

Sol-gel derived coatings with completely reversible photochromism

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Besides the photochromic glasses based on silver halides especially the cuprous halide containing materials are of practical importance. Due to their high absorption coefficient the cuprous halides are particularly suited for the preparation of thin photochromic films.

Using the sol-gel technique silicon alkoxide based coating solutions with continuously distributed photoactive components were prepared. From these sols single or multilayer coatings were produced by dipping. The precipitation of the cuprous halide microcrystals as carriers of the photochromic properties of the coatings proceeded during a subsequent heat treatment (temperature range of 100 to 800°C). Thus it was possible for the first time to produce photochromic coatings with a pronounced darkening and with complete reversibility of the photochromic reactions at room temperature.

Vollständig reversible Fotochromie in Sol-Gel-Schichten

Neben den fotochromen Gläsern auf Silberhalogenidbasis besitzen die silberfreien, kupferhalogenid-enthaltenden Gläser besondere Bedeutung. Aufgrund des höheren Absorptionskoeffizienten der Kupferkolloide sind solche Materialien zur Herstellung dünner fotochromer Schichten gut geeignet.

Mit Hilfe der Sol-Gel-Technik wurden Beschichtungslösungen auf Siliziumalkoxidbasis mit homogen verteilten fotoaktiven Komponenten erhalten. In den daraus hergestellten Tauchschichten erfolgte die Abscheidung der Kupferhalogenidkristalle während der Wärmebehandlung im Temperaturbereich von 100 bis 800°C. Auf diese Weise gelang es erstmals, tief eindunkelnde Materialien mit vollständiger Reversibilität des fotochromen Prozesses bei Raumtemperatur zu erzeugen.

1. Introduction

In contrast to the manufacturing of molten photochromic glasses, the preparation via sol-gel process is a fairly new field of research. The investigations concentrate on the precipitation of noble metal halide crystals in an oxide glass. In this way materials can be created which show a certain darkening under the influence of actinic radiation.

The greatest problem up to now was the control of the fading reactions. So far, the fading of materials, e.g. the restoration of the initial state, was possible only by an additional temperature treatment [1 to 3]. In this publication we present a way to produce photochromic coatings via sol-gel process with completely reversible photochromic reactions at room temperature.

Photochromism is defined as a light-induced, reversible change of the absorption state of a material. There are various classes of substances showing photochromic properties. The most important ones are, on the one hand, organic compounds like spiropyranes, acetanilides or fulgides [4 to 6]. On the other hand, there are the nanocrystals embedded in an inorganic matrix. Among them, the noble metal halides are of special importance.

The preparation of such materials is possible both by melting and by sol-gel process. The sol-gel process shows some specific advantages [7 to 9], above all the lower synthesis temperatures, connected with smaller evaporation losses of the photoactive substances. Further more, the sol-gel route allows a wider variation of the composition of the basic glass and makes it easier to modify the material properties.

Because of the comparatively low process temperatures, no stabilization of the photoactive substances in the system is necessary and so they can be incorporated into the sol-gel materials in considerably higher concen-

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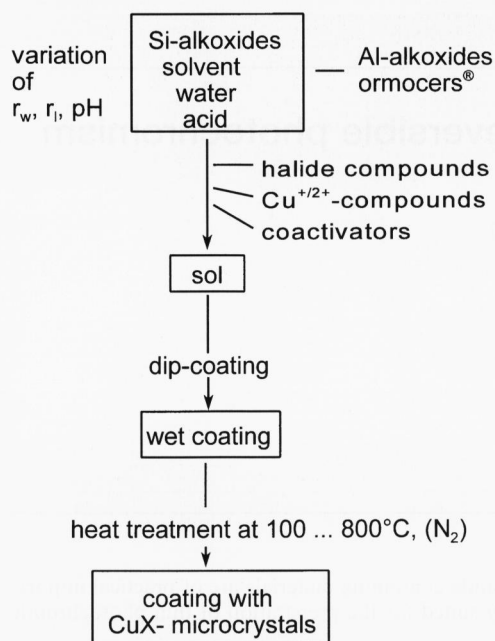


Figure 1. General preparation pattern of photochromic copper halide containing coatings; r_w : molar ratio of water to alkoxide, r_l : molar ratio of solvent to alkoxide.

trations. For this reasons, the sol-gel process is suited for the additional surface modification with thin coatings, whereas systems with cuprous halide crystals exhibit a particular suitability [10 and 11]. Their higher absorption coefficients compared to silver halides lead to a pronounced gradient in darkening. The subsurface layers show a very strong darkening and protect deeper areas from UV light. Therefore, it should be possible using copper halide containing materials to achieve a deep darkening at comparatively low film thicknesses.

