

# PREPARATION OF SILVER DOPED SILICA SOL-GEL LAYERS

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*Homogenous silicate layers containing silver nanoparticles were prepared by the sol-gel method and deposited on the glass substrate by the dip-coating technique. The sol consisted of tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTS), aminopropyltriethoxysilane (ATEOS), ethanol (EtOH), silver nitrate (AgNO<sub>3</sub>), nitric acid (HNO<sub>3</sub>) and demineralised water. The optimal ratio of components and conditions in relation to the quality and the homogeneity of the layers were established. The prepared layers were homogenous; with electron microscopy, a fine texture without silver particles was observed. Samples treated at temperatures up to 250°C and above 500°C were yellow, between 300 and 450°C were colourless. The coloration intensity increased with the treatment time. The immersion time of the substrate in the sol had no influence on the samples coloration. On the contrary, the increasing pull-up speed intensified the layers coloration. The optical quality of prepared layers deteriorated significantly above the pulling speed of 90 mm/min.*

## INTRODUCTION

Thin layers preparation is rapidly growing research area nowadays. The layer may be deposited by various methods, e.g. magnetron sputtering, chemical vapour deposition or by sol-gel process. Very pure materials with precise composition could be produced via these procedures. Silica or titanium oxides are often used to form layers on substrates from different kind of materials. These layered materials find the application possibilities in catalysis, optical wires, electrochromic devices and many other areas [1-3].

The properties of SiO<sub>2</sub> or TiO<sub>2</sub> layers can be improved by doping of small amount of different elements. Several elements can be used for the doping, e.g. Pd, Co, Cu, Mn, Cr, Au or Ag [4-10]. Silver appears to be very promising doping element, because silver doped glasses and layers are used in many areas, such as in catalyst, production of sensors, batteries and in preparation of photosensitive or antibacterial glasses [11-18]. By the properly selected conditions (composition, treatment time and temperature...) it is possible to control and modify the final product parameters. To understand better the process, several production parameters were selected and tested. It is the aim of this work to find out optimal conditions of the silver doped silica layers preparation especially with respect to their homogeneity, adhesion and coloration.

## EXPERIMENTAL

### Preparation of layers

Tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTS) and aminopropyl-triethoxysilane (ATEOS) were used as the precursors for sol preparation. Ethanol (EtOH) and water were used as dissolvent.

The preparation procedure is described in the Figure 1.

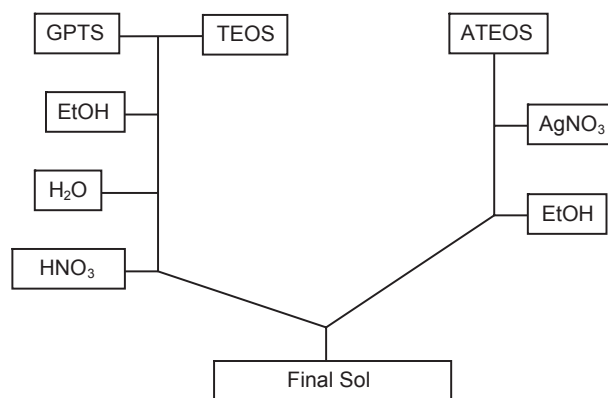


Figure 1. Preparation of Sol Containing Silver Particles.

In the first step, GPTS, TEOS, water and nitric acid ( $\text{HNO}_3$ ) were mixed together and stirred for 1 hour (Solution 1). Simultaneously, silver nitrate ( $\text{AgNO}_3$ ) was dissolved in ATEOS and ethanol and stirred for 1 hour as well (Solution 2). Both solutions were mixed together afterwards and stirred for 30 minutes. The best layer quality was achieved by the following molar ratio: TEOS : GPTS : ATEOS :  $\text{H}_2\text{O}$  : EtOH :  $\text{HNO}_3$  :  $\text{AgNO}_3$  1 : 3 : 0.7 : 25 : 45 : 5 : 0.3.

