

## Photochromic materials via sol-gel process<sup>1)</sup>

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Powders and thin films of photochromic glasses containing AgBr or AgCl microcrystals were synthesized via sol-gel process. Up to 10 wt%, of Ag<sup>+</sup>, bonded with suitable complexing agents, were introduced into the matrix system consisting of  $x\text{SiO}_2-(1-x)\text{Al}_2\text{O}_3$  ( $x = 0.7\dots 1$ ). After drying and heat treatment the AgX microcrystals (X = Cl, Br) were characterized by X-ray diffraction and high-resolution TEM. The photochromic properties were measured using a diode array UV-VIS spectrometer.

### Fotochrome Materialien über den Sol-Gel-Prozeß

Mit Hilfe der Sol-Gel-Technik gelang es, glasige fotochrome Pulver und Schichten mit AgBr- bzw. AgCl-Mikrokristallen herzustellen. Dem Matrixsystem, bestehend aus  $x\text{SiO}_2-(1-x)\text{Al}_2\text{O}_3$  ( $x = 0,7\dots 1$ ), wurden bis zu 10 Masseprozent komplexchemisch gebundenes Ag<sup>+</sup> zugesetzt. Die nach Trocknung und Temperung erhaltenen AgX-Mikrokristalle (X = Cl, Br) wurden mittels Röntgenbeugungsanalyse und elektronenmikroskopischen Untersuchungen charakterisiert. Die Messung der fotochromen Eigenschaften erfolgte mit einem Diodenarray UV-VIS-Spektrometer.

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## 1. Introduction

Sol-gel derived materials like powders, bulk glasses or thin coatings offer a larger number of new applications [1]. An important field is the surface refinement of glasses, metals or organic materials with thin layers [2 to 4]. Compared with molten photochromic glasses the specific advantages of the sol-gel process, low preparation temperature and more variation possibilities of the matrix system, allows the production of materials with higher concentrations of photoactive components.

But the basic disadvantage of the process is the spontaneous precipitation of the insoluble noble metal halides. Therefore, it is necessary to stabilize the light-sensitive components in the sols by complexation with suitable chelating agents. Such compounds have to fulfil special demands like high solubility and stability in the system and no self-coloration. The complexes have to bind to the gel network and should be decomposed in the temperature range of final heat treatment.

Another precondition is an inert matrix around the photochromic microcrystals (without double bonds, solvent residues or reactive groups) to prevent the irreversible bond of irradiation products. The crystals should have an optimal size of 10 to 50 nm in diameter.

Furthermore, they should be chemically disordered, e.g. through the introduction of ions like Cu<sup>2+</sup>, S<sup>2-</sup> or Cd<sup>2+</sup> or the formation of mixed crystals.

## 2. Experimental

A mixture of water and nitric acid and in some cases aluminium compounds (aluminiumtri-sec-butylate or aluminium-n-butylate) was added to a base system consisting of tetraethoxysilane (TEOS) and ethanol. The molar ratios of water and alcoxide, solvent and alcoxide and the pH values were varied in wide ranges.

Up to 10 wt% Ag<sup>+</sup> were introduced as activator component into this matrix system of  $x\text{SiO}_2-(1-x)\text{Al}_2\text{O}_3$  ( $x = 0.7\dots 1$ ). The complexation of Ag<sup>+</sup> was carried out with amino-substituted silicon alcoxides (3-aminopropyltriethoxysilane, n-(2-aminoethyl-3-aminopropyl)-trimethoxysilane, trimethoxysilylpropyl-diethylenetriamine). The halide ions were introduced using chloro- or bromoaryl substituted silicon alcoxides like chlorophenyltriethoxysilane, bromophenyltrimethoxysilane or (4-bromophenoxy)-trimethylsilane. Copper ions (as copper(II) acetate monohydrate) were used as coactivating agent. The molar ratios were as follows: Ag<sup>+</sup>: X<sup>-</sup> = 1:3; Ag<sup>+</sup>: Cu<sup>2+</sup> = 10:1 and chelating agent: Ag<sup>+</sup> = 3:1.