In order to possess photochromic properties, a material has to fulfil special demands, such as an inert matrix around the photochromic crystals which shows no reaction with the products of the photodarkening. The crystal size should amount from to 10 ... 50 nm in diameter and the crystals should be disordered, e.g. by implanting of foreign ions or by forming of mixed crystals.

2. Experimental

Figure 1 shows the general pattern of the synthesis of cuprous halide containing coatings via sol-gel process. The basic composition consists of partially substituted silicon alkoxides in a suited solvent. The hydrolysis is acid-catalyzed. The sol composition, especially the amounts of water and solvent, as well as the pH value can be widely varied.

To modify the film properties, it is possible to add other alkoxides as well as inorganic-organic hybrid polymers, the so-called ORMOCERS®. The copper com-

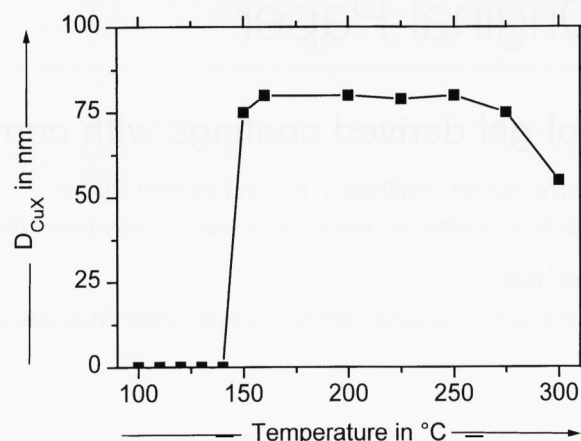


Figure 2. Diameter of precipitated photochromic crystals as a function of the temperature of heat treatment.

pounds may be introduced either in form of complexes or directly as dissolved copper(I) or copper(II) compounds. Besides chlorine- and bromine-substituted organic substances we used hydrochloric and hydrobromic acid and their mineral salts, respectively. Afterwards the addition of coactivating agents is carried out.

From the sol received in this way single or multilayer coatings on various substrates can be prepared. A following heat treatment in a temperature range between 100 and 800°C is necessary to obtain cuprous halide microcrystal containing photochromic coatings.

3. Results and discussion

A better handling of the sols and coatings as well as a controlling of the photochromic properties requires that the formation of crystals in the layers proceeds not during the synthesis but only during the subsequent heat treatment.

Figure 2 shows investigations of the crystallization in cuprous halide containing dip-coatings. The crystal diameter, calculated from X-ray diffraction pattern, was plotted versus the temperature of heat treatment. It can be seen that the crystal precipitation starts as desired only at heating temperatures of more than 150°C. At first, the crystals grow slowly with increasing temperature. With further temperature rise, evaporation losses lead to a continuous reduction in the crystal size. Besides the crystal size, the amount of precipitated cuprous halide influences the photochromic properties. Figure 3 presents the areas of the 100 % peaks of the X-ray patterns as a function of the temperature of heat treatment. A precipitation maximum was found at a temperature of about 250°C. With increasing temperature a growing surface opalescence is to be observed.

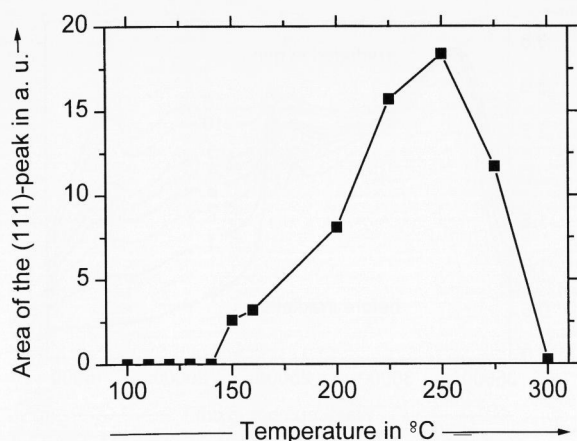


Figure 3. Amount of precipitated copper halide as a function of the temperature of heat treatment.

