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ScienceDirect
Ceramics International 34 (2008) 605–608
CERAMICS INTERNATIONAL
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Precipitation of metallic nanoparticles inside silicate glasses by femtosecond laser pulses

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Received 7 November 2006; received in revised form 17 November 2006; accepted 21 December 2006
Available online 2 February 2007

Abstract

Precipitation behaviors of metallic nanoparticles inside silicate glasses by femtosecond laser irradiation are studied in this work. Laser irradiation results easily in precipitation of metallic nanoparticles where colors depend in part on their sizes and quantities. Laser irradiation induced precipitation of metallic nanoparticles displays the different behaviors from that in the unirradiated area inside glasses and their mechanisms are investigated.

Keywords: B. Nanocomposites; C. Optical properties; D. Glass

1. Introduction

Recently, there have been intensive researches focused on the femtosecond (fs) laser-induced reactions. fs laser has become a powerful tool for the fabrication of integrated photonic devices, since it can induce various controllable microstructures inside transparent materials due to nonlinear optical absorption [1–3]. In our previous investigations, we have reported the space selective precipitation of metallic nanoparticles in glasses by irradiation of a focused fs laser and successive annealing [4–6]. The size and spatial distribution of the nanoparticles can be manipulated by modifying the laser irradiation conditions, such as light intensity, spot size of the focused beam, etc. In addition, the precipitated nanoparticles developed by this technique can be space-selectively ''dissolved'' by further fs laser irradiation, and re-precipitated via annealing process [7,8]. In this paper, we compare the different precipitation behaviors of metallic nanoparticles induced by fs irradiation with those in the unirradiated area inside glass. The mechanisms of the observed phenomena are also discussed.

2. Experimental

The compositions of the silicate glass samples used in this study were $0.01Au_2O_3{\cdot}20Na_2O{\cdot}10CaO{\cdot}70SiO_2$ (mol%) and $0.01Ag_2O{\cdot}20Na_2O{\cdot}10CaO{\cdot}70SiO_2$ (mol%), respectively. Reagent grades of Na_2CO_3, $CaCO_3$, SiO_2, $HAuCl_4{\cdot}4H_2O$, and $AgNO_3$ were used as raw materials. The silicate glasses were prepared by a melt-quenching method. The mixed batches were melted in a Pt crucible at 1550 °C for 4 h. Then the melts were quenched into transparent and colorless glass by pouring them onto a stainless steel mold kept at room temperature. After subsequent heat treatment near the glass transition temperature T_g, the resultant glasses were polished and cut into 10 mm × 10 mm × 2 mm plates.

A regeneratively amplified 800 nm Ti: Sapphire laser, which emitted 120 fs, 1 kHz mode-locked pulses was used in our experiments. The laser beam with an average power of 20 mW controlled by an attenuator was focused by a 10× objective lens, with a numerical aperture of 0.30. The spot diameter of the laser beam was calculated to be 3.3 μm. The position of the focal point was set 0.5 mm beneath the glass surface with the help of a computer controlled three-dimensional *XYZ* stage. The *XYZ* stage scanned the sample at a speed of 2500 μm/s and a spacing of 20 μm. Absorption spectra of the glass samples were acquired by a spectrophotometer (JASCO V-570). After

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0272-8842/$34.00
doi:10.1016/j.ceramint.2006.12.011

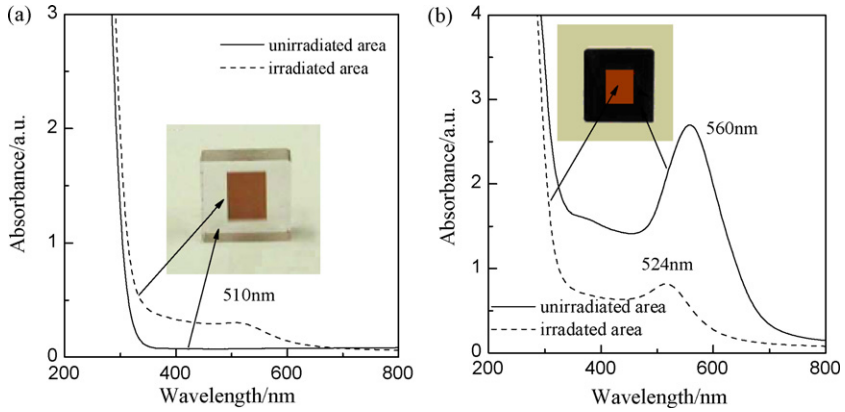

Fig. 1. (a) Absorption spectra of Au^{3+}-doped glass sample after further annealing at 520 °C for 30 min, and the inset of (a) shows the photograph of Au^{3+}-doped glass sample after further annealing at 520 °C and (b) absorption spectra of the unirradiated area of Au^{3+}-doped glass sample annealed at 600 °C for 30 min, and the inset is internal view of Au^{3+}-doped glass sample after annealed at 600 °C for 30 min.

exposure to the fs laser, the samples were subjected to heat treatment with various temperatures for 30 min.

