

# Synthesis of Ag-Colloids in Sol-Gel Derived SiO<sub>2</sub>-Coatings on Glass

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**Abstract.** Ag colloid-containing coatings on soda lime glass and fused silica are prepared via the sol-gel process. To incorporate Ag<sup>+</sup>-ions in the coatings homogeneously, they are stabilized by a functionalised silane (aminosilane) and then mixed with the basic sol prepared from 3-glycidoxypropyl trimethoxysilane (GPTS) and tetraethoxysilane (TEOS). Crack-free and transparent coatings with a thickness of 0.5 to 1.2 μm, are obtained by heat treatment between 120°C and 600°C. The Ag-colloid formation was monitored by UV-VIS spectroscopy as a function of temperature. The investigations reveal that the substrate has a deciding influence on the Ag-colloid formation caused by alkali diffusion from the substrate into the coating. High resolution transmission electron microscopy (HRTEM) investigations prove that poly-crystalline Ag<sub>x</sub>O<sub>y</sub>-nanoparticles are formed during thermal densification in the coatings and that this change is accompanied by a vanishing of the yellow colour of the coatings. A post-heat treatment in a reducing atmosphere (90% N<sub>2</sub>, 10% H<sub>2</sub>) turns back the yellow colour and single-crystalline Ag-colloids can be detected by HRTEM. A suitable choice of the temperature and time conditions allows the control of the colloid size during heat treatment in a reducing atmosphere. For comparison, ion-exchange experiments have been carried out which showed that a spontaneous Ag-colloid formation was achieved in the soda lime substrate at 400°C. Since Ag containing SiO<sub>2</sub>-coatings remained colourless after thermal treatment between 400°C and 600°C in air, on soda lime substrates, a remarkable diffusion of Ag<sup>+</sup> into the substrate was excluded.

**Keywords:** sol-gel coating, silver colloids, UV-VIS spectroscopy

## 1. Introduction

Ag colloids have been used for staining glasses yellow since several hundreds of years. The colouring effect is due to a surface plasmon resonance of the conductive electrons in the nano-sized Ag metal particles, leading to a Lorentzian-like absorbance band with a peak at about 400 nm to 430 nm wavelength and a full width at half maximum (FWHM) between 100 nm and 20 nm (depending on colloid size and refractive index of the embedding glasses). Ag colloids are grown from Ag<sup>+</sup>-containing melted glasses by a so called "striking" process [1, 2]. Since the diffusion coefficient of monovalent Ag<sup>+</sup>-ions in glasses is relatively high (e.g.,  $D = 2 \cdot 10^{-13} \text{ cm}^2 \cdot \text{s}^{-1}$  at 550°C in a sodium silicate glass [3]) Ag colloids also can be formed during or after an ion exchange process (e.g., Na<sup>+</sup>-Ag<sup>+</sup>-exchange) using Ag containing salt melts or pastes [4–6]. Investigations of the growth kinetics of Ag colloids in glass [3] lead to the conclusion that Ag<sup>+</sup>-ions are diffusing

towards Ag nuclei the formation of which may be induced either thermally or by UV-irradiation, and are reduced at the nucleus interface as far as polyvalent ions in the glass (e.g., Fe, Sn, Sb) assumed to act as redox compounds. Beside nucleation and growth from Ag<sup>+</sup>-ions, Ostwald ripening has been detected during long term thermal treatment of soda lime glasses [7].

There have been only a few attempts for the generation of Ag colloids in sol-gel materials [8, 9] by dissolving AgNO<sub>3</sub> in an appropriate sol prepared from tetraethoxysilane (TEOS) [8] or tetramethoxysilane (TMOS) [9]. Reduction was carried out using a reducing agent (formaldehyde [8] or Sn<sup>2+</sup> [9]), but using this route a broad size distribution and agglomeration of Ag colloids could not be avoided, even at room temperature. Hinsch and co-workers [10] added an aqueous colloidal Ag solution to a TEOS sol and prepared coatings. The Ag-colloid containing coatings showed a very broad absorbance band with a FWHM of about 250 nm, indicating a broad size

distribution and probably colloids of distorted spherical shape.

From investigations of metal colloid formation in aqueous solutions by Zsygmondy and Fischer [11] or Henglein et al. [12] it is known that the colloidal size and agglomeration can be controlled by surface ligands. In [13, 14] functionalized silanes are described to be suitable for the stabilisation of metal ions in  $\text{SiO}_2$  sols and the formation of metal colloids (including Ag) in appropriate  $\text{SiO}_2$  xerogel powders for catalytic applications. The authors assume that metal oxide nanoparticles are formed during thermal densification in air and can be reduced by a second thermal treatment in  $\text{H}_2$  atmosphere. The alternative mechanism, the formation of metal colloids at low temperatures and their oxidation at elevated temperatures, has not been taken into consideration so far.

