Available online at www.sciencedirect.com
ScienceDirect
Physica B 387 (2007) 32–35
PHYSICA B
www.elsevier.com/locate/physb

UV-laser-induced nanoclusters in silver ion-exchanged soda-lime silicate glass

Jiawei Sheng*, Jingwu Zheng, Jian Zhang, Chunhui Zhou, Liqiang Jiang

College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Zhaohui No.6, Hangzhou, Zhejiang 310014, China

Received 11 January 2006; received in revised form 16 March 2006; accepted 18 March 2006

Abstract

Excimer-laser irradiation (ArF: 193 nm) was performed on silver-exchanged commercial soda-lime silicate glass. Silver nanoclusters were obtained with an average size dependent on the irradiation time, without subsequent heating. Laser irradiation induces the reduction of silver ions and promotes the silver atoms aggregation.

PACS: 81.05.Kf; 61.46.+w; 61.43.Fs; 61.80.Ba

Keywords: Glass; Excimer-laser irradiation; Nanoclusters

Introducing nanosize metal clusters such as silver into glass has been used for changing the colour of decorative glass and recently for fabricating optical devices. During the past decades, the physical and, in particular, the linear and non-linear optical properties of metallic nanocluster in glass have been investigated using numerous experimental and theoretical approaches. Silicate glasses containing silver nanoclusters have attracted interest during the last years as materials for non-linear optical device fabrication. Ion exchange process with thermal treatments is a well-established technique for producing nanoclusters in a silicate glass [1–5]. Recently, the high-power laser annealing is an alternative way to form nanoclusters in silver ion-exchanged glass [5–7]. Although a substantial amount of literature is available on properties of silver nanoclusters in glass exhibiting high optical non-linear response [8], only minimal work has been reported on the optical spectroscopic investigations of silver ion-exchanged glass. In this work, we report on the silver nanoclusters formation behaviour in ion-exchanged soda-lime silicate glass by UV-laser irradiation. Once the formation mechanism of the silver nanoclusters is well characterized, the optimum annealing process for size-controlled silver nanoclusters may be obtained.

Commercially available soda-lime silicate glass substrates composed of (wt%): 74.2 SiO_2, 14.3 Na_2O, 1.9 Al_2O_3, 8.1 CaO, and 1.5 MgO were utilized for experimentation. Samples (2 mm thick and of approximately 15×15 mm), which had previously been scoured and dried, were preheated and subsequently dipped in a molten salt bath formed by a mixture of 98 mol% $NaNO_3$ and 2 mol% $AgNO_3$ in a crucible of Al_2O_3. The ion exchanges took place at a temperature of 320 °C with a processing time of 60 min. In order to ensure that the glass structure did not change during testing, the ion-exchange temperature was kept well below the glass-transition temperature of the specimen. After inter-diffusion, samples were removed from the molten bath and washed with several portions of distilled water and acetone to remove any silver nitrate adhering to their surface. An ArF UV laser (193 nm) was utilized at an output energy density of 30 mJ/(cm^2 pulse), with a repetition frequency of 10 Hz and a 20 ns pulse duration. With these parameter settings, the laser irradiation time ranged from 5 s to 30 min. Optical absorption spectra were recorded using a spectrophotometer in the wavelength range of 300–800 nm at ambient room temperature and all recorded optical spectra were referenced to

---

*Corresponding author. Tel.: 86 571 88320851; fax: 86 571 88320142.
E-mail address: jw-sheng@zjut.edu.cn (J. Sheng).

0921-4526/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2006.03.024

air. TEM images for representative samples were observed by a transmittance electron microscope (JEOL-2010 TEM) at electron beam energy of 300 keV.

Prior to the ion-exchange process, the glass samples were colourless and had no measurable absorption in the visible region. The soda-lime silicate glass was absent of any colour change following silver-exchange experimentation for 60 min. There was a lack of significant surface plasmon resonance (SPR) of the silver nanoclusters in glass (400–430 nm) during the ion-exchange process at these experimental conditions, indicating the silver aggregate formation did not occur, or the silver nanoclusters, if present, have size less than 1 nm. The formation of silver nanoclusters is limited, primarily, to the mobility of silver and the concentration of reducing elements present in the glass. In our experimental procedure, the silver mobility is minimal and the concentration of reducing agent is relatively low.

