Journal of Non-Crystalline Solids 147&148 (1992) 326–330
North-Holland

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Photoinduced formation of silver colloids in a borosilicate sol–gel system

M. Mennig, J. Spanhel, H. Schmidt and S. Betzholz
Institut für Neue Materialien, Universität Saarbrücken, Geb. 43, 6600 Saarbrücken, Germany

Silver ions are stabilized in a borosilicate glass sol by complex formation with a bifunctional amine compound. A UV-irradiation induced photochemical process reduced silver to form silver colloids with radii of several nanometers. The mean colloid size was controlled by irradiation time. The colloid concentration increases rapidly with irradiation, reaching a saturation level corresponding to total reduction of silver. Colloid formation was investigated by UV–VIS spectroscopy.

1. Introduction

Optical properties of nanoscale silver colloids embedded in glass are dependent on particle size. Such colloids cause a Lorentz-like absorbance band with a peak at about 400 nm wavelength and a halfband width between about 10 and 100 nm, for colloid radii between about 1 and about 10 nm [1,2]. Glasses prepared by fusion containing silver ions can produce silvercolloids with a relatively narrow size distribution by using UV-light induced nucleation in the presence of CeO_2. The nucleation is followed by a diffusion-controlled growth process at temperatures in the T_g range of the glass containing thermal reducing agents such as SnO or FeO [3,4].

Silver colloids can be generated in aqueous solutions by photochemical methods using UV-light in presence of acetone and isopropanol [5]. In this process, the light is absorbed by acetone to yield the triplet state which subsequently reacts with isopropanol to form two 1-hydroxy alkyl radicals. These radicals reduce Ag^+ to Ag^0.

The purpose of this study was to use this photochemical synthesis route to produce differently sized silver colloids in a borosilicate sol–gel system and to characterize the colloids by UV–VIS spectroscopy.

2. Experimental

A sol with 20 wt% B_2O_3 and 80 wt% SiO_2 was synthesized by diluting silver acetate in 0.6 mol N-(2-aminoethyl-3-aminopropyl)trimethoxysilane (H_2N–CH_2–CH_2–NH–$(CH_2)_3$–$Si(OCH_3)_3$). After adding 0.2 mol isopropanol and dilution in ethanol and water, the solution was mixed with 0.15 mol trimethylborate at 50°C for 15 h. Then 0.1 mol acetone was added at room temperature. The silver concentration in the final sol was 10^{-3} mol/l.

This sol was irradiated at 20°C in a closed 1 mm quartz cell with a 700 W xenon lamp at a distance of 25 cm for different times and UV–VIS transmission spectra were measured after UV exposure.

3. Results

Preliminary attempts to synthesize the silver colloids directly in a borosilicate sol using tetraethoxysilane and trimethylborate and adding an ethanolic solution of silver nitrate led to uncontrolled spontaneous silver colloid formation. In order to avoid the spontaneous colloid formation, the behaviour of the Ag–amine complex was

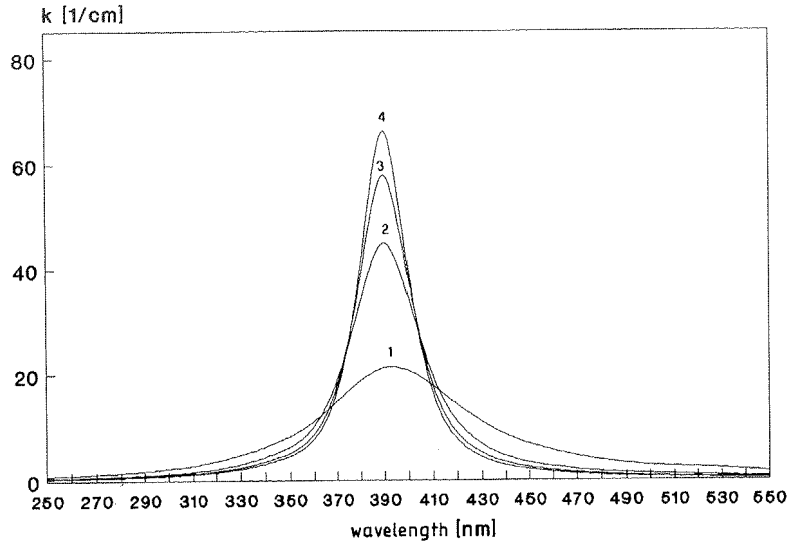

Fig. 1. Calculated spectra of silver colloids (volume fraction 10^{-5}) in glass sol ($n = 1.378$) for colloid radii: 1, $R = 1$ nm; 2, $R = 3$ nm; 3, $R = 5$ nm; 4, $R = 7$ nm.