Therefore the aim of the present study was to investigate the nucleation and crystallization of Ag colloids in gels in more detail. As the optical properties of noble metal colloids in a dielectric matrix are well understood it was decided to prepare coatings with a high optical quality on glass to follow the Ag-colloid formation by UV-VIS-spectroscopy. As substrates, both soda lime glass and fused silica were used to check the influence of alkali diffusion on the Ag-colloid formation. In order to consider the case that remarkable amounts of the silver from the coatings would diffuse into the soda lime substrate, ion-exchange experiments with a  $\text{Ag}^+$ -containing salt melt were carried out for comparison.

## 2. Experimental

For the preparation of Ag-containing  $\text{SiO}_2$ -coatings, 0,51 g  $\text{AgNO}_3$  was dissolved in a mixture of 10 ml methanol and 0,66 ml N-(2-aminoethyl)-3-amino-propyl trimethoxysilane (DIAMO) (molar ratio of Ag : DIAMO = 1 : 1). 21,9 ml of the  $\text{SiO}_2$  matrix sol, prepared from 160 ml 3-glycidoxypropyl triethoxysilane (GPTS) and 40 ml tetraethyl orthosilicate (TEOS), dissolved in 240 ml ethanol and pre-hydrolysed with 28,5 ml of 0,1 M  $\text{HNO}_3$ , was added and stirred for 15 minutes. Soda lime glass (8 wt.%  $\text{Na}_2\text{O}$ , 7 wt.%  $\text{K}_2\text{O}$ ) and fused silica slides were dip-coated with a withdrawal speed of 4 mm/s and dried at  $120^\circ\text{C}$ , before they were treated in ambient air between  $200^\circ\text{C}$  and  $600^\circ\text{C}$  in steps of 100 K for 1 h (heating rate: 60 K/h) and in a reducing atmosphere (volume fraction: 92%  $\text{N}_2$ /10%  $\text{H}_2$ ) at temperatures between  $100^\circ\text{C}$  and  $600^\circ\text{C}$  for 1 h and in the case of the soda lime

substrate additionally at  $500^\circ\text{C}$  up to 21 h (gasflow: 80 l/h, volume of the oven: 8 l).

$\text{Na}^+$ - $\text{Ag}^+$ -ion exchange experiments were carried out with the soda lime substrates in a salt melt of 5 wt%  $\text{AgNO}_3$  and 95 wt%  $\text{NaNO}_3$  at  $400^\circ\text{C}$  in air for 4 h and 18 h.

The Ag-colloid formation was investigated by UV-VIS-spectroscopy (Bruins Instruments, OMEGA 30) and high resolution transmission electron microscopy (HRTEM) (Philips, CM 200). The UV-VIS data were evaluated with regard to colloid size and colloid volume fraction according to [6] using spectra calculated [15] according to the Mie-theory [16] for comparison. The thickness of the coatings was determined by a profilometer (SAS Nanosurf 488).

## 3. Results and Discussion

For the investigation of the formation of Ag-colloids in  $\text{SiO}_2$ -coatings prepared via the sol-gel process the synthesis route as shown in Fig. 1 was developed.

