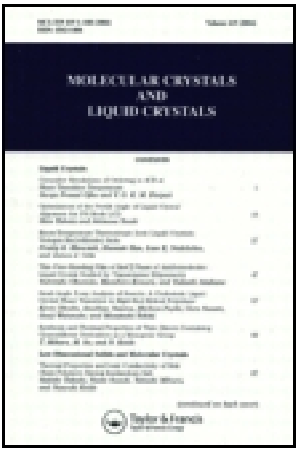

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Antje Kriltz [a], Matthias P. A. Müler [a], Regina Fachet [a] & Herbert Bürger [a]

[a] Otto-Schott-Institut für Glaschemie Friedrich-Schiller-Universität Jena, Fraunhoferstr. 6, D-00743, Jena, Germany

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GLASSY PHOTOCHROMIC LAYERS PRODUCED BY SOL-GEL PROCESS

ANTJE KRILTZ, MATTHIAS MÜLLER, REGINA FACHET, HERBERT BÜRGER
Otto-Schott-Institut für Glaschemie
Friedrich-Schiller-Universität Jena
D-00743 Jena, Fraunhoferstr. 6, Germany

Abstract Inorganic - organic composite materials on the basis of Tetraethoxysilane/3-Glycidoxypropyltrimethoxysilane containing microcrystals of AgBr, AgCl or $AgBr_xCl_{1-x}$ were synthesized as photochromic coatings via the sol-gel route. The bonding of halide ions to components of the matrix system, such as Bromophenyltrimethoxysilane or Chloropropyltrimethoxysilane and of Ag^+-ions with complexing agents such as 18-crown-6 and Aminopropyltriethoxysilane prevents the crystallization of silver halide crystals at room temperature and leads to a controlled growth of them. In the present work results of XRD- and AFM-measurements concerning crystal growth as function of the conditions of thermal treatment and UV-VIS spectroscopic investigations of the darkening and fading behaviour of the glassy coatings are shown.

INTRODUCTION

Glassy photochromic layers produced by the sol-gel method are suited for a subsequent refinement of glassy surfaces. In comparison to photochromic glasses the sol-gel route shows a series of advantages: The lower temperatures of synthesis cause, that the bonding of halide ions on borate groups is not necessary. Hence a wider range of the matrix composition is applicable. The possible higher concentration of silverhalide allows to produce thin films or powders. From investigations of photochromic glasses the authors know,[1-6] that, above all, there are three demands to a photochromic system: (1) The photochromic crystals should be included in an "inert" matrix system (without double bonds, reactive groups and relics of solvents - for preventing the irreversible bond of products of the irradiation process). (2) The optimal size of photochromic microcrystals ranges between 10...50 nm in diameter. (3) The microcrystals should be disordered by the introduction of strange ions, like Cu^+, S^{2-}, Cd^{2+}, Tl^+ or Pb^{2+} and by the formation of $AgBr_xCl_{1-x}$ crystals. The most problems at sol-gel route arise because of the higher diffusion rates at this synthesis in solution. This requires the preventing of the immediately crystallization of AgHal during synthesis.[9,10] In case of thin films, that is why we favour a bond of Ag^+ and/or Hal^--ions to components of the matrix system or complex reagents. Ideally these bonds decompose in the temperature range of the heat treatment of the gels (densification). A suitable complex reagent exhibits a high solubility in the sol, is colourless and has only an unimportant influence on the redox behaviour and pH-value of the system. The thermic/hydrolytic decompositon should occur without disturbing relics.

EXPERIMENTAL

Figure 1 shows the schedule of synthesis with all variations. This report primarily deals with the search for a suited complex reagent.