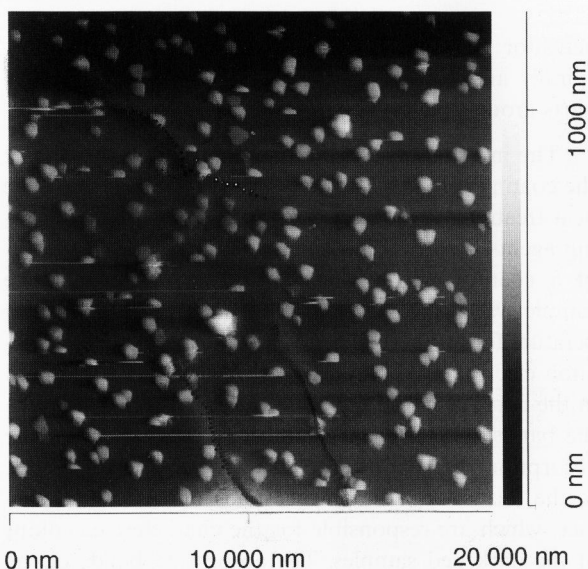


Figure 4. AFM of the surface texture of a copper halide containing coating without coactivators, heat-treated at 150 °C.

Besides electron microscopy, the atomic force microscopy is especially suited for the characterization of the coating surfaces. Figure 4 shows an atomic force micrograph (AFM) of the surface texture of a copper halide containing dip-coating which was prepared from a sol without coactivators. The sample was heat-treated at 150 °C for 10 min, e.g. in the initial stage of the crystal precipitation. The micrograph shows the photochromic crystals embedded in a silica matrix. The crystals jut out from the coating surface to about 200 nm. The average crystal size amounts to about 70 nm. It can be seen that in these conditions the matrix content is large compared with the content of crystals.

With rising temperature of heat treatment, the crystal precipitation increases, as already stated for the X-ray diffraction measurements. In figure 5, an atomic force micrograph is presented for a sample which was heat-

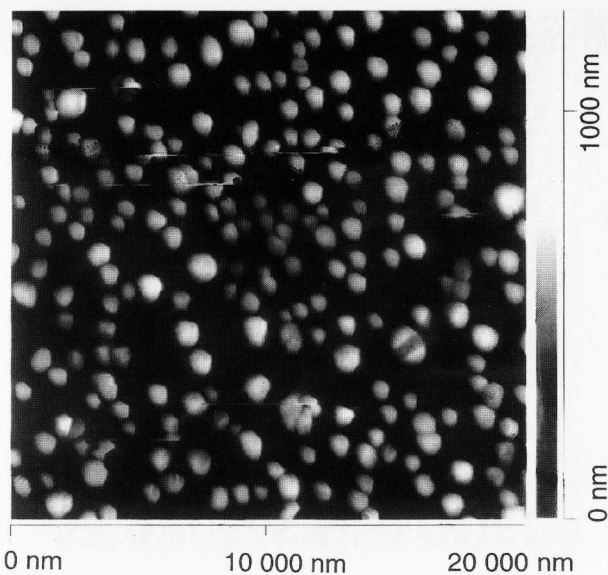


Figure 5. AFM of the surface texture of a copper halide containing coating without coactivators, heat-treated at 200 °C.

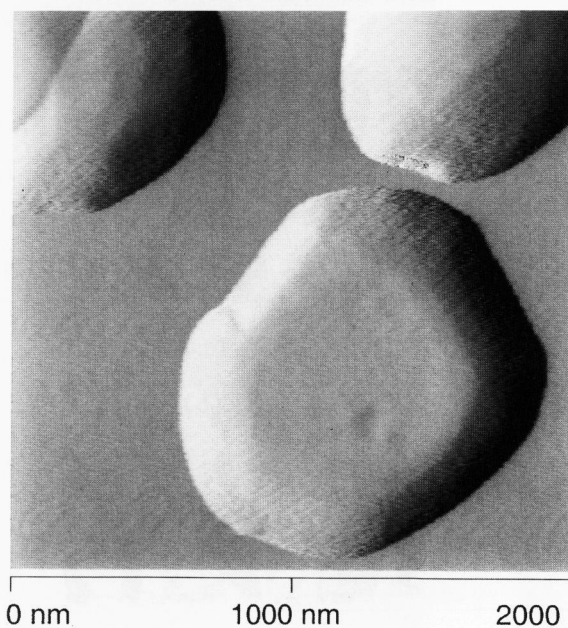


Figure 6. AFM of the habit of a monocystal sample without coactivators, heat-treated at 200 °C.