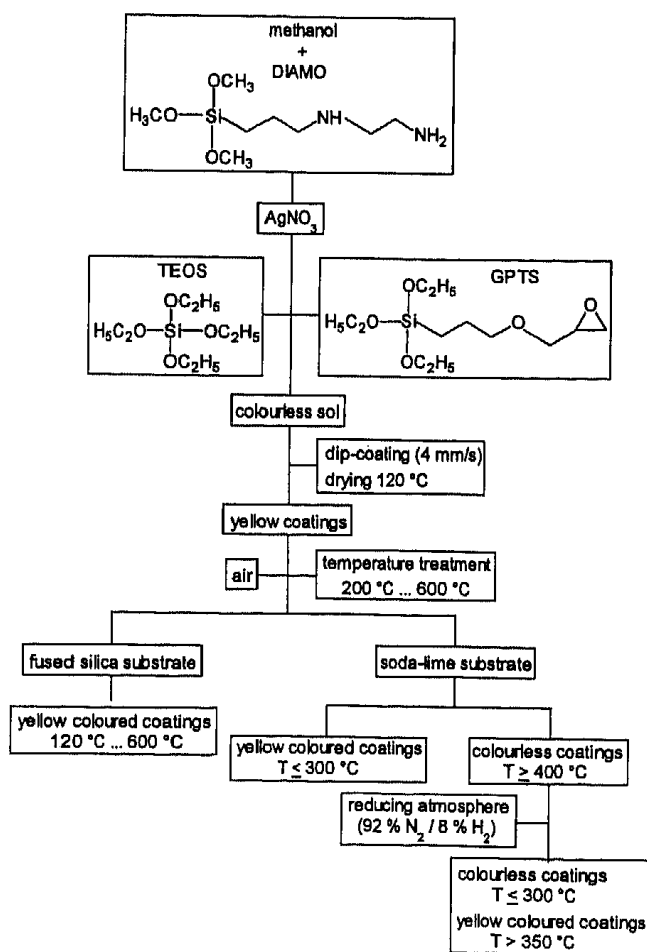


Figure 1. Flow chart of the preparation of  $\text{SiO}_2$ -coatings containing Ag-colloids on soda-lime and fused silica substrates.

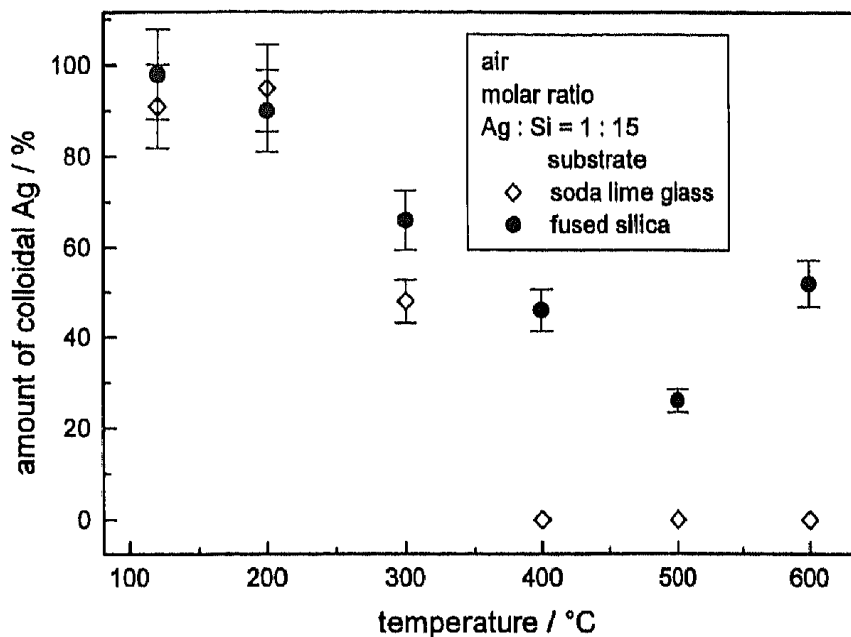


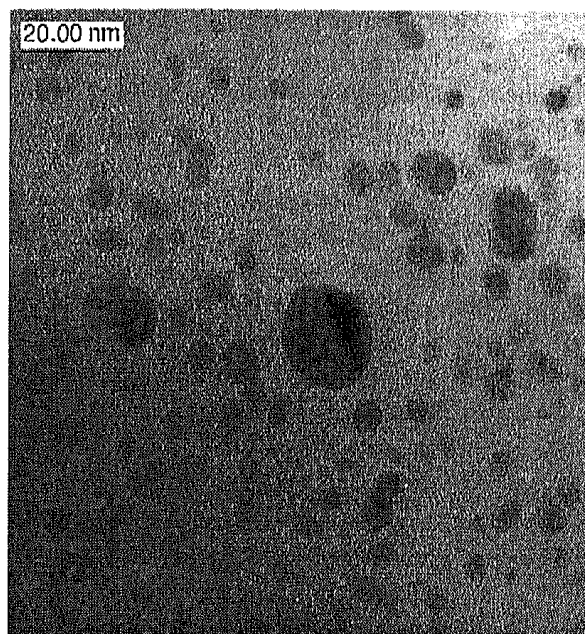
Figure 2. Amount of colloidal Ag of SiO<sub>2</sub>-coatings containing Ag in a molar ratio of Si : Ag = 15 : 1 densified between 120°C and 600°C in air on soda-lime and fused silica glass.

A mixture of methanol and DIAMO was used as a solvent for AgNO<sub>3</sub>, because silver is known to form stable ammine complexes. AgNO<sub>3</sub> was chosen as a precursor for silver because of the easy decomposition of nitrates during heating. The mixture of GPTS and TEOS as a SiO<sub>2</sub>-network forming sol was used because the organic compounds of the sol-precursors can act as a reducing agent and the organic compounds can easily be burnt off during thermal densification of the coatings [17, 18]. Thus, crackfree, transparent glass-like coatings up to 1 μm in thickness were obtained in air in a one-step coating process after the thermal densification. In order to reduce Ag<sup>+</sup>-Na<sup>+</sup>-ion exchange processes between the coating and the soda lime substrate at elevated temperatures, the molar ratio of Ag:DIAMO was chosen 1 : 1 to generate Ag colloids at rather low temperatures already. This molar ratio is also necessary to obtain sufficient solubility of Ag in the sol (molar Si : Ag-ratio = 15 : 1). Despite of the high ratio of complex formed, the activation energy of the Ag-colloid formation is low enough to form Ag-colloids during the drying of the coatings at 120°C in air. Yellow coloured coatings were obtained on both soda lime and fused silica substrates.