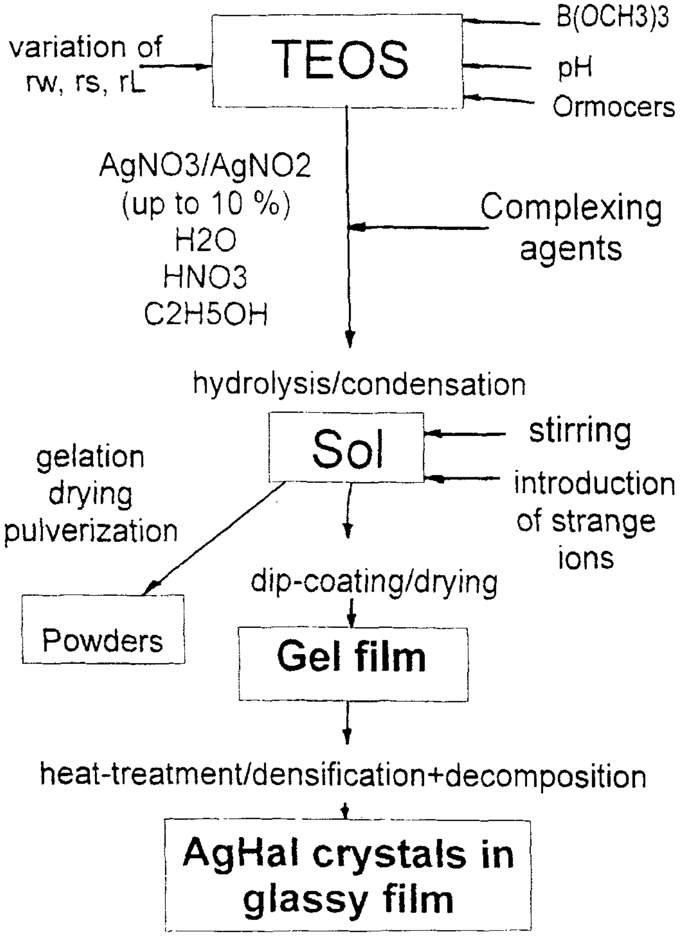


FIGURE 1: Schedule of synthesis

CHLOROETHYLTRIETHOXYSILANE/ DIAMO OR AMINOPROPYLTRIETHOXYSILANE

If only Ag^+ (to DIAMO: N-(2-Aminoethyl-3-aminopropyl)-trimethoxysilane) or Aminopropyltriethoxysilane, [Ag] : [complex] = 1 : 6) or Hal^- (as Chloroethyltriethoxysilane, [Ag] : [Cl] = 1 : 3) are bonded, bulk crystals of AgCl precipitate during sol synthesis. If both components are bonded, the diameters of the precipitated crystals in dried films (room temperature to 50 °C) range between 80... 90 nm. Figure 2 shows the development of diameters (XRD measurements) as function of heat treatment. All samples were heat treated for 2 hours, the samples of 400... 800 °C get a first treatment at 280 °C/2 h for removing of organics. Up to about 400 °C the crystals grow, at higher temperatures the crystal diameters decrease because of the evaporation of AgCl. At 800 °C only residues of Ag^0 are detectable, but this temperature is not enough for densification of the gel of TEOS basis to a glass. N_2-sorption (BET) and SAXS investigations show, that the average pore diameters (about 2 nm) are much smaller than crystals and the growth of the microcrystals is not limited by pore diameters. Hence the growth is also not strong influenced by variations of the matrix system and should controlled by better complexing agents.