3. Results

3.1. Precipitation of Au nanoparticles inside Au^{3+}-doped glass

The as-prepared Au^{3+}-doped silicate glass sample was transparent and colorless. After exposure to the focused fs laser, a faint gray color appeared in the irradiated area due to the generation of color centers such as non-bridging oxygen hole trap centers HC_1 and HC_2, etc. [4]. It became transparent and colorless again after annealing at 300 °C for 30 min. When the annealing temperature was increased to 520 °C, the irradiated area became red, whereas the unirradiated area was still colorless, as shown in the inset of Fig. 1(a). The corresponding absorption spectra of sample (Fig. 1(a)) displayed different characteristics. A visible absorption band peaked at 510 nm was observed for the fs irradiated area which is attributed to the surface plasmon resonance absorption of Au nanoparticles. However, no absorption in visible region was observed in the unirradiated area after annealing at 520 °C. It means that fs laser irradiation played an active role of promoting precipitation of Au nanoparticles precipitated within the scanned area of the glass.

When the Au^{3+}-doped glass sample was annealed at 600 °C, the color of the unirradiated area became purple, while the color of the fs irradiated area became deep red. The corresponding absorption spectra are shown in Fig. 1(b). An absorption band peaked at 560 nm can be observed in absorption spectrum of the unirradiated area (solid curve), whereas in the absorption spectrum of fs irradiated area, an absorption band peaked at 524 nm is visible (dashed curve). As we discussed above, they were assigned to the surface plasma resonance absorption from Au nanoparticles. Compared to the absorption spectrum of the glass annealed at 520 °C for 30 min (Fig. 1(a)), there is an obvious red shift of the absorption peak with increasing annealing temperature.

3.2. Precipitation of Ag nanoparticles in Ag^{+}-doped glass

For the Ag^{+}-doped glass sample, the fs laser irradiated area turned yellow after annealing at 500 °C for 30 min, whereas the unirradiated area remained colorless. In this case, the surface plasmon resonance absorption peak of Ag nanoparticles at

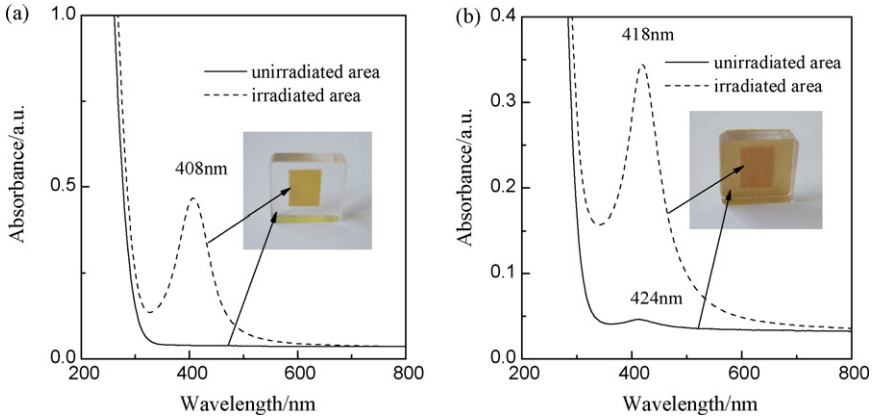

Fig. 2. (a) Absorption spectra of Ag^{+}-doped glass sample after further annealing at 500 °C for 30 min, and the inset of Fig. 1(a) shows the photograph of Ag^{+}-doped glass sample after further annealing at 500 °C and (b) absorption spectra of the unirradiated area of Ag^{+}-doped glass sample annealed at 600 °C for 30 min, and the inset is internal view of Ag^{+}-doped glass sample after annealed at 600 °C.

408 nm was observed, as shown in Fig. 2(a). No absorption in visible wavelength region was detected for the unirradiated area.