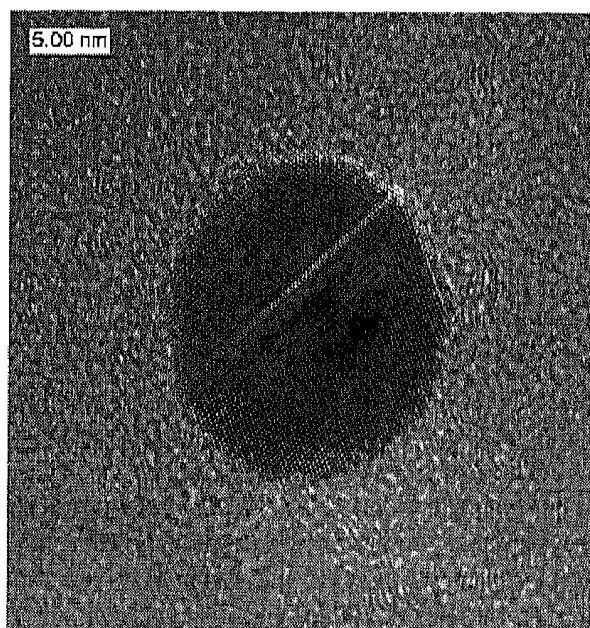
The change of the optical properties of the coatings during thermal densification between 120°C and 600°C in air and in a reducing atmosphere (H<sub>2</sub>/N<sub>2</sub>) was followed by UV-VIS spectroscopy. In a first approximation it was assumed that the peak areas,

determined from the products of full width at half maximum (FWHM) times peak absorbance, are directly proportional to the volume fraction of colloidal Ag independent on the colloid size. From calculated spectra the appropriate proportionality factor was determined ( $5,7 \cdot 10^{-8}$ ) and thus the relative volume fraction of Ag with regard to a complete conversion was determined as a function of the densification temperatures as shown in Fig. 2. It has to be taken into account that the refractive index of the coatings ( $n_e \cong 1,46$ ) is slightly changing during the thermal densification process because the organic compounds of the sol are burnt off, and additionally causing the formation of porosity. The influence of such slight refractive index changes on the absorbance spectra and therefore on the determination of the amount of colloidal Ag was also neglected. The uncertainty of this method can be estimated to be in the range of 10% to 15% only.

One can see that after drying at 120°C in air almost all of the Ag was converted to Ag colloids on both substrates. On soda lime glass, the amount of colloidal Ag decreases strongly with temperature and becomes zero at  $T \geq 400^\circ\text{C}$  (colourless coatings). HRTEM investigations showed that, after thermal treatment at 200°C in air, single-crystalline particles with a mean diameter of about 5 nm and some larger particles up to 20 nm in diameter with a bi-crystalline structure are formed and attributable to metallic silver as can be seen in Figs. 3(a) and 3(b).



(a)



(b)

Figure 3. (a) HRTEM picture of Ag-colloids in a SiO<sub>2</sub>-coating containing Ag with a molar ratio of Si : Ag = 15 : 1 densified at 200°C in air on a soda-lime substrate. (b) HRTEM picture of a bicrystalline Ag-particle in a SiO<sub>2</sub>-coating containing Ag densified at 200°C in air on a soda-lime substrate.

The coatings on fused silica do not show a significant difference in the absorbance spectra up to 200°C compared to coatings on soda lime glass. But at  $T \geq 400^\circ\text{C}$  Ag-colloids are still present in the coatings on fused silica. With increasing temperature a continuous decrease of the amount of colloidal Ag was observed reaching

a minimum at 500°C. Between 500°C and 600°C a remarkable increase of the amount of colloidal Ag takes place.