investigated. Therefore, amino groups bonded to polycondensable silanes were used, since they allow incorporation of the complex in a sol–gel matrix. The use of the amine compound led to the formation of a silver complex [6], which completely suppressed spontaneous colloid generation.

Results of spectroscopic measurements were used to compute the colloidal absorption coefficient, $k(\lambda)$, as described earlier [7]. These were

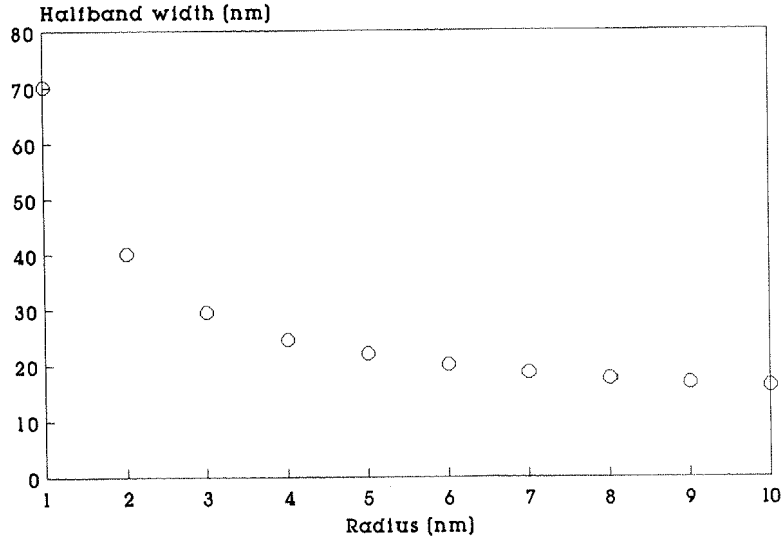

Fig. 2. Halfband widths of calculated spectra as a function of colloid radius.

based on a refractive index of the silver free sol determined to about 1.378. The calculation is based on a Mie theory approximation for small colloids and therefore the results are only valid for colloids small enough to neglect scattering (maximal colloid radius in glass of about 15 nm). Following the example given in ref. [1], quantum size effects are taken into account and the dielectric function of the silver is modelled according to the Drude theory of the free electron gas. The contributions of the bonded electrons to the real and the imaginary part of the dielectric function were estimated numerically using data from ref. [8].

Figure 1 shows calculated spectra, $k(\lambda)$, for various colloid radii, R. The peak position slightly shifts to shorter wavelengths with increasing colloid size. For $R = 1$ nm, the peak is at 395 nm and for radii greater than 3 nm it remains constant at 390 nm. The maximal absorption increases and the halfband width decreases with increasing particle size, as can be seen from fig. 2, where the halfband width is plotted versus the colloid radius. It decreases from about 70 nm for $R = 1$ nm down to about 16 nm for $R = 10$ nm. It can be shown that the area beneath the calculated absorption bands, approximated by the product of the maximal absorption coefficient and the halfband width, is independent of the particle size and is directly proportional to the colloidal silver concentration. The proportionality