The uniform distribution of silver in the sol was achieved by using of ATEOS. This compound contains amino groups that form stable silver amino-complexes. The glycidic group, present in GPTS, is easily oxidizable and allows the silver ions reduction to neutral particles by lower temperature.

#### Thermal treatment

Layers were deposited by the dip-coating method on microscopic slides produced by float process.

The slides were cleaned by detergent, rinsed by distilled water and ethanol and dried. By the standard procedure, samples were immersed into the sol for 60 s and pulled up 1mm/s afterwards. It was followed by the drying at 60°C for 30 minutes and burning in the air atmosphere. The treatment temperature ranged from 100 to 550°C for 1, 2, 4 and 6 hours.

Influence of different settings parameters, such as the dipping time, the pull-up speed and the treatment time and temperature were tested in the further steps.

## RESULTS AND DISCUSSION

### Optical Microscopy

The optical microscopy showed homogenous yellow or colourless layers according to the treatment temperature. Samples were burnt out at 550°C for 6 hours

and cut to observe different diffusion profile on the air and the tin side (see Figure 2a,b).

Coloured layer on the tin side is deeper and more intensive than on the air side of the glass substrate. In the case of tin side, this effect is caused by the presence of reducing agents in the substrate, especially by tin diffused from the tin bath. Air side coloration was due to the presence of iron (+II) ions in the glass or by the tin, which evaporated from the tin bath and diffused in the glass surface from the float chamber atmosphere.

### Electron Microscopy

The surface structure, particles size and particles distribution was observed by the electron microscopy (Hitachi S-4700). Two different kinds of samples were prepared. First of them was dried by 60 °C for 6 hours, the second one was burnt at 550 °C for the same time.

A slightly cracked silica surface was observed by the electron microscopy. These cracks were reduced by the firing temperature of 550 °C. No visible silver particles were observed and detected by EDS analyzer on the samples surface. This fact might be explained either due to the small dimension of silver particles or due to diffusion of silver into the bulk of the glass.

### Factors influencing the quality of layers

The influence of various factors on the coloration and the final quality of the layers was tested and subsequently characterized by the UV-VIS spectrophotometry.

### Heat-treatment time and temperature

The glasses with deposited layers were dried at 60°C and fired in the temperature range of 100-550°C for 2 hours. Absorbance in the dependence on the wavelength was measured afterwards (see Figure 5).

