

Micro-modification of Metal-doped Glasses by a Femtosecond Laser

Bin Hua, Yasuhiko Shimotsuma, Masayuki Nishi, Kiyotaka Miura and Kazuyuki Hirao

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

We report the precipitation and control of silver and copper nanoparticles inside transparent glasses, respectively. A metal-doped silicate glass sample was first irradiated by using an 800 nm femtosecond laser at room temperature and then annealed at 550 °C. A portion of silver or copper ions near the focused part of the laser beam inside the glass were reduced to silver or copper atoms after the laser irradiation. These atoms aggregated to form nanoparticles after further annealing. A mechanism is suggested that consists of multiphoton reduction, which is induced by the fundamental light of the laser beam, and diffusion of metal atoms driven by heat energy to form nanoparticles. The observed phenomenon may have promising applications for the fabrication of three-dimensional multicolored images inside a transparent material and for integrative micro-optical switches.

Keywords: glass, silver, copper, nanoparticles, femtosecond laser

1. Introduction

Noble-metal-nanoparticle-doped glasses exhibit large third-order nonlinear susceptibility and ultrafast nonlinear response [1, 2]. They are expected to be promising materials for an ultrafast all-optical switch in the THz region [3]. There have been extensive studies conducted on the fabrication and characterization of metal-nanoparticle-doped glasses [4-11]. The fabrication methods discussed so far include traditional melting and annealing, sol-gel, chemical vapor deposition, sputtering, ion exchange, and ion implantation [4-11]. Of the aforementioned fabrication processes, ion exchange and ion implantation can realize space-selective precipitation of nanoparticles. However, both the composition of the glass matrix and the nanoparticle-precipitated area after further treatment are restricted in the ion-exchange method. In the case of ion implantation, the glass matrix is usually damaged severely and some impurities may be induced. In addition, both the size and space distribution of nanoparticles are broad from the surface to the inside of the glass sample.

Recently, an ultrashort pulsed laser has been used as a powerful tool to make microscopic modifications inside transparent materials [12-19]. The reason for using this laser is that its electric field intensity can reach 100 TW/cm², which is sufficient for inducing nonlinear optical effects in materials by the use of a focusing lens when the pulse width is 100 fs and the pulse energy is 1 μJ. The photoinduced reaction is expected to occur only near the focused part of the laser beam due to nonlinear optical processes.

Herein, we report on the space-selective precipitation and control of silver and copper nanoparticles in transparent materials, respectively. We observed space-selective photoreduction of metal ions to the metal atoms in a silicate glass by focusing 120 fs laser pulses from a regeneratively amplified Ti: Sapphire laser through a microscope objective lens. The mechanism of the occurrence of the phenomenon is also discussed.

2. Experimental procedures

The copper- and silver-doped glass compositions in this study were 70SiO₂ · 20Na₂O · 7.5CaO · 2.5Al₂O₃ · 0.15SnO · 0.1CuO and 70SiO₂ · 10CaO · 20Na₂O · 0.1Ag₂O (in mol %), respectively. Reagent grade SiO₂, CaCO₃, Na₂CO₃, Al₂O₃, SnO, Ag₂O and CuO were used as starting materials. Details of the glass-preparation procedure have been described elsewhere [20].

A regeneratively amplified 800 nm, 120 fs, 1 kHz Ti: sapphire mode-locked laser (Spectra-Physics Company) was used in this study. The laser beam was focused into the glasses about 1 mm beneath the surface by a 10× objective lens with a numerical aperture of 0.30. To write an image inside the glass samples, the irradiated locus was controlled by a computer-driven three-dimensional XYZ stage at the scanning rate of 1000 μm/s. The diameter of the laser beam was about 9 μm. The glass samples were then annealed in an electric furnace at various temperatures for one hour.

Absorption spectra of the glass samples were measured by a spectrophotometer (JASCO V-570). Electron spin resonance (ESR) measurements were carried out at X-band frequency (9.8 GHz) by an ESR spectrophotometer (JEOL-FE3X). The microwave power, time constant, modulation amplitude, and sweep time were 1 mW, 0.03 s, 1×100, and 4 cm/min, respectively. Electron probe micro-analyzer (EPMA, JEOL JXA-8900-RL) was also used in this study. All of the experiments were carried out at room temperature.