treated at 200 °C for 10 min. It demonstrates that both crystal size and amount are distinctly increasing with rising temperature. Besides the spherical growth the crystals exhibit an increasing six-fold symmetry. In figure 6 the habit of a monocystal (same sample as in figure 5) is presented.

Adding small amounts of coactivating agents during the sol synthesis, we found strong influences on the surface crystallization. The crystal sizes of coactivated and noncoactivated samples differ only slightly, but we observed a strong increase in the degree of crystallinity of

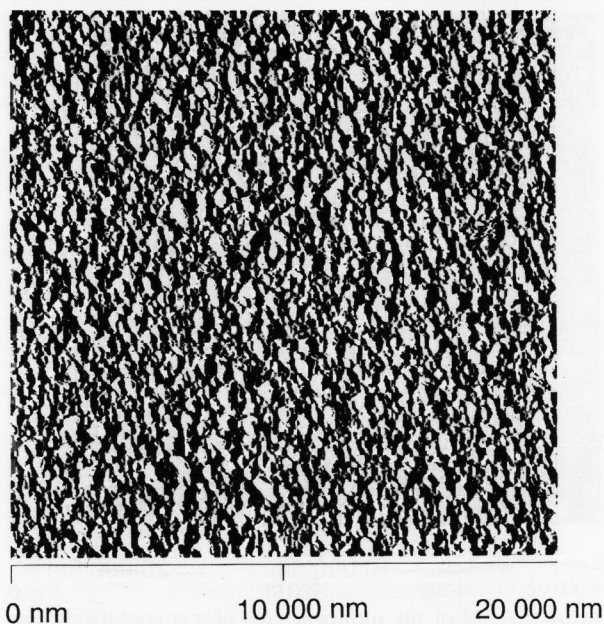


Figure 7. AFM of the surface texture of a sample with low content of coactivators, heat-treated at 200°C.

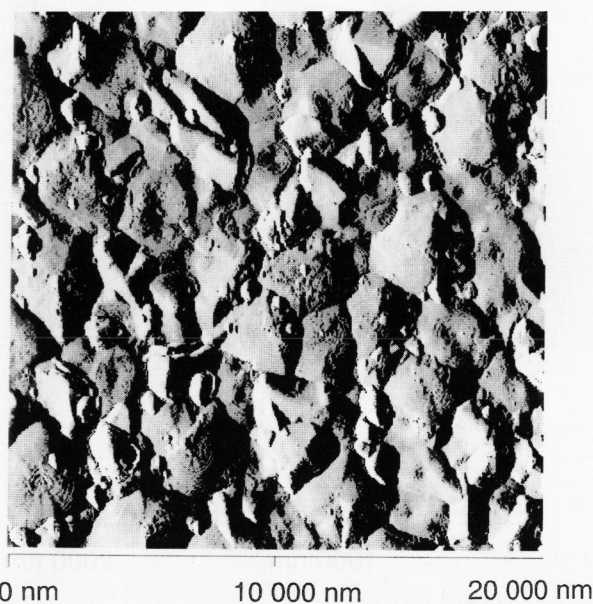


Figure 8. AFM of the surface texture of a sample with doubled content of coactivators, heat-treated at 200°C.

the coating surface of coactivated samples. Figure 7 shows the atomic force micrograph of a copper halide sample with a low content of coactivating agents. The coated substrate was heat-treated at 200°C for 10 min. After the heat treatment the coating surface is nearly densely crystallized, only at high magnitudes small parts of the matrix are perceptible. Using higher amounts of coactivating agents, the coating surfaces are completely covered with photochromic crystals after the heating. This is shown in figure 8 for a sample with doubled co-