When the annealing temperature reached 600 °C, the unirradiated area of the glass became light yellow while the fs irradiated area turned dark yellow (deep amber). Fig. 2(b) exhibits the internal view of the glass sample after fs irradiation and annealing at 600 °C from which the fs scanned area was distinguished by its dark color from its surrounding area. The related absorption spectra are shown in Fig. 2(b) where a slight absorption band peaked at around 424 nm is observed in the unirradiated area while a more pronounced absorption band peaked at 418 nm is observed in fs irradiated area. They both display a red shift with respect to absorption peak of the glass annealed at 500 °C.

4. Discussion

The above results clearly indicate that, metallic nanoparticles have been precipitated space-selectively in metallic ions doped glasses by fs laser irradiation and successive annealing even at low temperature, while no any detectable metallic nanoparticles were observed in the unirradiated glass sample. fs laser irradiation reduces the annealing temperature for the precipitation of metallic nanoparticles, i.e. the temperature threshold of irradiated area for coloration occurrence is significantly lower than that of unirradiated area. For the unirradiated area of glass samples annealed at high temperature (600 °C), the absorption peaks show a significant red shift.

Noble metallic nanoparticles have been used for the coloration of glasses. Variation in color can be readily attributed to the different sizes and quantities of the nanoparticles in glass samples. It has been reported that gold particles with 10 nm diameter result in pink glasses, with diameter ranging from 10 to 20 nm produce red glasses, and those with diameter ranging from 20 to 50 nm form deep purple glasses, respectively [9]. Usually, when the approximate size of nanoparticles is smaller, the light reflection can be ignored, the absorption peak can be assigned to the surface plasmon resonance absorption of metallic nanoparticles. Based on Mie's theory, $R \propto \lambda_p^2/\Delta\lambda$, the average radii ($R$) of metal nanoparticles could be associated with the characteristic wavelength of surface plasmon resonance (λ_p) as well as the full-width at half-maximum of absorption band ($\Delta\lambda$) [10,11]. In the present work, the value of $\lambda_p^2/\Delta\lambda$ increases with increasing annealing temperature from 520 to 600 °C, indicating that the average size of the Au and Ag nanoparticles increases with increasing the annealing temperature.

In addition, the corresponding value of $\lambda_p^2/\Delta\lambda$ calculated by absorption spectra in Figs. 1(b) and 2(b) indicates that at higher annealing temperature (600 °C), the average size of the metallic nanoparticles (including both gold and silver nanoparticles) in fs laser irradiated area is smaller than that of in the unirradiated area.

Mechanism concerning the different precipitation behaviors of metallic nanoparticles as discussed above could be explained with respect to the multi-photon ionization process induced by the focused laser beam with high intensity up to is 1.95×10^{15} W/cm^2 in this study. It is well known that noble metal has a low solubility in glasses. During melt-quenching process, there are maybe various states of metal in glass samples, such as metallic ions, metallic atoms and small invisible metallic nuclei. fs laser irradiation produces a high concentration of free electrons due to the multi-photon ionization effect, and the reduction of the metallic ions to metallic atoms can be brought about as a result of the subsequent electrons captured by the metallic ions. Based on the view of literatures [4,12], electrons are driven out from the 2p orbital of the non-bridging oxygen (NBO) in the SiO_4 polyhedron via the multi-photon absorption of the incident photon.

We assume that the reduction of metallic ions in irradiated area is initiated from multi-photon absorption, inducing the reactions $Au^{3+}+3e \rightarrow Au^0$ and $Ag^+ + e \rightarrow Ag^0$, in which the electrons come from NBO's of the glass. Diffusion and aggregation of the metallic atoms are accelerated at elevated temperatures and metallic nanoparticles form and grow eventually. We propose that the high-intensity fs laser irradiation produces a high concentration of reduced metallic atoms per unit volume, and in turn, a high concentration of nucleation centers. As a result, under the same annealing process, irradiation by fs laser induces smaller and denser particles. At the same time, fs laser irradiation induces microstructural changes and defects in the glass, leading to reduction of the free energy of nucleation and crystallization. It is thus easier for metallic atoms to grow into nanoparticles at low temperature. On the other hand, structural defects may interfere with the diffusion and coalescence of metallic atoms in the glass matrix. Smaller and denser metallic nanoparticles are precipitated under lower annealing temperature.