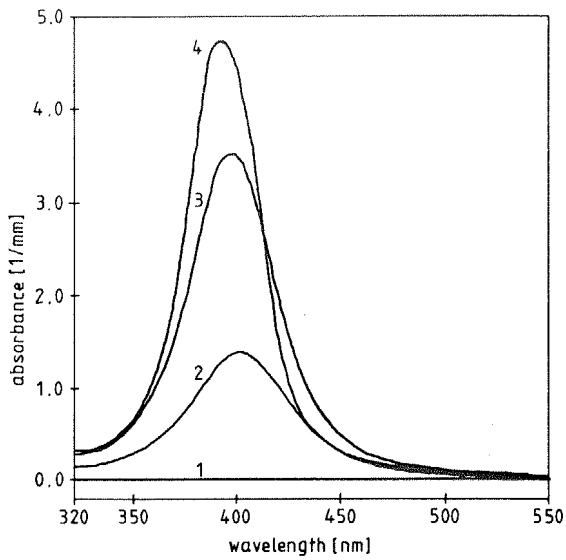

Fig. 3. Measured absorption spectra of silver colloids. 1, Before UV-irradiation; 2, after 2.5 min UV-irradiation; 3, after 6.5 min UV-irradiation; 4, after 14 min UV-irradiation.

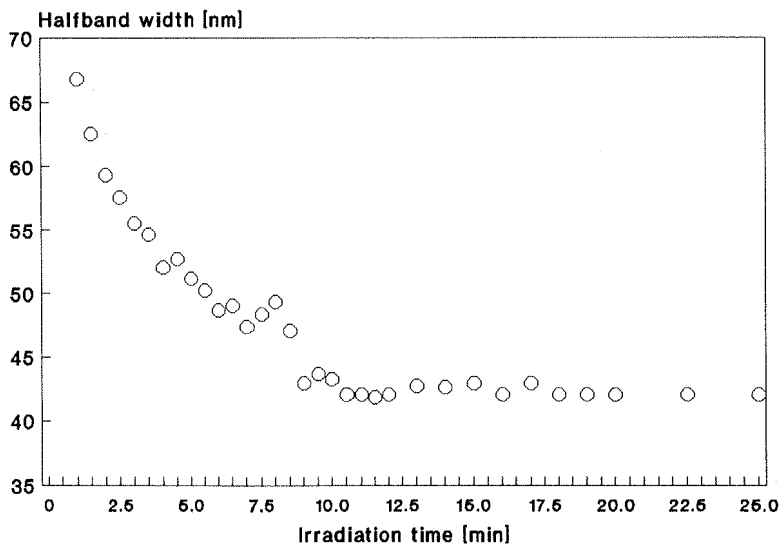

Fig. 4. Halfband widths of measured absorption bands as a function of irradiation time.

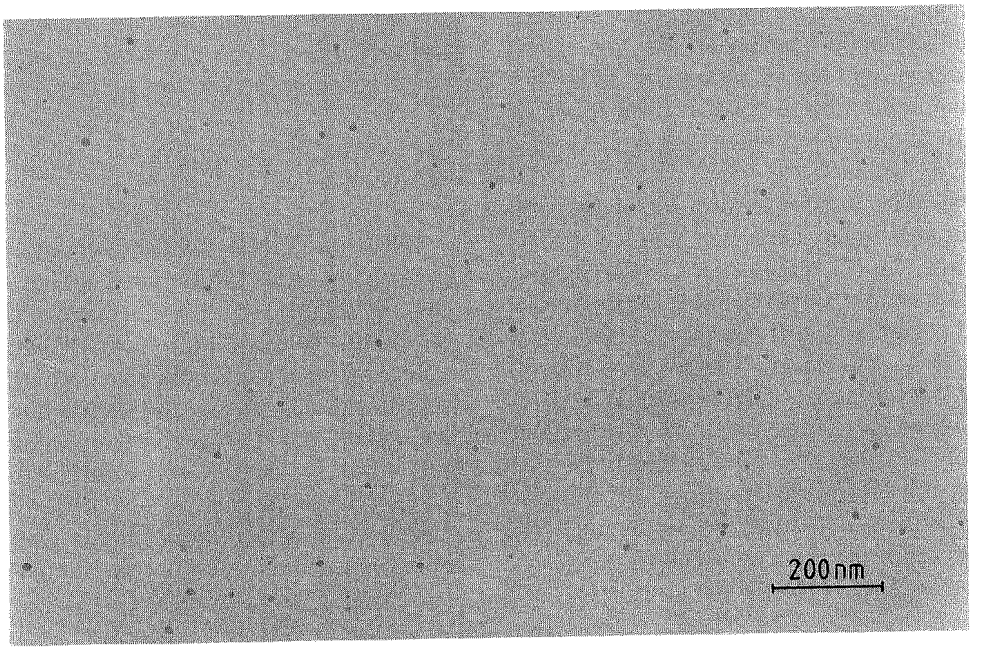

Fig. 5. Electron micrograph of silver colloid containing sol after 20 min irradiation.

factor depends on the refractive index of the matrix (sol) and was determined to 0.154 l/mol from the data of the calculated spectra.