Powders which show photochromic properties were obtained after gelation, drying and heat treatment of the sols. By addition of drying control chemical additives

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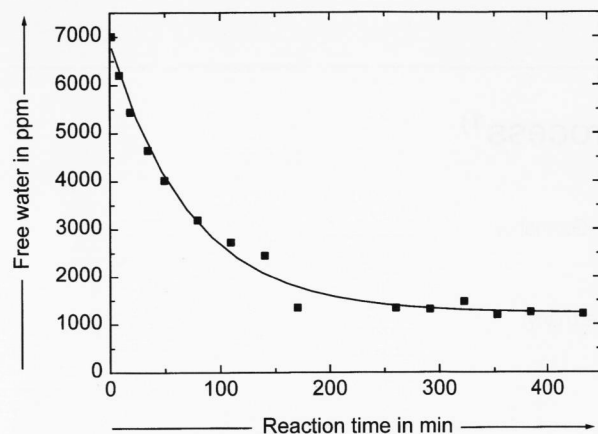


Figure 1. Content of free water versus reaction time of a sol with  $r_w = 0.95$ .

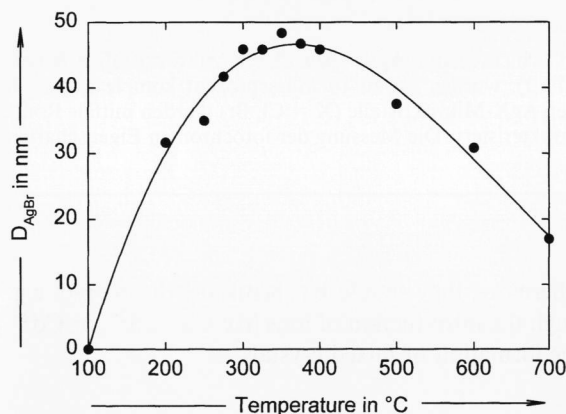


Figure 2. Diameter of precipitated AgBr crystals as function of heat treatment.

bulk glasses were made. Moreover, single- and multilayer coatings on various substrates were prepared by dip coating of the mentioned sols at withdrawal speeds of 5 to 30 cm/min. In order to increase the film thickness, in some cases the tetraethoxysilane was partly or completely replaced by 3-glycidoxypropyltrimethoxysilane. After dipping the coatings were dried at 100 °C and then heat-treated at 250 °C and 350 °C for each one hour. The layers densified in this way were analyzed by X-ray diffraction and high-resolution electron microscopy to determine the size and distribution of the precipitated crystals.

In order to investigate their photochromic properties the coatings were irradiated with a 150 W XBO-lamp for several times and simultaneously the darkening behaviour and optical bleaching were measured with a photodiode array UV-VIS spectrometer. The fading at higher temperatures was analyzed using a microscope heating stage.

### 3. Results and discussion

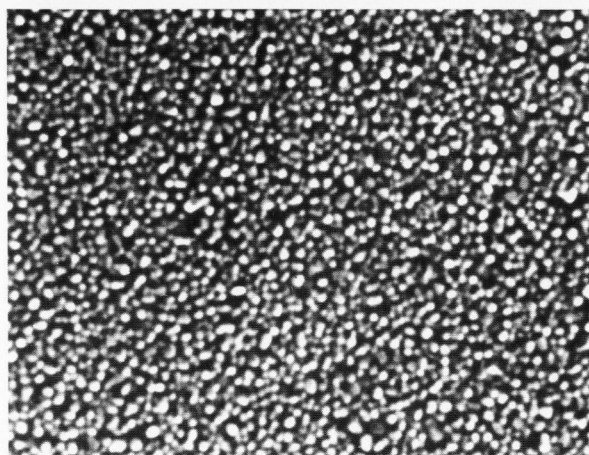
The authors have shown in a previous work [5] that only by complexation of both photoactive components a spontaneous precipitation of large silver halide crystals can be prevented. Since silver atoms act as a soft Lewis acid, compounds with soft ligands (e.g. nitrogen- or sulphur-coupling atoms) are best suited for their complexation. Due to the  $S_N2$  mechanism of the  $X^-$  against  $OH^-$  substitution, aromatic compounds are more stable against attacks of water or solvents than aliphatic molecules. Therefore, the best halide supplier are chloro- or bromoaryl substituted silicon alcoxides.

Using bromophenyltrimethoxysilane, chlorophenyltriethoxysilane or (4-bromophenoxy)trimethylsilane as halide supplier and 3-aminopropyltriethoxysilane or n-(2-aminoethyl-3-aminopropyl)-trimethoxysilane as complexing agent, any crystal formation at room temperature was avoided. Due to the new preparation techniques and the mentioned sol compositions no prehydrolysate consisting of TEOS, water, nitric acid and solvent is necessary. The halide carrier is now homogeneously distributed in the matrix network and smaller crystals are generated. In the case of progressed condensation processes of network through the pre-hydrolysis, the binding of bulky photoactive components takes place at the surfaces of formed clusters.