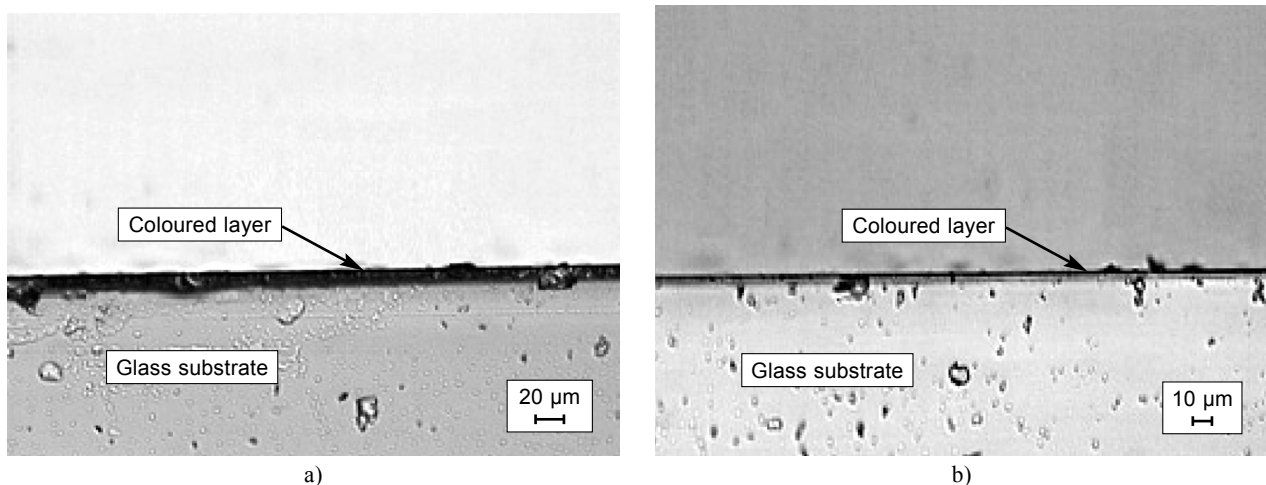


Figure 2. Coloured layers on the tin side (a) and on the air side (b). Heat-treatment at 550 °C for 6 hours.

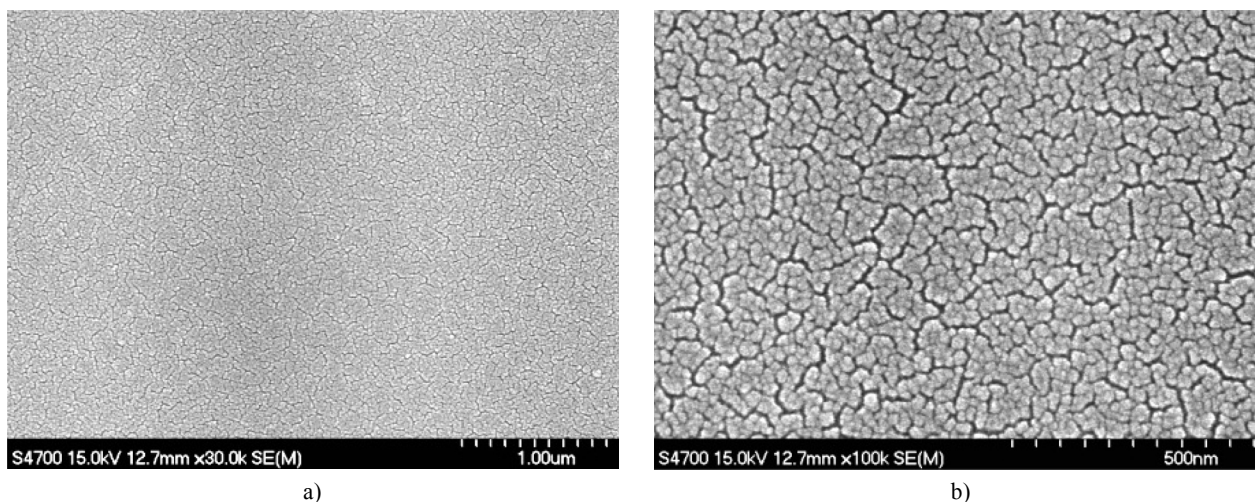


Figure 3. Layer treated at 60 °C for 6 hours (tin side, different resolutions).