The fact that already formed colloids disappear has not been observed in Ag colloid containing melted glasses at comparable temperatures. For this reason, it is assumed that on both substrates the Ag-colloids, formed at a temperature of about 120°C, are oxidised to Ag<sub>x</sub>O<sub>y</sub> particles with increasing temperatures, but only on soda lime glass the oxidation of the Ag-colloids is completed. As shown in [19], a reversible change of the UV-VIS-spectra of Ag-colloids in a porous SiO<sub>2</sub>-matrix during heating in an oxidizing and a reducing atmosphere was observed and it was concluded that oxygen adsorbed at the colloid surface causes a change of the colloid shape responsible for the change of the absorbance spectra. The authors excluded an oxidation of the Ag-particles because bulk Ag<sub>2</sub>O is not stable above 400°C [20]. HRTEM investigations of coatings on soda lime glass thermal treated at 500°C in air revealed that poly-crystalline particles in the size range of 2 nm to 10 nm are obtained and that their electron diffraction pattern can be attributed to an Ag<sub>x</sub>O<sub>y</sub>-compound (Fig. 4). This means that Yanase's et al. formulated hypothesis could not be proved in the present system.

The increased stability of the Ag<sub>x</sub>O<sub>y</sub> colloids on soda lime substrates has either to be attributed to the glassy

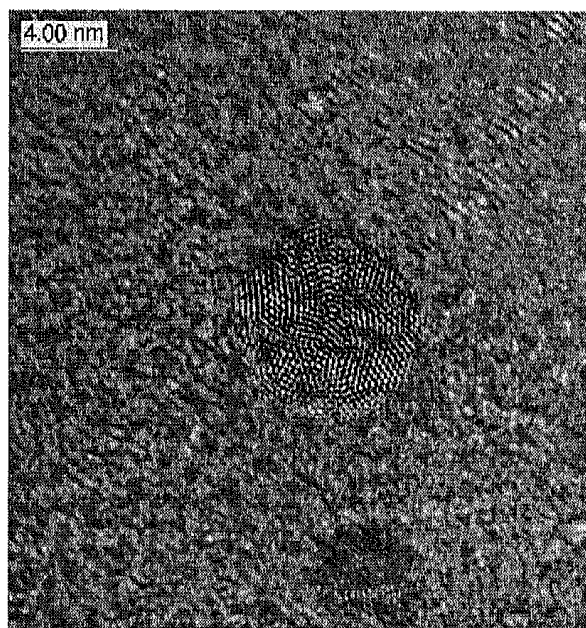


Figure 4. HRTEM picture of a polycrystalline Ag<sub>x</sub>O<sub>y</sub>-particle in a SiO<sub>2</sub>-coating containing Ag with a molar ratio of Si : Ag = 15 : 1 densified at 500°C in air on a soda-lime substrate.

matrix obtained by diffusion of  $\text{Na}^+$  into the porous  $\text{SiO}_2$  with an interface stabilisation effect or the effect of the formation of a glassy film around the particles with a strongly reduced  $\text{O}_2$  diffusivity. Another fact supporting the existence of an oxidised form of Ag at higher temperatures may be related to the basicity of the matrix system. As shown in [21], SNMS investigations of Au containing coatings proved a remarkable  $\text{Na}^+$  diffusion into the coatings above  $300^\circ\text{C}$  leading to a strong increase of the basicity [22], favouring higher oxidation states by thermodynamic reasons [23]. The decrease of the Ag colloid formation above  $400^\circ\text{C}$  on fused silica cannot be explained by the hypothesis shown in [19], since no deformation of Ag colloids could be detected. It also has to be attributed to a matrix stabilisation effect. Matrix stabilisation is a common phenomena in catalysis. For example it is possible to stabilize  $\text{Cr}^{6+}$  on  $\text{SiO}_2$  up to  $600^\circ\text{C}$  (otherwise decomposition to  $\text{Cr}_2\text{O}_3$  takes place above  $300^\circ\text{C}$ ). Above  $500^\circ\text{C}$ , the  $\text{Ag}_x\text{O}_y$  decomposition on fused silica begins.

A complete oxidation of the Ag-colloids and dissolution to single  $\text{Ag}^+$  ions, as it is observed in Ag containing glass melts, should lead to an ion exchange on a soda lime glass substrate at temperatures higher than  $400^\circ\text{C}$ . But this can be excluded from the fact that  $\text{Ag}^+$  ions after undergoing an  $\text{Na}^+$ - $\text{Ag}^+$ -ion exchange spontaneously are staining the glass yellow by an Ag-colloid formation, as observed on identical soda lime substrates during an  $\text{Ag}^+$ - $\text{Na}^+$ -ion exchange in a salt melt at  $400^\circ\text{C}$  for 4 h which does not take place with the Ag-containing coatings.