To control the content of free water in the final sols, the water determination with the Karl Fischer technique [6] was carried out. Figure 1 shows the relation between water content and reaction time of a sample with  $r_w = 0.95$  ( $r_w$  = molar ratio of water to alcoxide). The water content decreases with increasing reaction time and reaches a stable value after about 5 h. At this time the hydrolysis process is almost finished and coatings of uniform quality can be drawn.

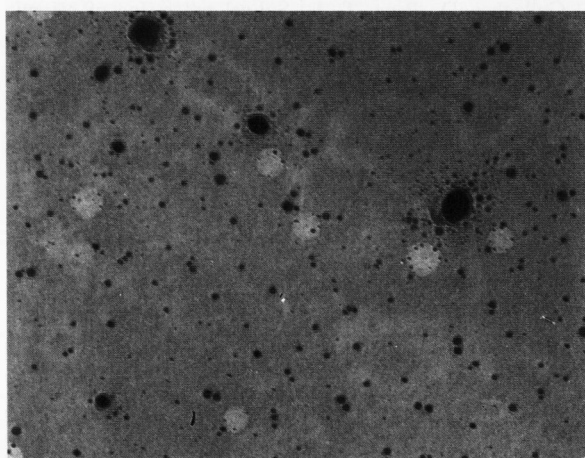
During the heat treatment the release of bonded silver and halide takes place and leads at  $T > 150^\circ\text{C}$  to AgX crystals of average diameters of 20 to 50 nm depending on the sample thickness. Figure 2 demonstrates the influence of annealing temperature on the particle size for a photochromic powder containing bromophenyltrimethoxysilane and n-(2-aminoethyl-3-aminopropyl)-trimethoxysilane. The particle size was calculated from X-ray patterns. Due to the effective binding of photoactive components at room temperature, no AgBr crystals are detectable. Up to about 400 °C the average crystal diameter increases with increasing temperature, above 400 °C evaporation of AgBr becomes more and more important and the crystal size decreases again. Due to the rather low sample thickness, the crystals of the coatings are smaller and therefore surface evaporation of photoactive components plays a more important role.

Figure 3 shows the scanning electron micrograph of a heat-treated photochromic layer prepared by use of bromophenyltrimethoxysilane and n-(2-aminoethyl-3-aminopropyl)-trimethoxysilane. The silver content was 10 wt% and the coating thickness about 800 nm. The



500 nm

Figure 3. Scanning electron micrograph of a heat-treated photochromic layer containing AgBr crystals



125 nm

Figure 4. Electron micrograph of a heat-treated photochromic layer containing AgBr crystals

sample surface is completely covered with AgBr microcrystals, the average crystal size is in the range of 40 to 50 nm. Atomic force microscopy measurements showed that these crystals stick out of the coating surface to 1/5 to 1/10 of their size. High-resolution electron microscopy indicated that besides them a fraction of smaller crystals (5 to 10 nm in diameter) exists inside the layers (figure 4). Intermediate crystal sizes beyond these populations were not found. The two average crystal sizes are probably caused by different nucleation places of different growing times of AgBr during the heat treatment. Preparation effects can be excluded, because different techniques (dimpling and ion etching, elutriation) gave the same results. A more exact investigation of these effects will be the subject of future works.

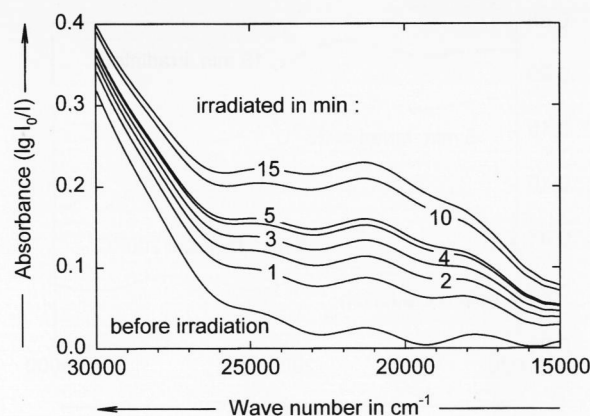


Figure 5. Darkening behaviour of an 800 nm thick coating.