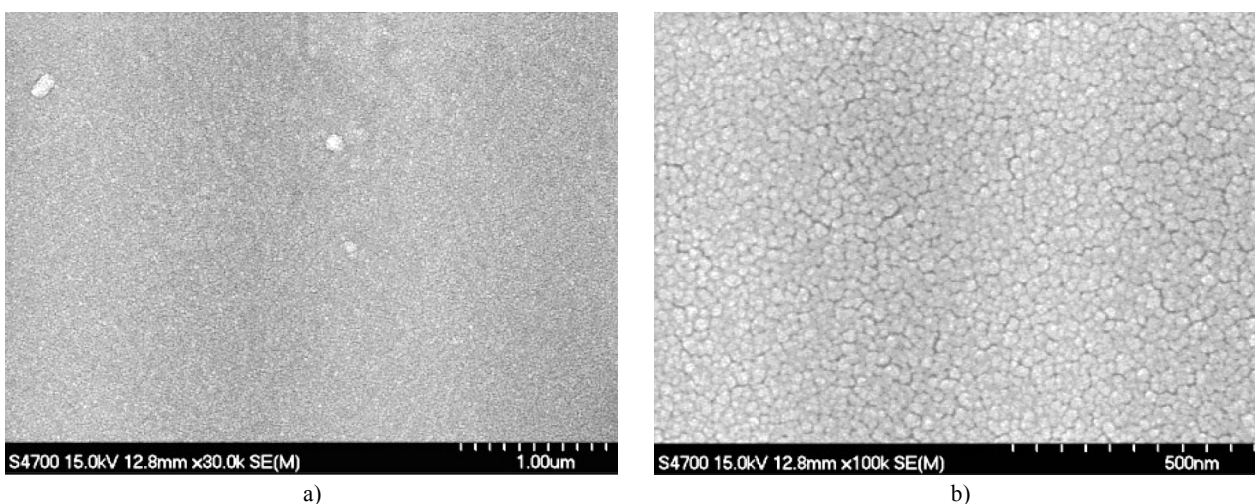


Figure 4. Layer treated at 550 °C for 6 hours (tin side, different resolutions).

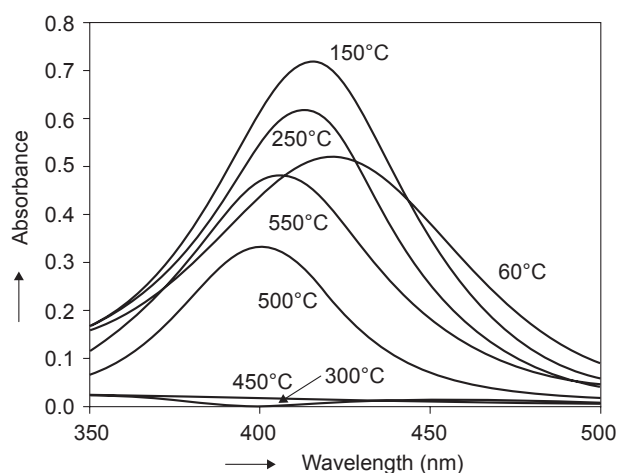


Figure 5. Influence of Treatment Temperature on the Layers Coloration.

The heating up to 250°C and above 500°C caused the coloration of layers because of silver ions reduction. Characteristic peaks from 390 to 420 nm correspond to the yellow colour of samples. The layers treated in the temperature range from 300 to 450°C were colourless.

The existence of coloration in these two temperature intervals can be explained by different silver reduction mechanisms. In the first firing range (from 60 to 250°C), silver was reduced by organic groups included in the precursors. With the increasing temperature, above 300°C, all organic groups were burnt out, silver was oxidized by air and the samples became colourless.

Above 500°C, the second reduction mechanism was initiated. Silver particles moved easily into the glass substrate thanks to the exchange diffusion with sodium ions and thanks to the higher temperature. Redox reaction with reducing agents, mainly with tin and iron (+II) ions followed (1).



The explanation can be supported by the Differential Thermal Analysis (DTA) and Thermal Gravimetry (TG) curves (see Figure 6). The prepared sol was dried at 80°C for a long time to remove most of the solvents. Prepared xerogel was heated up to 800°C and compared with the aluminium oxide as the reference.

Two endothermic and four exothermic peaks were found on the DTA curve. Both endothermic peaks, at 250 and at 330°C, are probably caused by water evaporation, which was physically and chemically bonded in the xerogel. Four exothermic peaks (at 200, 300, 370 and 530°C) are linked with the weight loss. This fact indicates the burning of the organic residues.

The evaporation of all residues together with the layers compaction is finished above 650 °C. Hence, the best mechanical and chemical durability of the layered glass might be expected in the temperatures near the  $T_g$  value of the glass substrate.

Firing at 550°C for 1, 2, 4 and 6 hours were chosen to describe the heat-treatment time influence (see Figure 7).

