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A SOL-GEL DERIVED AgCl PHOTOCROMIC COATING ON GLASSES

M. MENNIG, C. FINK, H. SCHMIDT

Institut für Neue Materialien, Saarbrücken, Germany

ABSTRACT

A new sol-gel synthesis route for the preparation of a transparent photochromic coating based on silver halide crystals is described. Therefore a sodium aluminoborosilicate sol synthesized for dip coating glass surfaces is used. Porous layers of about $2\ \mu\text{m}$ in thickness have been obtained after drying. Silver ions were introduced into the layer by an infiltration process with an aqueous silver nitrate solution, forming small silver colloids that can be converted into silver chloride particles by HCl vapour. The so prepared coatings show a reversible photochromic behaviour. After 15 minutes of UV illumination transmittance decreases from about 86 % to 36 %. The darkened coatings recover completely after thermal bleaching at about $400\ ^\circ\text{C}$. The reversible formation of silver colloids after UV irradiation could be followed directly by x-ray diffraction and electron microscopy. Surprisingly the photo efficiency is much higher in the prepared coating than in molten photochromic glasses.

INTRODUCTION

The sol-gel process is a low temperature route, enabling the synthesis of glasses and ceramics, new glass compositions and special products such as fibers, foils, monolithes, composites and coatings (1,2).

The preparation of photochromic sol-gel glasses or glass like materials is of particular interest. Levy et al. incorporated organic photochromic dyes (spiropyranes) in sol-gel matrices (3). The coatings cannot be densified to glasses without losing their photochromic properties due to the low thermal stability of the organic dye. In opposition to this, silver halide based photochromism in inorganic glasses is obtained through a controlled phase separation step at elevated temperatures (4-7). The question arises, whether it is possible to obtain similar properties by the sol-gel synthesis route. As already shown elsewhere (8,9) in principle it is possible to prepare photochromic sol-gel glass powders. In this paper it was investigated whether thin coatings can be obtained by this route.

EXPERIMENTAL

The sol for a glass composition of 59.5 mole-% SiO_2 , 20.5 mole-% B_2O_3 , 9.5 mole-% Al_2O_3 and 10.5 mole-% Na_2O (10) was synthesized by dissolving tetraethoxy silane and methyltriethoxy silane in ethanol at room temperature and hydrolysing it in the presence of 1 M nitric acid as a catalyst. Subsequently, the trimethyl borate was added dropwise at $50\ ^\circ\text{C}$. After stirring for 2 h the sol was cooled down and alumina isopropoxide and sodium methylate were

added. For increasing the thickness of the coatings ethylene glycol and hydroxypropyl cellulose were added to the sol as drying control chemical additives (11). Microscopy slides of soda lime glass and fused silica were coated by dipping at withdrawal speeds of about $20 \text{ cm}\cdot\text{min}^{-1}$ and dried for 15 minutes at $130 \text{ }^\circ\text{C}$, yielding to a thickness of about $2 \mu\text{m}$. After exposing the coating to a 0.1 M silver nitrate solution for 1 minute at $25 \text{ }^\circ\text{C}$ and drying for 30 minutes at $55 \text{ }^\circ\text{C}$ (the thickness decreased down to $1.2 \mu\text{m}$), the films were treated with HCl vapour at $25 \text{ }^\circ\text{C}$. The coatings were irradiated with a 700 W mercury-xenon-lamp at a distance of about 30 cm and then kept at temperatures between 100 and $400 \text{ }^\circ\text{C}$ for 30 minutes. The photochromic properties were investigated using UV/VIS-spectroscopy and the crystalline precipitates within the coatings were characterized by x-ray diffraction and transmission electron microscopy. The infiltration process was investigated by atomic emission and atomic absorbance spectrometry and energy disperse x-ray analysis.

RESULTS AND DISCUSSION

The Ag concentration in molten photochromic glasses ranging from about 0.1 to 1 weight-% (12, 13) are too small for remarkable colouring effects in a thin layer. Because the colouring efficiency of AgCl in a sol-gel matrix was not known, high Ag concentrations were applied first. Therefore either a sol containing high concentrations of Ag^+ can be used or the Ag can be infiltrated into the pores of a predried silver free gel using a soluble Ag compound. For the conversion into AgCl Cl^- ions have to be introduced through a liquid or a gaseous phase. We chose the gaseous infiltration route to prevent migration and coagulation of the AgCl particles.