In order to investigate how far the discolouring process is reversible on soda lime substrates and on fused silica, the coatings fired for 1 h at  $500^\circ\text{C}$  in air were treated at temperatures between  $100^\circ\text{C}$  and  $600^\circ\text{C}$  (50 K-steps) for 1 h in a reducing atmosphere (volume fraction: 90%  $\text{N}_2$ /10%  $\text{H}_2$ ). HRTEM investigations showed that after thermal post-treatment in  $\text{N}_2/\text{H}_2$  for 1 h at  $500^\circ\text{C}$  the  $\text{Ag}_x\text{O}_y$ -nanoparticles are reduced to colloidal silver and single-crystalline Ag-particles in the range of 3 nm to 20 nm are detectable (Fig. 5).

UV-VIS absorbance spectra were measured and evaluated in the same kind as the UV-VIS spectra of the coatings fired in air. The results are plotted in Fig. 6 for coatings on soda lime glass and on fused silica.

Figure 6 shows that Ag-colloids in coatings on soda lime glass are formed at temperatures higher than  $300^\circ\text{C}$  and that a remarkable Ag-colloid formation is observed with increasing temperature. In case of the

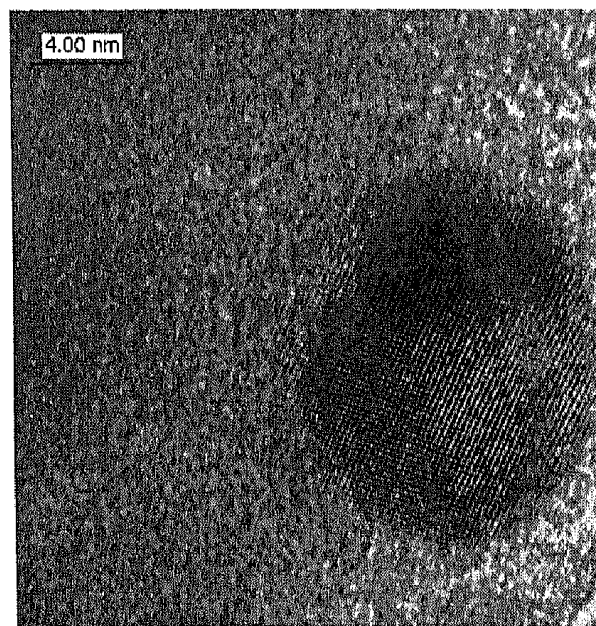


Figure 5. HRTEM picture of a single-crystalline Ag-colloid in a  $\text{SiO}_2$ -coating containing Ag with a molar ratio of  $\text{Si}:\text{Ag}=15:1$  densified at  $500^\circ\text{C}$  in air and then post-treated for 1 h in a reducing atmosphere (90%  $\text{N}_2$ /10%  $\text{H}_2$ ) at  $500^\circ\text{C}$  on a soda-lime substrate.

coatings on fused silica (Fig. 6) no remarkable change of the colloid concentration is observed up to  $300^\circ\text{C}$  in the reducing atmosphere. Above  $300^\circ\text{C}$ , the colloid concentration increases slightly compared to the soda lime substrates. At temperatures between  $500^\circ\text{C}$  and  $600^\circ\text{C}$  almost the same amounts of colloidal Ag are obtained on fused silica and on soda lime glass. For the determination of the Ag concentration on soda lime glass at  $600^\circ\text{C}$  the peak area was determined by a numerical method since very large particles were obtained causing a dominant light scattering effect. One can see in Fig. 6 that after 1 h treatment in a reducing atmosphere between  $500^\circ\text{C}$  and  $600^\circ\text{C}$  only 50% conversion to colloidal Ag can be obtained. In order to check whether Ag was evaporated during the heat treatments long term experiments at  $500^\circ\text{C}$  in  $\text{H}_2/\text{N}_2$  were carried out. Since a complete conversion could be obtained after 18 h a remarkable loss of Ag has to be excluded. In case of the post-heat treated samples on soda lime substrates the spectroscopic data were in good agreement with those obtained from calculated spectra using a computer model [15] based on the Mie-theory [16]. In coatings on fused silica the obtained absorbance bands were broad and showed long wavelength tails similar to those observed in [19]. In order to give a proper explanation for this difference further investigations using HRTEM and XPS will be necessary, but nevertheless