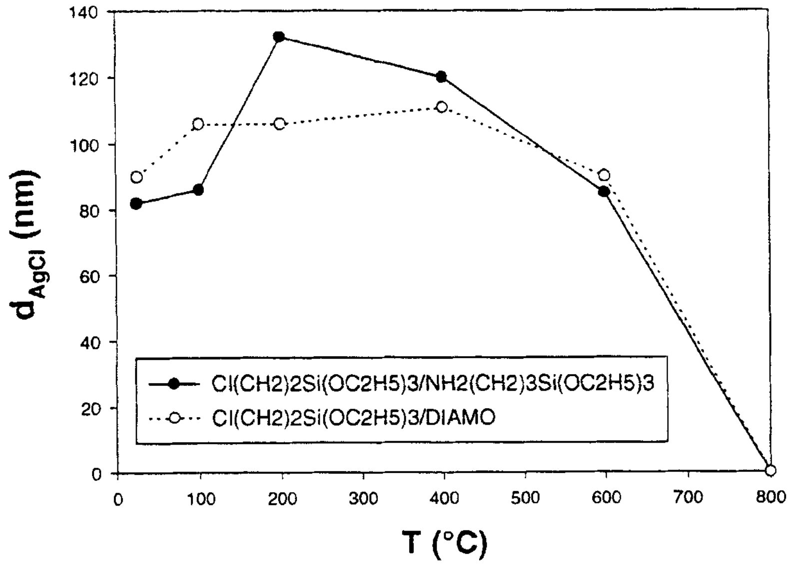


FIGURE 2: Diameters of precipitated AgCl crystals as function of heat treatment

18-CROWN-6/CHLOROETHYLTRIETHOXYSILANE

The use of 18-crown-6 as complexing reagent for Ag^+ ([Ag] : [complex] = 1 : 6) and Chloroethyltriethoxysilane as Cl carrier leads to a preventing of the precipitation of AgCl microcrystals in not heat treated films. Figure 3 shows the obtained diameters of AgCl crystals after a heat treatment at 410 °C for several times (first heat treatment: 280 °C/2 h). A longer time at this temperature causes a reduction of diameters as a result of AgCl evaporation. Despite the optimale crystal sizes, films show only a transmission change < 1%, since concentration of Ag^+ (up to 3 mol%) and filmthickness (about 250 nm) are, in consequence of problems with crown ether solubility, not increasable.

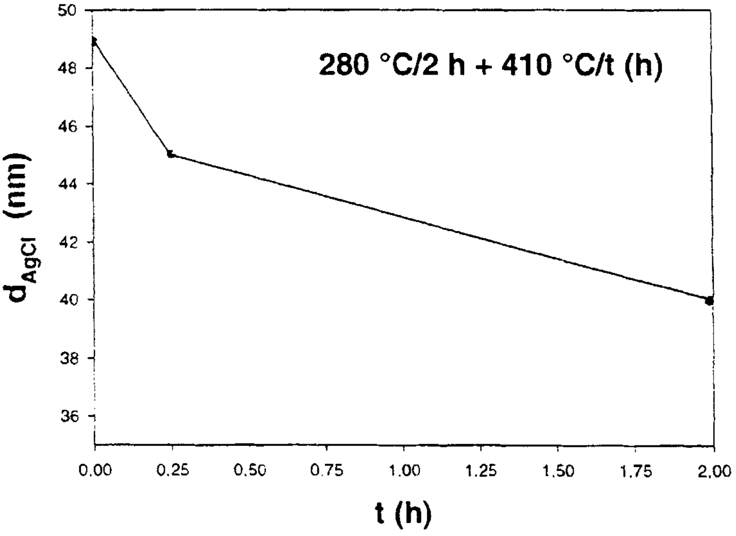
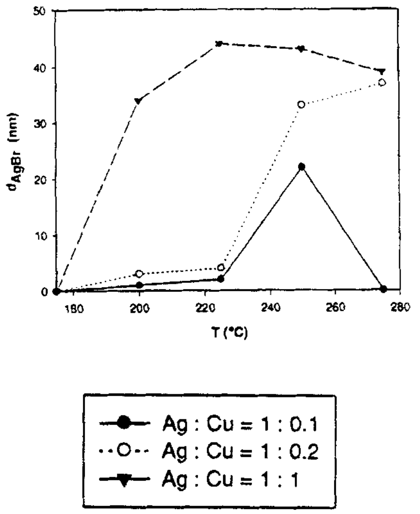


FIGURE 3: AgCl diameters as function of heat treatment (280 °C/2 h + 410 °C/t (h))