3. Results

3.1 Silver-doped glasses

Fig. 1 shows the absorption spectra of the Ag⁺-doped glass samples before (a) and after (b) femtosecond laser irradiation, and after further annealing at 550 °C for 1 hour (c). Before the femtosecond irradiation, the glass samples were transparent and colorless in visible wavelength region. It should be noted that there is no intrinsic absorption at the wavelength of 800 nm for the glass sample. However, the focused part of the samples became darkish gray after the femtosecond laser irradiation. The average power of the

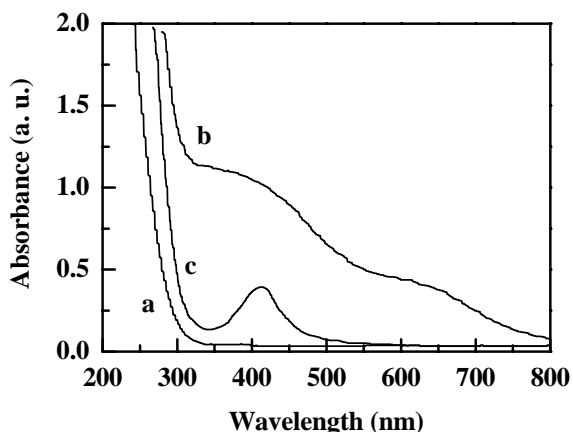


Fig. 1 Absorption spectra of the Ag^+ -doped silicate glass samples before (a) and after (b) the femtosecond laser irradiation, and after further annealing at $550\text{ }^\circ\text{C}$ for 1 hour (c).

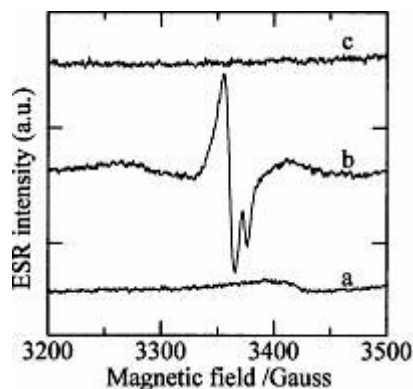


Fig. 2 ESR spectra of the glass sample before (a) and after (b) the femtosecond laser irradiation, and after further annealing at $550\text{ }^\circ\text{C}$ for 1 hour (c).

laser beam was set to 80 mW in this study. There was an apparent increase in the absorbance in the wavelength region from 300 to 800 nm in the irradiated region. The characteristic absorption bands at about 430 and 650 nm can be assigned to hole trap centers (HC) at nonbridging oxygen near Ag^+ ions, e.g., HC_1 and HC_2 [21]. The HC_1 and HC_2 are holes trapped at the nonbridging oxygen in the SiO_4 polyhedron with two and three nonbridging oxygen, respectively. Therefore, an electron was driven out from the $2p$ orbital of a nonbridging atom near the Ag^+ ions after femtosecond laser irradiation, while Ag^+ captured the electron to form an Ag atom. After further annealing at $550\text{ }^\circ\text{C}$ for 1 hour, the irradiated area in glass sample became yellow. Fig. 1 also shows that a new peak appeared at 450 nm in the absorption of the glass sample after further annealing at $550\text{ }^\circ\text{C}$. The peak can be assigned to the absorption due to the surface plasmon of the silver nanoparticles [22]. The photon-reduced Ag atoms aggregated to form nanoparticles after the heat treatment. An unirradiated glass sample precipitates nanoparticles only at temperatures above $600\text{ }^\circ\text{C}$. Therefore, we suggest that the neutralized Ag promotes nucleation. Femtosecond

laser irradiation can be used to separate and control the nucleation and growth processes.

Fig. 2 shows the ESR spectra of the glass sample before (a) and after (b) the femtosecond laser irradiation at room temperature, and after further annealing at $550\text{ }^\circ\text{C}$ for 1 hour (c). No apparent signal was detected in the unirradiated glass sample, while the spectrum of the glass sample after femtosecond laser irradiation showed a broad signal at $g \sim 2.10$ and two signals at $g \sim 2.00$. The broad signal at 2.10 may be due to the Ag atom [23], while two signals at $g \sim 2.00$ can be assigned to hole trap centers, HC_1 and HC_2 [24].