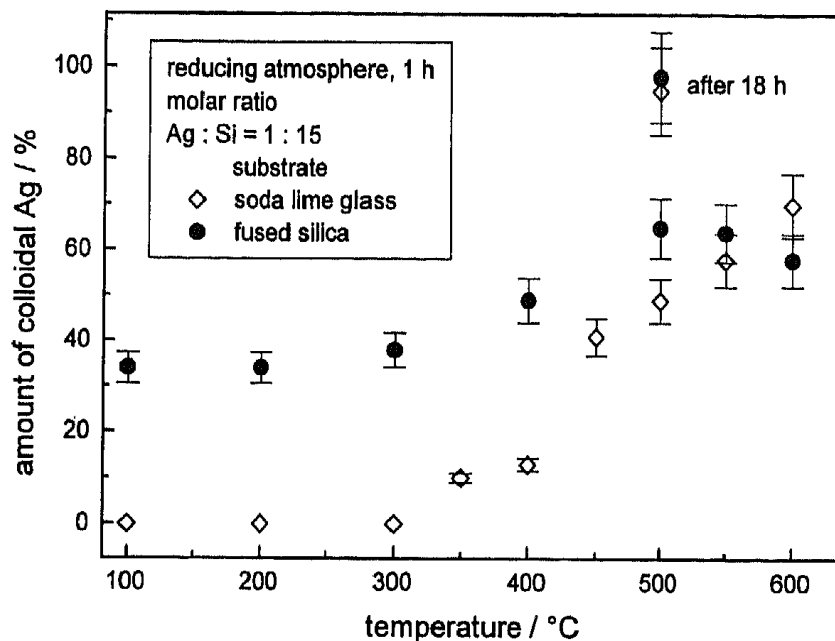


Figure 6. Amount of colloidal Ag of SiO<sub>2</sub>-coatings containing Ag in a molar ratio of Si:Ag = 15:1 densified first at 500°C in air and then post-treated for 1 h in a reducing atmosphere (90% N<sub>2</sub>/10% H<sub>2</sub>) between 100°C and 600°C on soda-lime and fused silica glass.

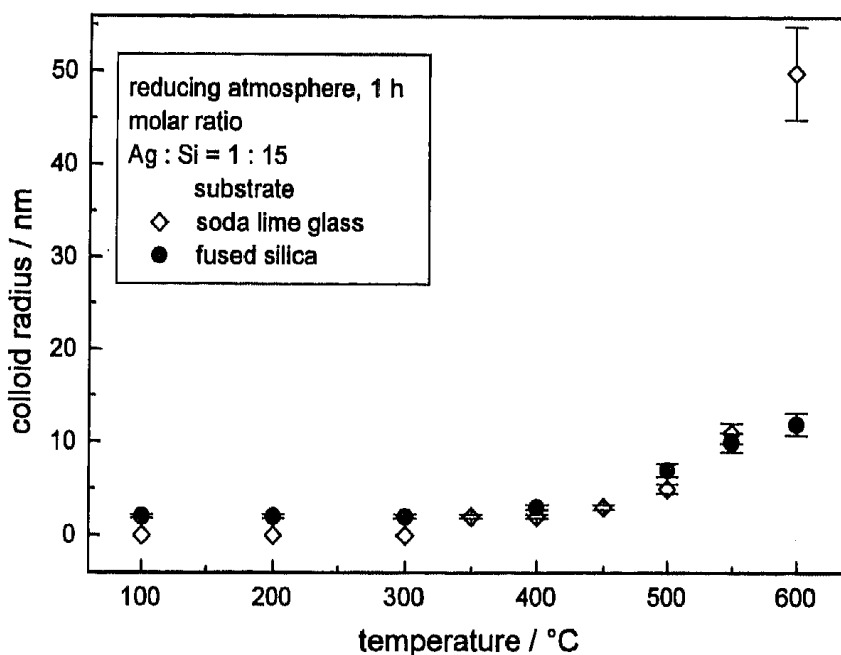


Figure 7. Colloid radii of Ag-colloids of SiO<sub>2</sub>-coatings containing Ag in a molar ratio of Si:Ag = 15:1 densified first at 500°C in air and then post-treated for 1 h in a reducing atmosphere (90% N<sub>2</sub>/10% H<sub>2</sub>) between 100°C and 600°C on soda-lime and fused silica glass.

the absorbance spectra were calculated with regard to the colloidal size as shown in Fig. 7.

On soda lime glass rather small colloids with radii <5 nm are formed during the thermal treatment between 350°C and 500°C. On fused silica similar colloids were present already before the post-heat treatment and the colloid size does not change significantly up to 400°C. For temperatures up to 550°C colloids of

about 7 nm in radius are obtained on both substrates. Only for 600°C a strong difference between both cases is obtained since very large colloids are generated in coatings on soda lime glass but not in coatings on fused silica. It is assumed that the Na<sup>+</sup>-content of the SiO<sub>2</sub> coatings on soda lime glass decreases the viscosity at 600°C to such an extent that Ostwald ripening can occur due to an increased diffusion coefficient of Ag. As