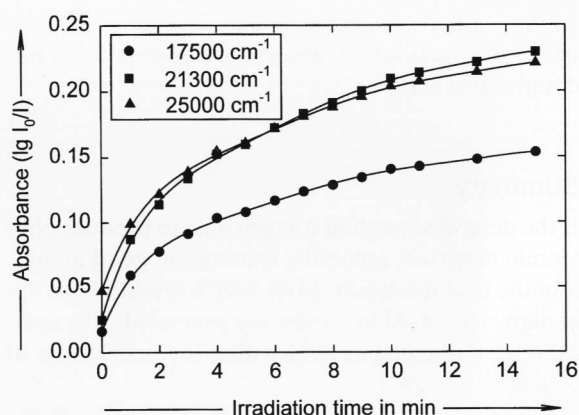


Figure 6. Darkening as function of irradiation time of an 800 nm thick coating.

The photochromic behaviour of the coatings was examined by irradiation with an XBO lamp and subsequent optical bleaching. Figure 5 presents the absorbance spectra of an irradiation process of an 800 nm thick coating. The lowest curve shows the state before irradiation; the time interval between the following spectra was one minute respectively. It can be seen that the layers reach a 50% darkening in the first 15 min with a half darkening time of 2 min. This corresponds to an absorption coefficient of about  $5500 \text{ cm}^{-1}$  at a wave number of  $21300 \text{ cm}^{-1}$ . Figure 6 presents the absorbance values as function of the irradiation time for the three curve maxima (at  $17500 \text{ cm}^{-1}$ ,  $21300 \text{ cm}^{-1}$  and  $25000 \text{ cm}^{-1}$  of the nonirradiated sample). It shows that during the first 15 min of irradiation process no saturation level is reached. The darkening proceeds rather slowly.

After irradiation is finished the coatings show a noticeable fading even at room temperature, about 10% during the first 5 min. Total fading can be achieved by thermal bleaching at  $200^\circ\text{C}$  for 5 min (figure 7). The coatings show good long-term stability during the irradiation process. A tenfold irradiation and thermal

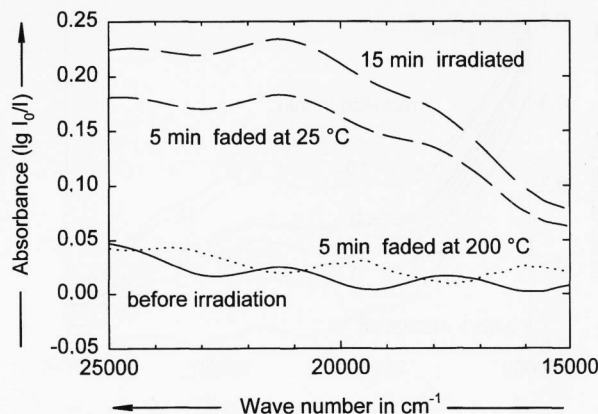


Figure 7. Fading behaviour of an 800 nm thick coating.

bleaching caused no considerable changes but only statistical fluctuations of absorbance spectra of darkened and faded state.

#### 4. Summary

With the described method it is possible to produce photochromic materials, especially coatings, in good quality. During the heat treatment, silver halide crystals with optimal diameters of 40 to 50 nm are generated. The coatings show a darkening of 50% within the first 15 min of

UV irradiation, the half darkening time amounts to 2 min. After irradiation is finished, the coatings exhibit even at room temperature a fading of 10% within the first 5 min. A complete fading of the samples is reached through thermal treatment at 200 °C.

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#### 5. References

- [1] Mackenzie, J. D.: Applications of sol-gel methods for glass and ceramics processing. In: Hench, L. L.; Ulrich, R. R. (eds.): *Ultrastructure processing of ceramics glasses and composites*. New York: Wiley, 1984, p. 15–26.
- [2] Uhlmann, D. R.; Rajendran, G. P.: Coatings: the land of opportunity for sol-gel technology. In: Mackenzie, J. D.; Ulrich, D. R. (eds.): *Ultrastructure processing of advanced ceramics*. New York: Wiley, 1988, p. 241–253.
- [3] Brinker, C. J.; Hurd, A. J.; Schunk, P. R. et al.: Review of sol-gel thin film formation. *J. Non-Cryst. Solids* **147 & 148** (1992) p. 424–436.
- [4] Gallagher, D.; Ring, T. A.: Sol-gel processing of ceramic films. *Chimia* **43** (1989) p. 298–304.
- [5] Kriltz, A.; Müller, M.; Facht, R. et al.: Glassy photochromic layers produced by sol-gel process. *Mol. Cryst. Liq. Cryst.* **297** (1997) p. 41–48.
- [6] Hydranal® – Praktikum: Wasserreagenzien nach Eugen Scholz für die Karl-Fischer-Titration. Riedel-de-Haën, Seelze, 1987.

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