Due to the ion-exchange process, the silver diffused up to several micrometers in the soda-lime silicate glass. Effects of laser irradiation were clearly visible with the glass exemplifying a yellow colour after laser irradiation. Moreover, the colour density increased with increasing irradiation time. Fig. 1 shows the absorption spectra for silver-exchanged glasses after laser irradiations. An absorption band at approximately 425 nm was clearly observed, which was due to the SPR band of silver nanoclusters formed in the glass matrix. A small blue shift of the SPR is visible in Fig. 1 for the longest irradiation time, indicating differences in the refractive index properties of matrix or differences in sizes of silver nanoclusters as function of time. The laser irradiation promotes nanocluster formation, as witnessed by the appearance of the SPR band. The intensity of the SPR band sharply increases with the irradiation time. Fig. 2 shows the concordance of theoretically calculated and experimentally recorded optical absorption spectra of silver nanoclusters formed after 10 min laser irradiation. The theoretical spectrum was calculated using the Mie theory with the electric dipole approximation [9–11]. For nanocluster sizes below 20 nm, optical scattering contributions are negligible, and only the electric dipole term in the Mie expression has to be taken into account,

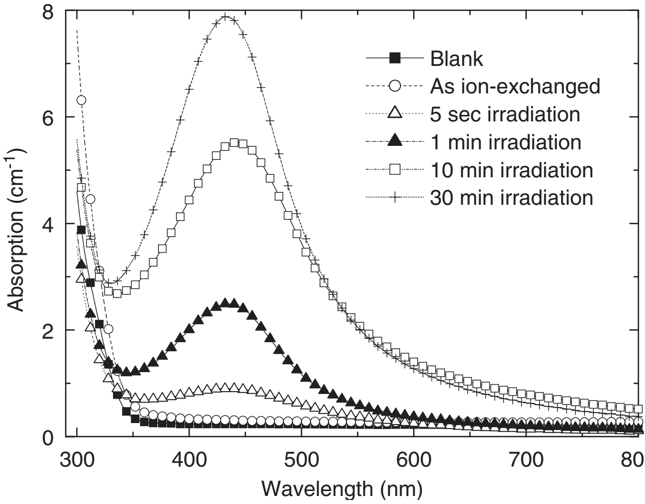

Fig. 1. Optical absorption spectra of silver ion-exchanged glass, before and after excimer-laser irradiation.

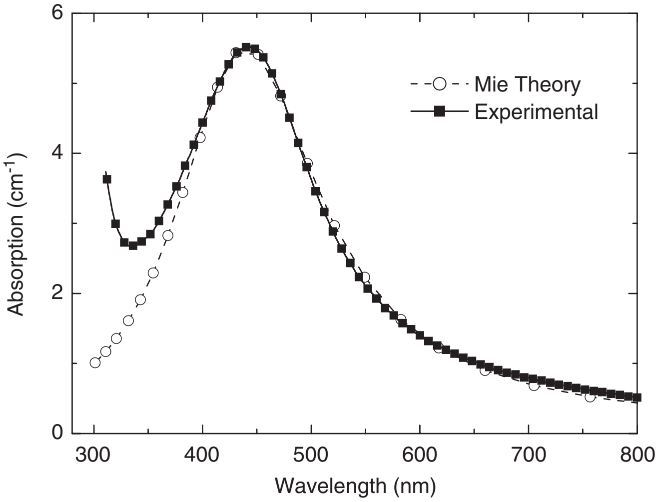

Fig. 2. Experimentally recorded and theoretically calculated optical absorption spectra of silver nanoclusters in glass.

$$\alpha\,(\mathrm{cm}^{-1}) = 18\pi Q n_0^{3/2} \frac{\varepsilon_2}{\lambda\left[(\varepsilon_1 + 2n_0^2)^2 + \varepsilon_2^2\right]}, \tag{1}$$

where $\alpha(\mathrm{cm}^{-1})$ is the absorption coefficient at the wavelength of the incident light, λ, Q is the volume fraction of metallic silver per unit of the irradiated area, and n_0 is the effective dielectric constant of the matrix. ε_1 and ε_2 are the frequency-dependent real and imaginary part of the nanocluster, calculated from the optical constants of their bulk metal. The absorption coefficient has its maximum value when $(\varepsilon_1 + 2n_0^2) = 0$, which is the condition for the SPR. The SPR frequency depends on the dielectric function as well as the nanocluster size and composition. The average radius of silver nanoclusters, r, can be determined by means of the equation [2,12,13].