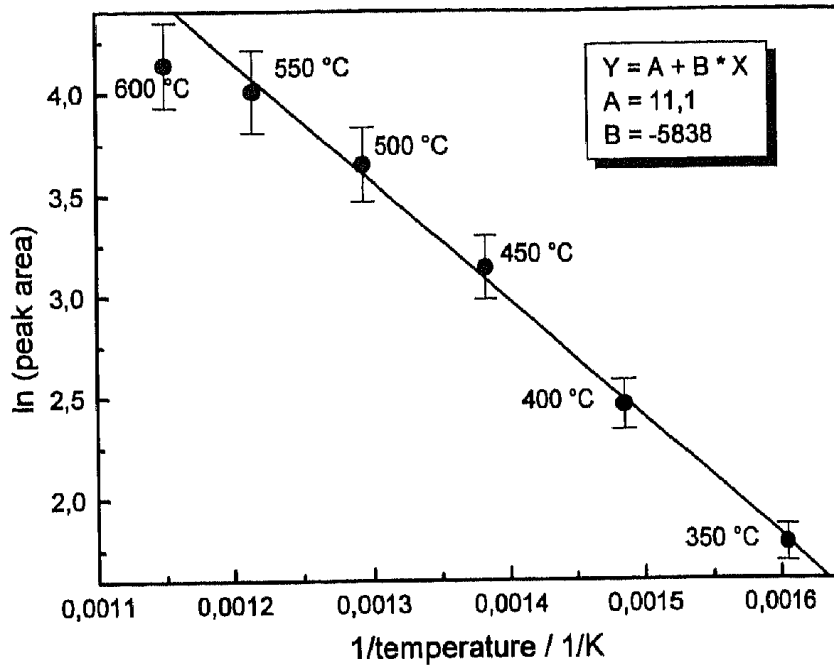


Figure 8. Arrhenius-plot of the peak areas of the UV-VIS-absorbance bands of  $\text{SiO}_2$ -coatings containing Ag in a molar ratio of Si : Ag = 15 : 1 densified first at 500°C in air and then post-treated for 1 h in a reducing atmosphere (90%  $\text{N}_2$ /10%  $\text{H}_2$ ) between 350°C and 600°C on soda-lime glass.

mentioned above, the long term treatment at 500°C lead to a complete conversion of  $\text{Ag}_x\text{O}_y$  particles and probably  $\text{Ag}^+$ -ions to Ag colloids but no remarkable particle growth could be determined from the appropriate spectra within the precision of the measurement and the applied method ( $\pm 1$  nm). Two possible explanations may be found for this surprising result. A small increase in particle size is not detectable in the UV-VIS spectra, because the peak position nearly remains unchanged and the FWHM decreases for a few nm only but it causes an enormous increase of the volume fraction of the colloids. For example, an increase of the colloid radius from 4 nm to 5 nm leads to an increase of the volume fraction of nearly 100%. That means that a growth of the Ag-colloids by diffusion and reduction of  $\text{Ag}^+$ -ions available in the matrix probably could not be detected. Another possible explanation might be the successive reduction of the  $\text{Ag}_x\text{O}_y$ -nanoparticles of Ag-colloids.

Since the results obtained so far indicate a colloid formation mainly by the reduction of  $\text{Ag}_x\text{O}_y$  particles and not by nucleation, diffusion and reduction of  $\text{Ag}^+$ -ions in the coatings, it was interesting to determine the activation energy for the colloid formation on the soda lime substrates as shown in Fig. 8 in which the logarithm of the peak area is plotted against the reciprocal absolute temperature.

For temperatures below 550°C a nearly linear relation is noticeable. Since the determination of the peak area of the sample treated at 600°C is doubtful this value was not taken into account. From the slope of the straight line in Fig. 8, an activation energy of about 48,5 kJ/mol can be evaluated for the Ag-colloid formation. Shelby and Vitko [24] determined an activation energy of about 120 kJ/mol for the Ag-colloid formation in ion exchanged glass in air. It seems plausible that the activation energy of the colloid formation in the sol-gel derived  $\text{SiO}_2$ -coatings is much less than in the case of glass, because  $\text{H}_2$  is a better reducing agent than polyvalent ions in glasses. For the future, it will be interesting to determine the activation energy for the colloid formation in soda lime glass in  $\text{H}_2/\text{N}_2$  atmosphere for comparison of the results obtained in the sol-gel coatings.

#### 4. Conclusions

The investigations show a new way for the formation of Ag-colloids in sol-gel derived glass-like coatings. A complete conversion of ionic silver to colloidal silver at low temperatures and the following oxidation to  $\text{Ag}_x\text{O}_y$ -nanoparticles and a suitable reduction process of these particles allow the control of the colloid size

in a wide range (5 nm to 100 nm). Furthermore a good technique for suppressing an  $\text{Ag}^+$ - $\text{Na}^+$ -ion exchange at higher temperatures may be achieved by this method. But further investigations, e.g., SNMS and XPS have to be undertaken to prove these assumptions.

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