Figure 3 shows spectra for different irradiation times. The intensity of the absorption increases with increasing irradiation time. After about 10 min irradiation, no further change in the absorption spectra occurs. The peak position decreases slightly with increasing irradiation time. It shifts from about 405 nm after 1 min down to about 394

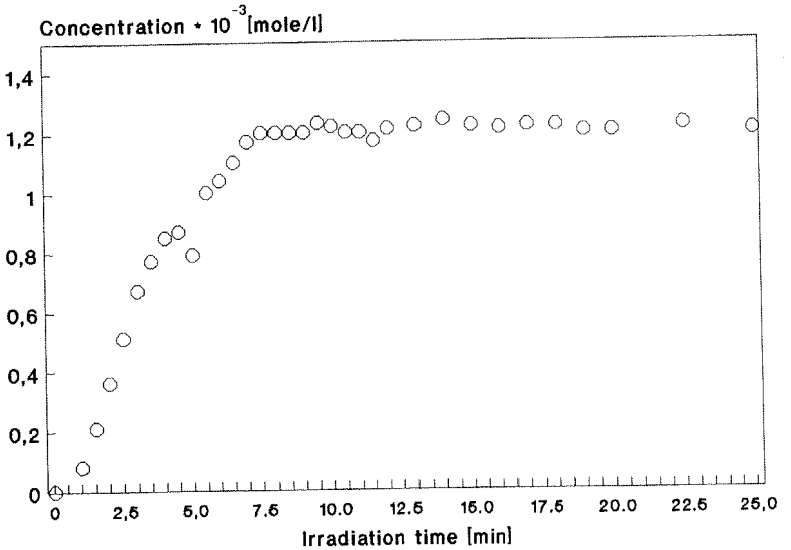

Fig. 6. Concentration of colloid silver as a function of irradiation time.

nm after about 10 min irradiation. These values are in relatively good agreement with the calculated peak positions for small colloids (395–390 nm). The halfband width decreases from about 70 nm down to about 40 nm within the first 10 min irradiation, as shown in fig. 4.

This behaviour indicates a growth of the colloid size in the range between 2 and 4 nm in diameter (see fig. 2) assuming a monodisperse size distribution. An electron microscope sample holder was coated with a silver colloid containing sol irradiated to saturation. The electron micrograph (see fig. 5) shows silver colloids with a remarkable size distribution and an average radius of about 7 nm. For a colloid radius of 7 nm, the calculated halfband width is about 20 nm (see fig. 2), but a measured halfband width must be larger in presence of smaller particles.

4. Discussion

One may thus conclude that there is a good agreement between calculated and measured absorption spectra and that differences in the halfband widths may result from the size distribution of the silver colloids.

Based on this assumption, the concentration of the silver colloids was calculated from the measured spectra using the theoretically determined proportionality factor of 0.154 l/mol and plotted versus the irradiation time as plotted in fig. 6.

It can be seen that the colloidal silver concentration increases rapidly with irradiation and the saturation level is in the same range as the total silver concentration in the sol (10^{-3} mol/l).

5. Conclusions

Silver ions in a borosilicate glass sol, stabilized by a complexing bifunctional amine compound, can be reduced by UV-irradiation to Ag^0 and completely converted into colloids. During irradiation, the mean particle size and the colloidal concentration grows. Although a distribution of the colloid size is obtained, the method described can be used to controllably form nanometer-sized silver colloids in glass sols. Further study is required to investigate gelation and glass formation in order to obtain glasses containing Ag colloid.

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