While during the successive annealing at higher temperature (600 °C), there are high degrees of super saturation of metallic nanoparticles, the diffusion and congregation actions are confined. Hence it cannot supply the necessary source (atomic metal in the form of a super saturation) to make the nanoparticles grow to large-size. Also, it is difficult for the primary nanoparticles to recrystallization or congregate to secondary particles. That is, the mean particle size in fs irradiated area is smaller than that of unirradiated area.

Metallic nanoparticles can also precipitate in the unirradiated glass which is annealed at a certain high temperature. This is because in the as-prepared glass sample, there are also some metallic atoms, which act as precursors of metallic nanoparticles. Annealing process can promote the diffusion and aggregation of metallic atoms, and finally leads to the formation of nanoparticles. The above results show that the nanoparticles precipitation induced by fs laser technique may be useful in the fabrication of three-dimensional multi-color images and integrated all-optical switches, etc.

5. Conclusion

To summarize, we have shown that metallic nanoparticles can be space-selectively precipitated in metallic ion-doped glasses by fs laser irradiation followed by successive annealing. fs laser irradiation lowers the annealing temperature for the

precipitation of metallic nanoparticles as well as confines their diffusion and growth. The average size of metallic nanoparticle in the irradiated area is smaller than that in unirradiated area at the higher annealing temperature.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 50572027). The authors would like to thank Dr. Ya Cheng at University of Missouri-Rolla for helpful discussions and staffs at State Key Laboratory of High Field Laser Physics (Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences) for experimental assistance.

References

[1] K. Miura, H. Inouye, J. Qiu, T. Mitsuyu, K. Hirao, Optical waveguides induced in inorganic glasses by a femtosecond laser, Nucl. Instrum. Meth. Phys. Res. B 141 (1998) 726–732.

[2] C.B. Schaffer, A. Brodeur, J.F. García, E. Mazur, Micromachining bulk glass using femtosecond laser pulses with nanoJoule energy, Opt. Lett. 26 (2001) 93–95.

[3] Y. Cheng, K. Sugioka, K. Midorikawa, M. Masuda, K. Toyoda, M. Kawachi, K. Shihoyama, Control of the cross-sectional shape of a hollow microchannel embedded in photostructurable glass by use of a femtosecond laser, Opt. Lett. 28 (2003) 55–57.

[4] J. Qiu, X. Jiang, C. Zhu, M. Shirai, J. Si, N. Jiang, K. Hirao, Manipulation of gold nanoparticles inside transparent materials, Angew. Chem. Int. Ed. 43 (2004) 2230–2234.

[5] H. Zeng, Y. Yang, X. Jiang, G. Chen, J. Qiu, F. Gan, Preparation and optical properties of silicate glasses containing Pd nanoparticles, J. Cryst. Growth 280 (2005) 516–520.

[6] X. Hu, Q. Zhao, X. Jiang, C. Zhu, J. Qiu, Space-selective co-precipitation of silver and gold nanoparticles in femtosecond laser pulses irradiated Ag^{+}, Au^{3+} co-doped silicate glass, Solid State Commun. 138 (2006) 43–46.

[7] X. Jiang, J. Qiu, H. Zeng, C. Zhu, K. Hirao, Laser-controlled dissolution of gold nanoparticles in glass, Chem. Phys. Lett. 391 (2004) 91–94.

[8] H. Zeng, J. Qiu, X. Jiang, S. Qu, C. Zhu, F. Gan, Influence of femtosecond laser irradiation and heat treatment on precipitation of silver nanoparticles in glass, Chin. Phys. Lett. 20 (2003) 932–934.

[9] N.R. Wilk Jr., H.D. Schreiber, Optical properties of gold in acetate glasses, J. Non-Cryst. Solids 239 (1998) 192–196.

[10] G. Mie, Beitrage zur optik truber Medien speziel kolloidaler Metallosungen, Ann. Phys. 25 (1908) 377–445.

[11] D. Manikandan, S. Mohan, P. Magudapathy, K.G.M. Nair, Blue shift of plasmon resonance in Cu and Ag ion-exchanged and annealed soda-lime glass: an optical absorption study, Physica B 325 (2003) 86–91.

[12] O.M. Efimov, K. Gabel, S.V. Garnov, L.B. Glenov, S. Grantham, M. Richardson, M.J. Soileau, Color-center generation in silicate glasses exposed to infrared femtosecond pulses, J. Opt. Soc. Am. B 15 (1998) 193–199.