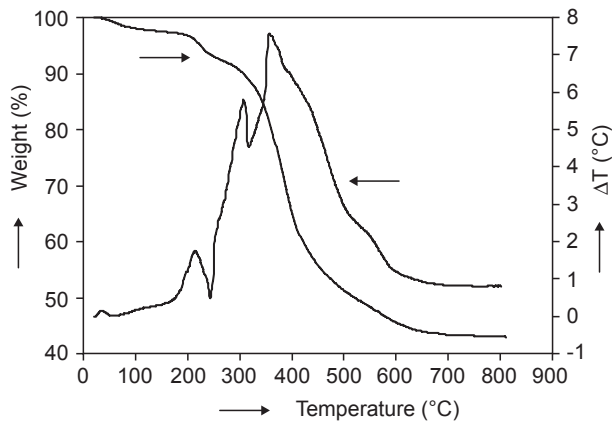


Figure 6. DTA and TG Analysis of xerogel prepared by thermal treatment at 80°C for 48 hours.

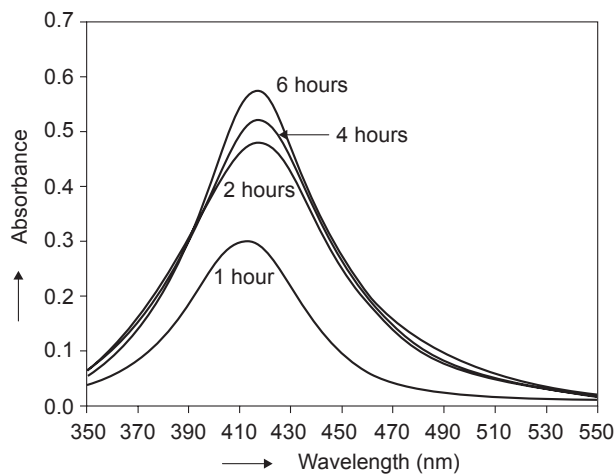


Figure 7. Influence of Firing Time on the Coloration Intensity.

Significant absorption peak's growth was observed with the increasing time. This effect was probably caused by the higher diffused and reduced silver amount in the glass substrate.

#### Dipping time

The influence of the dipping time on the coloration of layers was measured to characterize the speed bond ability between the sol and substrate.

The glasses were pulled down and immersed in the sol for 10, 30, 60, 90 and 450 seconds. The pulling up, the drying (30 minutes by 60°C) and the firing at 550°C for 6 hours followed afterwards.

Absorption curves are demonstrated below (Figure 8). Resulting UV-VIS curves had almost the same shape. Because the dipping time was the only different parameter in the preparation process, no influence of dipping time on the layers coloration might be assumed.

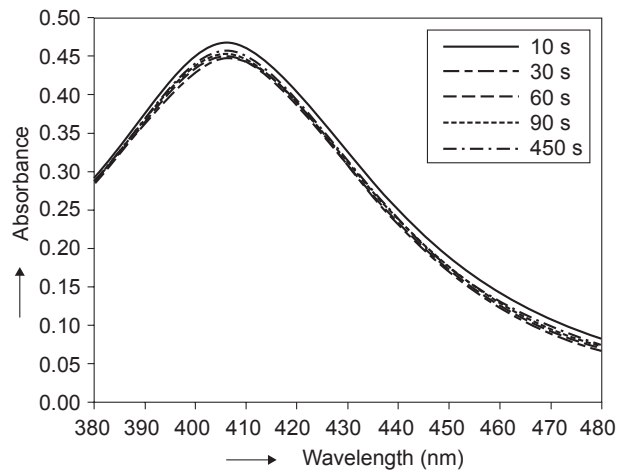


Figure 8. Influence of Dipping Time on the Layers Colour Intensity.