BROMOPHENYLTRIMETHOXYSILANE/DIAMO

The phenyl-group in Bromophenyltrimethoxysilane causes a slower hydrolysis in comparison to former used halide carriers with alkyl-groups. In addition to the use of Bromophenyltrimethoxysilane ([Ag] : [Br] = 1 : 3), the composition of the matrix was varied by the introduction of an ormocer (3-Glycidoxypropyltrimethoxysilane, GPTMS). This decreases the densification temperature to 350 °C. A two step heat treatment of the film samples was carried out. The first step at 200...275 °C should serve to remove the organics and the second at 300...375 °C should densificate the gel. Figures 4 and 5 demonstrate the effect of these heat treatments on crystal growth. The best precipitation conditions are at 250 °C, a rise in $Cu^{+/2+}$- concentration enlarges the range of precipitation and the size and amount of microcrystals, possibly by nucleation effects. The crystals do not contain detectable amounts of $Cu^{+/2+}$. The treatment in the densification range leads to a small reduction of average diameters (evaporation effect). The use of Bromophenyltrimethoxysilane/DIAMO in a TEOS/GPTMS matrix allows to increase the Ag^+-concentration up to 10 weight%. Figures 6 and 7 show AFM results of these films with 3 weight% and 10 weight% Ag^+, respectively. In the last case the surface of the film is almost completely covered by crystals.



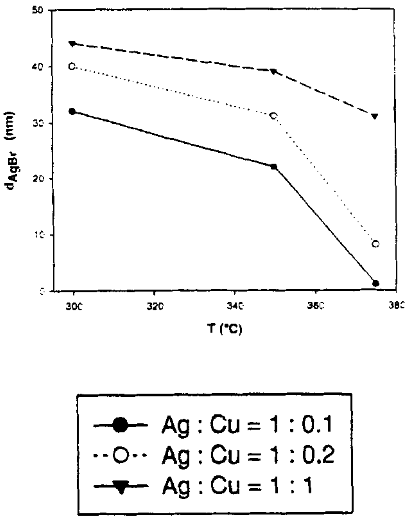


FIGURE 4: AgBr diameters as function of first heat treatment (T (°C)/1 h + 350 °C/1 h) and $Cu^{+/2+}$-content

FIGURE 5: AgBr diameters as function of second heat treatment (250 °C/1 h + T (°C)/1 h) and $Cu^{+/2+}$-content

Figure 6: AFM results, Br-C_6H_5-$Si(OCH_3)_3$/
DIAMO/TEOS
3 weight% Ag^+
350 nm x 350 nm
250°C/1h+350°C/1h
(See Color Plate II).

FIGURE 7: AFM results,
BrC_6H_5-$Si(OCH_3)_3$/
DIAMO/TEOS/GPTMS
10 weight% Ag^+, 350 nm x 350 nm
250°C/1h+350°C/1h
(See Color Plate III).

PHOTOCHROMIC BEHAVIOUR

The UV-VIS spectroscopic measurements were carried out at a photodiode array spectrometer L.O.T. ORIEL including a microscope heating stage for measuring fading at higher temperatures.[7] Irradiation is done by a XBO lamp (150 W) in a distance of 5 cm for 5...10 min. The absorption spectra after irradiation show three distinct absorption bands. The peak at about 23000 cm^{-1} results from colloids of Ag (size about 1...3 nm in diameter), sitting on the surface of the AgHal microcrystal. At oblate ellipsoids of colloidal silver specks this peak splits into two other ones. The ellipsoid with rotation axis parallel to the electrical field vector has an absorption peak at about 33000 cm^{-1}, perpendicular to the electrical field vector the peak lies at 18000 cm^{-1}.[5, 8] Figure 8 shows the darkening (room temperature) and fading (at 200 °C) as function of time. After 10 min at 200 °C the fading is terminated.