By EDX analysis it could be proved that during the AgNO_3 infiltration an ion exchange between Ag^+ and Na^+ took place, because the Na^+ signal was decreased drastically after the infiltration. This result is supported by AAS and ICP analysis. The molar silver content of the layer (about $1.1 \mu\text{mole}/\text{cm}^2$) was significantly lower than the former Na^+ content (about $6.1 \mu\text{mole}/\text{cm}^2$). A comparison with an adequate infiltration experiment in pure water (same pH-value) showed a weight loss of the layer of about 60% that could be related either to the ionic exchange between Na^+ and H_3O^+ and/or the dissolution of the gel layer caused by pH increase from leached Na^+ ions. The silver content introduced by infiltration is roughly estimated to be in the range of $3 - 4$ weight-% (molten photochromic glasses: $0.1 - 1$ weight-%). It can be expected that the incorporation of Ag instead of Na also changes the thermochemical behaviour (T_g) of the gel layer and therefore influences the densification. This important point of view has to be the subject of further investigations.

The transparent Na-Al-B-Si-coatings showed different colours after the infiltration in silver nitrate and subsequent drying. They were slightly brown at lower drying temperatures and turned to dark brown at $100 \text{ }^\circ\text{C}$. Figure 1 represents the UV /VIS spectra of these coatings in

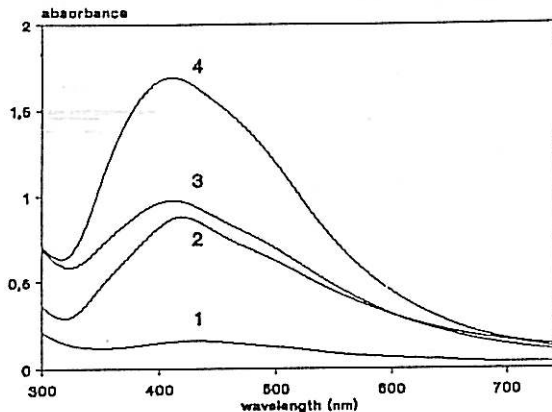


Figure 1. Optical absorption spectra of sodium aluminoborosilicate coatings after AgNO_3 infiltration and different temperatures of drying 1) 50°C 2) 60°C 3) 70°C 4) 100°C

and 425 nm (14,15), which fits quite well to the spectra given in Fig. 1.

After treatment with HCl -vapour at room temperature the transformation to silver chloride took place as detected by a colour change from brown to colourless till slightly milky white and proved by x-ray diffraction. But this conversion was only possible in the films heat treated at 50 or 60°C after Ag infiltration. At higher temperatures than 60°C no transformation of the silver colloids to silver chloride was observed by UV/VIS spectroscopy. The reason for this behaviour is not clear and will be a subject of further investigations.

The photoirradiated coatings turned brownviolet as observed in previous studies on powders (8). Figure 2 shows the transmission spectra of a nonirradiated and the darkened coatings after different irradiation times. The transmission at 545 nm (highest sensitivity of the human eye) continuously decreases with increasing irradiation time, down to 36% after 15 minutes and to 28% after 2 hours (saturation). Comparing the darkening effects, a typical molten photochromic glass (Corning, HC-SB, $0.213\text{ weight-\% Ag}$ as analysed by AAS) was irradiated under same conditions of illumination. From the measured optical densities at 545 nm wavelength and the thicknesses of the photochromic glass and the sol-gel coating respectively the coefficient of extinction (k) was calculated it has been shown, that its value for the molten glass ($k = 2.21\text{ cm}^{-1}$) can be multiplied by 300 compared to the prepared coating ($k = 633\text{ cm}^{-1}$). Because the silver concentrations are different in the two materials these k values were related to the total amount of Ag in the appropriate materials obtaining of $47\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for the molten glass and $932\text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for the coating respectively. These values in the dimension of the molar coefficient of extinction represent the photo efficiency of the two

the region from 300 to 740 nm as a function of the drying temperature. All four coatings showed a broad absorption band peak at a wavelength of 410 nm . With elevated drying temperature the intensity of the peak increases. An interpretation can be given by comparing the spectra with those of silver colloids in glasses from melts. These colloids (around $1\text{-}3\text{ nm}$ in diameter) show broad bands (half band widths $> 100\text{ nm}$) with peaks between 410 and

materials and it is clearly to be seen that photo efficiency of the prepared coating is surprisingly much higher than of the glass in this example.