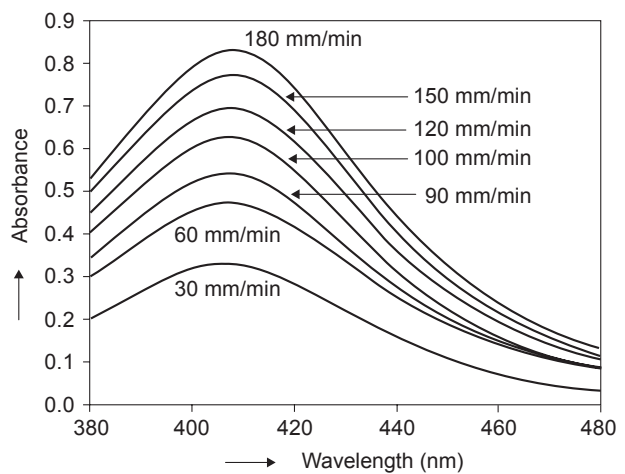


Figure 9. Influence of Pull-up Speed on the Layers Coloration.



These results indicate the fast bonding ability of the sol on the substrate surface and the fast formation of chemical and physical linking.

#### Pull-up speed

The glass substrate was dipped in the sol for 30 seconds and pulled up at seven different speeds (30, 60, 90, 100, 120, 150 and 180 mm/min) subsequently. All the samples were dried at 60°C for 30 minutes, fired at 550°C for 6 hours and characterized by UV-VIS spectrophotometry (see Figure 9).

The absorbance of samples (in other words, the amount of silver in the layer forming coloured centres) grows with the increasing pull-up speed. This conclusion is well-known and was described by Brinker-Scherer [19] or Landau-Levich [2]. In this case, the pull-up speed had a significant impact on the quality of deposited layers. 90 mm/min was the limit pull-up speed for preparation of good quality layers. Above this value, linear vertical inhomogeneities were observed on the surface after the heat-treatment.

#### CONCLUSION

The homogeneous silver containing silica layers on the glass substrate were prepared by the sol-gel method. Small cracks in the structure of dried layers were observed by the electron microscopy. These cracks were reduced by the heat-treatment at 550°C.

The firing temperature had a significant impact on the samples coloration. Yellow layers were obtained after the firing at the temperatures up to 250°C and above 500°C. In the temperature range of 300-450°C samples were colourless due to the silver oxidation. The firing time intensified the coloration intensity.

The influence of the dipping time and the pull-up speed were tested as well. The dipping time has no influence on the samples absorbance (and thus on the amount of silver in the layer). On the other hand, the absorbance grew with the increasing pull-up speed. Linear vertical defects were examined at the speeds above 90 mm/min. The DTA and TG analysis showed that the final compaction of the coloured layers comes on between 500 and 550°C.

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#### PŘÍPRAVA KŘEMIČITÝCH SOL-GEL VRSTEV DOPOVANÝCH STŘÍBREM

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Metodou sol-gel byly připraveny homogenní křemičité vrstvy obsahující nanočástice stříbra a nanoseny na skleněný substrát technikou dip-coating. Výchozí sol byl připraven z tetraethoxysilanu (TEOS), glycidoxypropyltrimethoxysilanu (GPTS), aminopropyltriethoxysilanu (ATEOS), ethanolu (EtOH), dusičnanu stříbrného (AgNO<sub>3</sub>), kyseliny dusičné (HNO<sub>3</sub>) a demineralizované vody. Poměr mezi použitými složkami a podmínky přípravy solu byly optimalizovány s ohledem na kvalitu a homogenitu vrstev. Připravené vrstvy byly homogenní. Pomocí elektronového mikroskopu byla zjištěna jejich textura, v níž nebyly identifikovány částice stříbra. Vrstvy připravené za teplot do 250°C a nad 500°C měly žluté zbarvení, vrstvy připravené v rozmezí teplot 300-450°C byly bezbarvé. Intenzita zbarvení u žlutých vrstev vzrůstala s časem. Zbarvení žlutých vzorků nebylo ovlivněno časem imerze substrátu v solu. S rostoucí rychlostí tažení substrátu ze solu vzrůstala intenzita zbarvení vrstev. Optická kvalita vrstev značně klesla, jestliže rychlost tažení ze solu překročila hodnotu 90 mm/min.