The additional introduction of Cl (as Chloropropyltrimethoxysilane) leads to a precipitation of mixed crystals from $AgBr_xCl_{1-x}$-type. Contrary to photochromic glasses the part of Cl in the crystals is always higher than in synthesis. In this case the rate of hydrolysis is probably the reason of this precipitation behaviour. With increasing of Br^-

content the darkening (and fading) ability also increases (see fig. 9 and 10). The best values are obtained at pure AgBr microcrystals with transmission changes of 26.5 % by a 5 min UV-irradiation with an XBO 150 W-lamp. This corresponds to a molar absorption coefficient of about 2000 lmol^{-1}cm^{-3}.

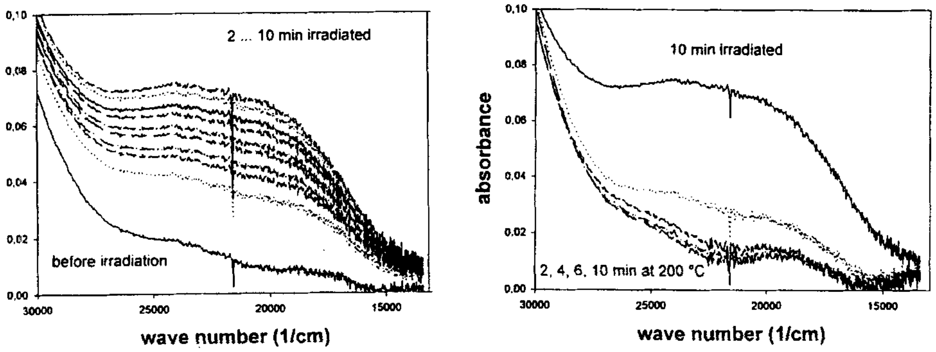


FIGURE 8: Darkening (a) and fading (b) as function of time at a Br-C$_6$H$_5$-Si(OCH$_3$)$_3$/ DIAMO/TEOS/GPTMS/ containing sample

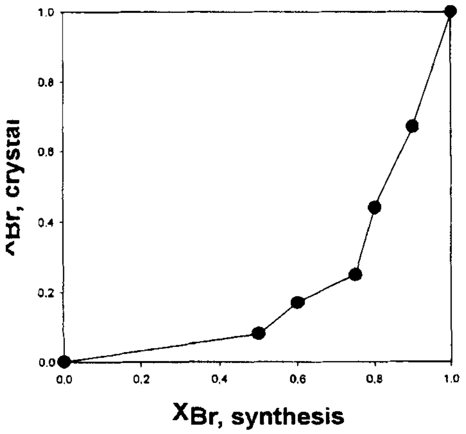


FIGURE 9: Relations of [Br] : [Cl] in synthesis and crystal

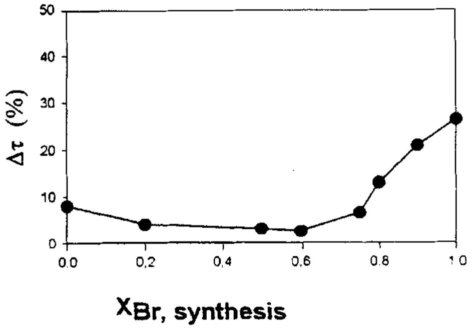


FIGURE 10: Influence of [Br]:[Cl] on the darkening behaviour (Δτ)

RESULTS

The sol-gel method allows to synthesize photochromic films on glassy surfaces with a good quality of the layer. By the introduction of complex reagents for Ag^+ and halide carriers from siloxane type, it is possible to increase the Ag^+-concentration up to 10 weight% and to control the crystal growth of the AgHal microcrystals. Parameters of the growth process are composition ([Br] : [Cl], [Cu]) and time and temperature of a heat treatment of the gel films in the range of 200...375 °C. By controlling of these parameters crystals with optimal diameters (20...40 nm) were obtained. The best films show a transmission change of 26.5 % by UV-irradiation at a film thickness of about 400 nm. Fading is terminated within 10 minutes at 150...200 °C.

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