$$r = \frac{v_\mathrm{f}}{\Delta\omega}, \tag{2}$$

where $v_\mathrm{f} = 1.39 \times 10^8\,\mathrm{cm/s}$ is the Fermi velocity for bulk silver and $\Delta\omega$ is the bandwidth at half maximum (FWHM) of the SPR band. The FWHM is determined by assuming the absorption peak as a normal Gaussian distribution and fitting the flank of the absorption band on the long wavelength side. The value of $\Delta\omega$ is determined using $\Delta\omega = 2\pi c(1/\lambda_1 - 1/\lambda_2)$, where c is the speed of light in vacuum, λ_1 and λ_2 are the wavelength at FWHM. For the measured FWHM of Fig. 1, the calculated radii ranged from 0.51 to 0.98 nm, as given in Table 1. The average nanocluster radius increased with increased irradiation time. The sizes of nanoclusters observed from the sample after 30 min irradiation is shown in Fig. 3, where the

Table 1
Nanocluster sizes after laser irradiation, calculated from the Mie theory

Irradiation time	Nanocluster radii (nm)
5 s	0.51
1 min	0.76
10 min	0.84
30 min	0.98

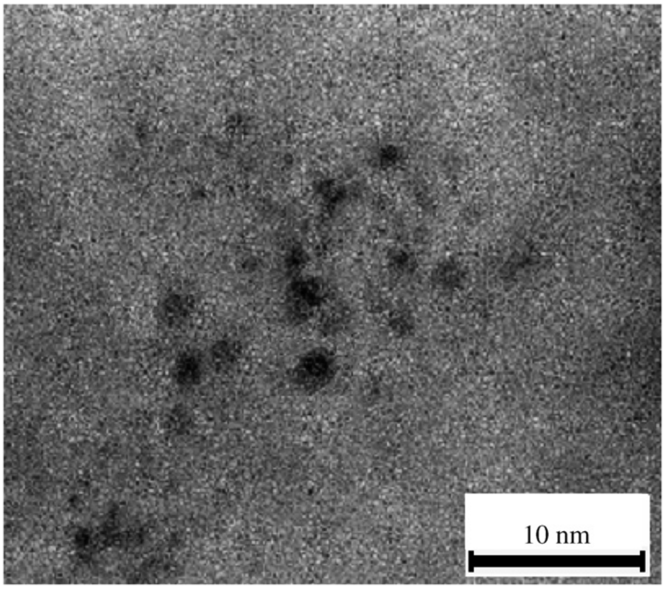

Fig. 3. TEM image of a glass sample after 30 min of irradiation.

spherical individual particles, with an average diameter of 2 nm, were observed.

Elemental metallic nanoclusters are generally formed in the laser-irradiated area following heat treatment in a reducing atmosphere. Interestingly, our results showed the formation of silver nanoclusters only by excimer-laser irradiation without subsequent heating, yielding a yellow colour of glass. Currently, the mechanisms responsible for the formation of the silver nanoclusters solely by laser irradiation are not fully understood. In the as-exchanged glass, silver atoms are expected to be bound to non-bridging oxygen (NBO) atoms, after the substitution for the sodium atoms in the glass matrix. The silver introduced by ion-exchange process is comprised of Ag^+ as the major state, with a minor population of Ag^0 atoms [4]. The Ag^0 atoms have an absorption wavelength of approximately 200 nm and have no visible absorption. The development of appreciable colour occurs only after the aggregation of Ag^0 atoms to form nanoclusters larger than 1 nm. When the silver-exchanged glass was subjected to laser irradiation, a reduction of silver atoms was induced. An electron was driven out from the 2*p* orbital of a NBO near the silver ions after laser irradiation, while silver ion captured the electron to form an atom. The following equations presented the effects during irradiation.

$$\text{Glass} \xrightarrow{\text{laser}} h^+ + e^-, \tag{3}$$

$$Ag^+ + e^- \longrightarrow Ag^0, \tag{4}$$

where h^+ is a hole and e^- is the electron. Substrate temperature plays a fundamental role in the formation of silver precipitates in silver-exchanged glass, with silver nanoclusters usually aggregating only at a high temperature (i.e., temperatures $\geq$ 500 °C) in air. According to the above discussion, the silver ions introduced in glass materials by ion-exchange processes have been observed to partly reduce to the neutral silver atom species, possibly aggregating to form silver nanoclusters with diameter of less than 1 nm. Although the temperature of the laser irradiation area was far less than 500 °C, we suggest that the neutralized silver promotes nucleation with resultant aggregation during irradiation.

