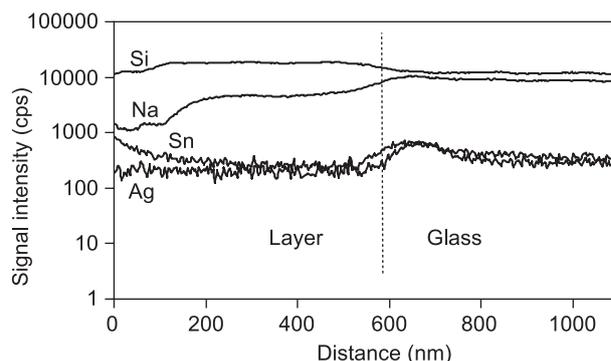


Figure 6. Concentration profiles of Si, Ag, Na and Sn at the interface between “tin” side of the substrate and surface layer prepared by heat treatment at 550°C for 2 hours.

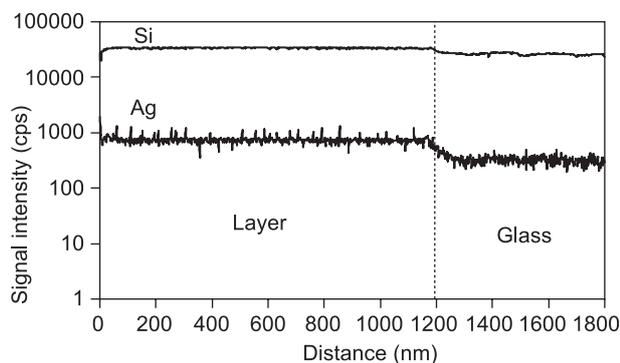


Figure 4. Concentration profiles of Ag and Si at the interface between “tin” side of the substrate and surface layer prepared by drying at 60°C for 6 hours.

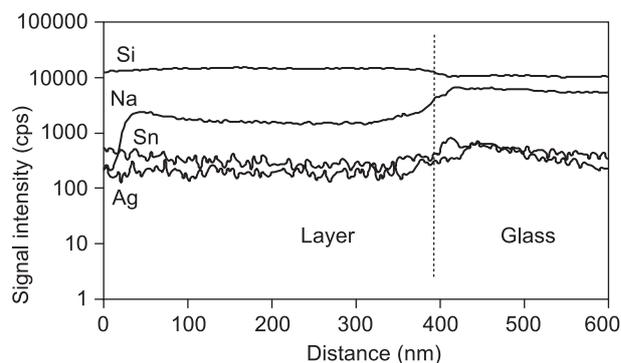


Figure 7. Concentration profiles of Si, Ag, Na and Sn at the interface between “tin” side of the substrate and surface layer prepared by heat treatment at 550°C for 4 hours.

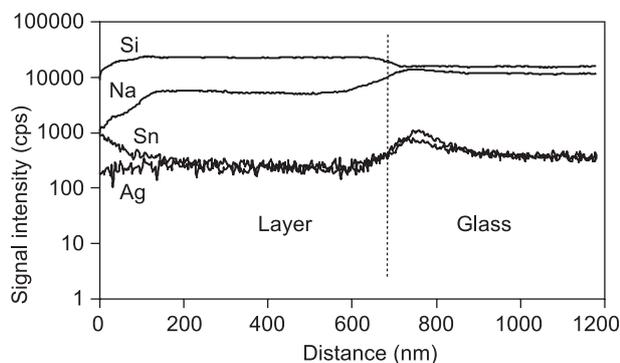


Figure 5. Concentration profiles of Si, Ag, Na and Sn at the interface between “tin” side of the substrate and surface layer prepared by heat treatment at 550°C for 1 hour.

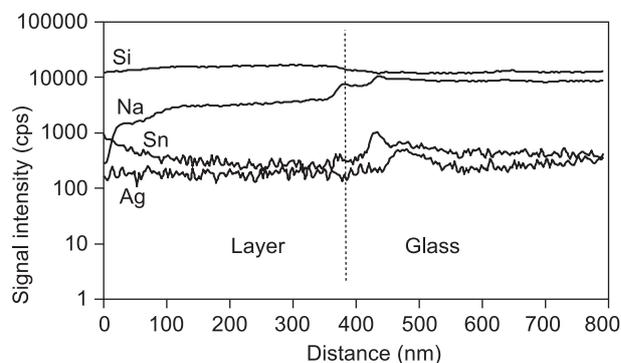


Figure 8. Concentration profiles of Si, Ag, Na and Sn at the interface between “tin” side of the substrate and surface layer prepared by heat treatment at 550°C for 6 hours.

concentration in the layer and in the substrate; the sol-gel layer consists almost completely of SiO<sub>2</sub> in contrary to the glass substrate, where weight SiO<sub>2</sub> concentration amounts about 72 %.

Concentration profiles of Si, Na, Ag and Sn at the interface between sol-gel layers prepared by treatment at the temperature of 550°C for different time periods (1, 2, 4, and 6 hours) and the substrate are summarized in the Figures 5-8.

The concentration profiles in the Figures 5-8 show the time development of some elements distribution at the interface between the sol-gel layer prepared by heat treatment at 550°C and the "tin" side of the substrate. Concentration profiles of Si do not show any significant change with time. The small break of the profiles at the interface can be again considered as the boundary between the layer and the substrate and the concentration profiles of other elements can be assessed in relation to the position of the break. Concentration profiles of Na indicate diffusion of Na from the substrate into the sol-gel layer. The layer is also enriched by Sn which can be explained by diffusion of Sn from the glass substrate. The concentration profiles of Ag confirm the expected exchange diffusion mechanism  $\text{Na}^+_{(\text{substrate})} \leftrightarrow \text{Ag}^+_{(\text{layer})}$  which is accompanied by diffusion of Sn from the substrate into the layer. It is probable that tin moves slowly in the form of Sn<sup>2+</sup> ions. The diffusion movement of Sn<sup>2+</sup> ions can be complicated by reaction between those ions and Ag<sup>+</sup> ions moving in the opposite direction. As a result the reaction  $\text{Sn}^{2+} + \text{Ag}^+ \rightarrow \text{Sn}^{4+} + \text{Ag}$  proceeds and silver atoms are formed [14-18]. The existence of diffusion processes accompanied by chemical reactions (reduction of Na<sup>+</sup> ions into Na is also not excluded) is probably the reason of maximum formation on the Ag, Sn and Na concentration profiles. The existence of those maximum in the substrate can be explained by high rate of  $\text{Ag}^+ \leftrightarrow \text{Na}^+$  exchange which enables Ag<sup>+</sup> ions quickly penetrate into the substrate and react with the Sn<sup>2+</sup> ions.

## CONCLUSION

Silica glass layers enriched by silver were prepared via sol-gel method at the temperatures of 60°C and 550°C and various time periods. Fine structured cracked surface without any isolated particles was observed by electron microscopy. Secondary Neutral Mass Spectrometry was used for diffusion profiles determination. The concentration profiles of Ag and Na confirmed exchange

diffusion mechanism at 550°C by which silver moves quickly from the surface layer into glass substrate. The silver diffusion is probably complicated by chemical reaction with Sn<sup>2+</sup> ions moving from the substrate into sol-gel layers. The chemical reactions between diffusing ions can be the reason of maximum existence on the silver, tin and sodium concentration profiles.

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