In comparison to the silver colloid containing films (Fig. 1) the optical spectra in Fig. 2

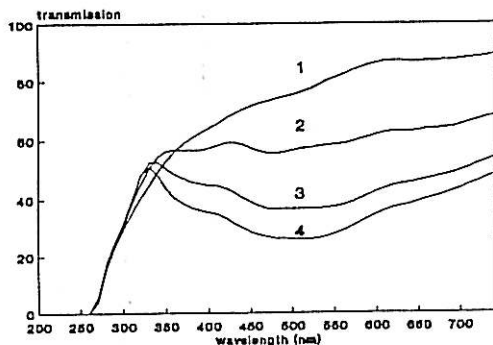


Figure 2. Transmission spectra of the darkened coatings at different irradiation times 1) 0 min 2) 1 min 3) 15 min 4) 2 h

also depicts principle changes. They are characterized by broad absorption bands between 360 and 600 nm as observed in molten photochromic glasses doped with silver halides (12,16).

After irradiation the coatings do not recover at room temperature, they had to be bleached thermally. Raising the temperature stepwise (30 minutes) up to 400 °C in air the initial values of the transmission spectra are reached (100 °C: 30 %, 200 °C: 36 %, 300 °C: 52 %, 400 °C: 86 %).

The process was repeated for 30 times without observable decay. The mechanisms for the slow recovery behaviour are not clear so far, but from literature is known that high silver containing glasses recover very slowly too. Therefore the process has to be investigated as a function of glass composition and Br⁻ and Cu⁺ addition. At temperatures of about 500 °C the AgCl decomposed and the coatings became yellow forming silver colloids.

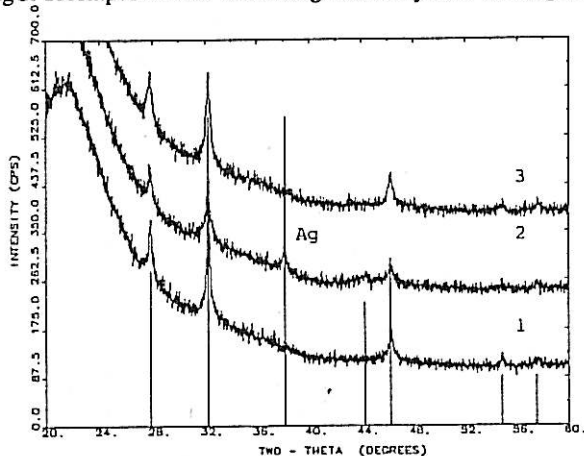


Figure 3. x-ray diffraction spectra of AgCl-containing coating on fused silica: 1) before, 2) after 15 min UV and 3) after thermal treatment

Figure 3 shows the x-ray diffraction spectra of a coating deposited on fused silica before irradiation, after 15 min irradiation with UV and after thermal treatment.

The position and the intensity of the observed peaks correspond to the JCPDS data as one would expect for crystalline silver chloride. The darkened coating (2 in figure 3) has an additional peak at about 38° identified as crystalline silver. Correspondingly, the intensities

of all AgCl-peaks decreased. After the coating was thermally bleached, the intensities of the AgCl-peaks increased again while the silver peak disappeared. The diffraction pattern proves that during UV-irradiation a transformation from AgCl to Ag colloids occurred, which was observed to be reversible by thermal treatment.

The d-spacings calculated from the diffraction pattern of appropriate electron micrographs correspond to crystalline silver. A broad particle size distribution is obtained by picture analysis of the micrographs. The average crystallite size of the crystalline silver formed during irradiation is about 5.1 nm.

CONCLUSIONS

The present work has shown that it is principally possible to generate optically transparent silver halide based photochromic coatings on glass by the sol-gel route. The starting point is the synthesis of the sodium aluminoborosilicate sol. By the described infiltration step a sufficient silver content for remarkable optical effects could be achieved, but the key for realising photochromic properties is the exact control of silver colloids formed within the coating, responsible for the appropriate formation of the Ag-halide phase. The high concentration of AgCl in the relatively thin coating obtained by sol-gel also allows interesting analysis of the photochromic process by direct imaging of Ag formation by x-ray diffraction. This has to be investigated systematically and statistically insured by further investigations. The bleaching kinetics of the so prepared coatings are not satisfying yet, but one can be optimistic to improve them by using sensitizers as for instance Cu^+ or by generation of a mixed crystal phase with other halides. Increasing the kinetics, the darkening effect decreased (17), but we are encouraged preparing sol-gel derived thin coatings, relating to the much higher efficiency of the photochromic effect than in molten glasses. Another powerful tool should be the control of the microstructure of the matrix during densification.

Therefore future experiments will focus on the optimization of the synthesis and process parameters for the development of systems with predetermined photothermal behaviour with respect to applications in the field of smart materials.

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