Diffusion of silver towards the surface, with consequential precipitation, are caused by thermal relaxation of the surface tensile stress introduced by the size differential between Ag^+ and Na^+ during the ion exchange process. Tensile stress introduced by this size difference is still present after cooling [4,14]. Following laser irradiation, more Ag^+ ions acquire sufficient energy to overcome the static barrier potential produced by oxygen bonding and move towards the still considerably stressed surface. The activated Ag^+ ions mobilize toward a more relaxed surface, resulting from precipitation or nanocluster formation of silver atoms. Conversely, the dissociation of Ag–O bonds to form Si–O and Ag–Ag bonds result in a net loss in the system free energy [4]. Thus, the silver inclusion of the glass network will move toward the surface and form nanoclusters in order to maintain a minimum-energy state within the system. Since the diffusion of silver in the glass matrix is nominal, the above-discussed processes of silver nanocluster formation are commonly carried out through heat treatment.

In summary, we have been able to form silver nanoclusters in a silver-exchanged commercial soda-lime silicate glass by a single process of excimer-laser irradiation. Moreover, it was observed that laser irradiation promotes silver aggregation.

The author gratefully acknowledges the financial support for this work from Zhejiang Provincial Natural Science Foundation of China (R404108), Zhejiang Provincial Special Hired Professor Foundation, and Scientific Research Foundation of Zhejiang Provincial Education Department (20040251). Dr. Satjit Brar and Bill X. Huang of NIH/NIAAA are acknowledged for the English improvement.

References

[1] D. Ricard, P. Roussignol, C. Flytzanis, Opt. Lett. 10 (1985) 511.

[2] W.P. Halperin, Rev. Mod. Phys. 58 (1986) 533.

[3] D. Ila, E.K. Williams, R.L. Zimmerman, D.B. Poker, D.K. Hensley, Nucl. Instr. and Meth. B 166–167 (2000) 845.

[4] P.W. Wang, Appl. Surf. Sci. 120 (1997) 291.

[5] A. Miotello, M. Bonelli, G. De Marchi, G. Mattei, P. Mazzoldi, C. Sada, F. Gonella, Appl. Phys. Lett. 79 (2001) 2456.

[6] F. Gonella, G. Mattei, P. Mazzoldi, E. Cattaruzza, G.W. Arnold, G. Battaglin, P. Calvelli, R. Polloni, R. Bertoncello Jr., R.F. Haglund, Appl. Phys. Lett. 69 (1996) 3101.

[7] M. Kaempfe, H. Hofmeister, S. Hopfe, G. Seifert, H. Graener, J. Phys. Chem.B 104 (2000) 11847.

[8] G. De Marchi, F. Gonella, P. Mazzoldi, G. Battaglin, E.J. Knystautas, C. Meneghini, J. Non-Cryst. Solids 196 (1996) 79.

[9] P.B. Johnson, R.W. Christy, Phys. Rev. B 6 (1972) 4370.

[10] G.W. Arnold, J.A. Borders, J. Appl. Phys. 48 (1977) 1488.

[11] D.P. Peters, C. Strohhofer, M.L. Brongersma, J. van der Elsken, A. Polman, Nucl. Instr. and Meth. B 168 (2000) 237.

[12] G. Battaglin, A. Boscolo-Boscoletto, P. Mazzoldi, C. Meneghini, G.W. Arnold, Nucl. Instr. and Meth. Phys. Res. B 116 (1996) 527.

[13] U. Pal, A. Bautista-Hernandez, L. Rodriguez-Fernandez, J.C. Cheang-Wong, J. Non-Cryst. Solids 275 (2000) 65.

[14] G. Battaglin, E. Cattaruzza, F. Gonella, R. Polloni, F. D'Acapito, S. Colonna, G. Mattei, C. Maurizio, P. Mazzoldi, S. Padovani, C. Sada, A. Quaranta, A. Longo, Nucl. Instr. and Meth. Phys. Res. B 200 (2003) 185.