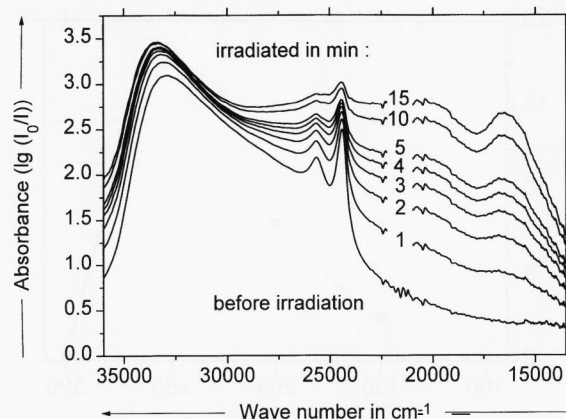


Figure 9. Darkening as function of irradiation time of a sample with doubled content of coactivators.

activator content. The crystals grow more and more spirally and have one or more growth centers. Matrix parts around the crystals are not detectable.

The investigation of the photochromic properties of the coatings proved that they are a function of both the heat treatment conditions and the content of coactivating agents. Figure 9 illustrates the darkening behaviour of a coating with a higher coactivator content. The sample was heated up to 150°C and kept at this temperature for 10 min. Under the influence of actinic radiation electron-hole pairs, so called excitons, are formed in the cuprous halide crystals. In the absorbance spectra the bands at 25660 and 24390 cm^{-1} are caused by the absorption of these excitons. The UV irradiation leads to the formation of copper colloids on the crystal surface, which are responsible for the characteristic colour of the darkened samples. The absorption bands of the colloids are detected at 20370 and 16480 cm^{-1} . The presented spectra show a strong dependence of the absorbance of the coatings on the irradiation time. The absorbance time behaviour resembles that of normal photochromic glasses. In the case of the described sample the transmission lowering amounts to about 45% after 5 min of irradiation and to more than 50% after 15 min.

For the first time to our knowledge the characterization of the fading behaviour of the developed materials shows a complete fading at room temperature without any additional temperature treatment or treatment with oxidizing agents.

Figure 10 illustrates the transmission behaviour of the described sample during one irradiation cycle. As described above, the coatings show a fast darkening reaction under the effect of UV-irradiation. The so-called half-darkening time amounts to about 60 s. After a 15 min irradiation the coatings reach transmission values of less than 5%. That corresponds to a transmission decrease of more than 50% compared with the initial state. The fading process starts at room temperature im-

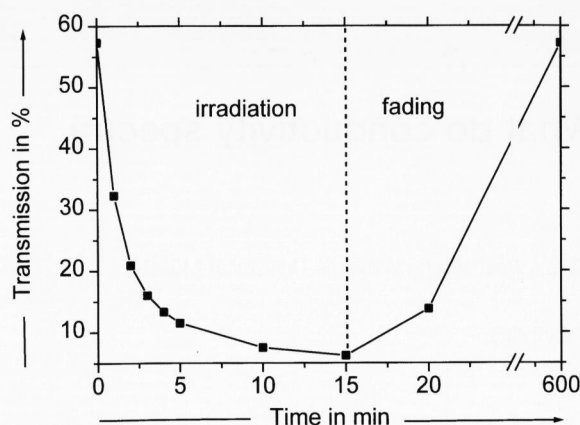


Figure 10. Photochromic behaviour of a sample with doubled content of coactivators during one irradiation cycle.

mediately after the switch off of the irradiation. Already 5 min after stopping the UV irradiation, the sample shows a noticeable fading, in the case of the described sample this makes about 10 % increase in transmission. A complete fading can be reached after about 10 h.

The described photochromic properties of the samples are reproducible, the manifold repetition of the darkening and fading processes did not show any significant changes in the photochromic behaviour.

4. Summary

Using the new materials, we succeeded for the first time in producing photochromic coatings via sol-gel process with complete reversibility of the photochromic reactions at room temperature. The carriers of the photochromic properties are cuprous halide microcrystals precipitated preferably on the coating surfaces. As demanded, the precipitation of crystals proceeds only during a heat treatment. Both crystallization behaviour and photochromic properties depend on the content of coactivating agents.

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Under UV irradiation, the darkening of the coatings amounts to about 45 % for the first 5 min and to more than 50 % for the first 15 min. The half darkening time amounts to about 60 s.

After the switch off of the irradiation, the samples fade already at room temperature, that means without any additional heat treatment. In the first 5 min the fading amounts to about 10 %. A complete fading takes place within a few hours.

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