3.2 Copper-doped glasses

As expected, Cu^{2+} ions are also possible to reduce in glasses as well as silver ions. When prepared, copper-doped glass appeared transparent and blue color, indicating that the copper present in the glass existed mainly in the divalent state. Fig. 3 shows the absorption spectra of Cu^{2+} -doped glass samples before (a) and after laser irradiation (b) and successive annealing at $550\text{ }^\circ\text{C}$ for 1 hour (c). The absorption band of the as-prepared glass sample from 700 to 800 nm was due to the absorption of Cu^{2+} ions, and there was no apparent absorption from 500 to 600 nm. But after laser irradiation and further annealing, the irradiated area in glass appeared red color. Here, the average power of the laser beam was 80 mW as well. In absorption spectra, there was a clear absorption band at peak about 570 nm in the sample after annealing at $550\text{ }^\circ\text{C}$, which should result from surface plasma resonance absorption of copper nanoparticles [25]. These results indicated portions of copper ions were reduced after laser irradiation. Furthermore, the glass after annealing at $650\text{ }^\circ\text{C}$ did not show any absorption at 570 nm. We estimated that copper nanoparticles dissolved away at this temperature and transformed to copper ions in glass.

Furthermore, we carried out EPMA measurement of the red area in the irradiated glass sample after annealing at $550\text{ }^\circ\text{C}$ for 1 hour. As shown in Fig. 4, in backscattering

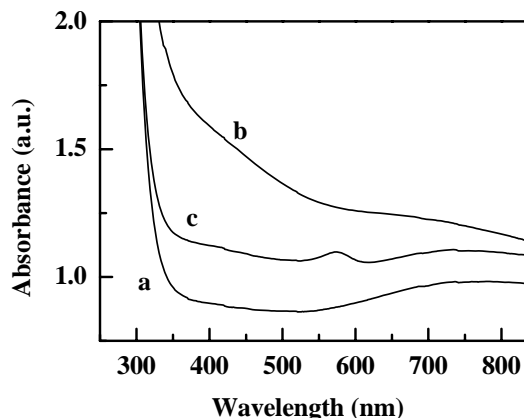


Fig. 3 Absorption spectra of the Cu^{2+} -doped glass samples before (a) and after femtosecond laser irradiation (b), and subsequent annealing at $550\text{ }^\circ\text{C}$ for 1 hour (c).

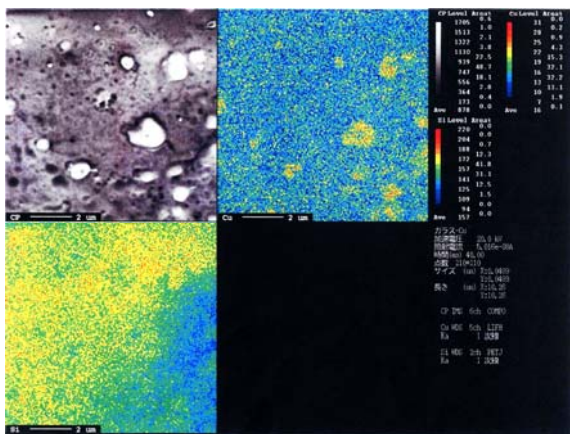


Fig. 4 Backscattering electron image (left upper) and Cu (right upper), Si (left lower) spectrum mapping image of the irradiated area in copper-doped glass. The sample was annealed at 550 °C for 1 hour. The scale bar is 2 μm.

electron image, the white area was corresponding to the red area in glass sample. Copper spectrum mapping confirmed that copper concentration in the red area was clearly higher than that in the surrounding glass sample, while further element composition analysis showed the differences of the other element concentrations in glass, e.g. oxygen, silicon, sodium et al. were little between the red area and the surrounding glass. Thus, it was estimated that the copper nanoparticles were precipitated after laser irradiation and were agglomerated to form red area inside silicate glasses.

4. Discussion

The reduction of metal ions to atoms by femtosecond laser irradiation is the key process of this method. Silver or copper ions capture the “free” electrons created by multiphoton processes and are then reduced to atoms, which aggregate to form nanoparticles during annealing.

The light intensity of the focused laser beam used in this study is of the order of 10^{15} W/cm². In general, the light intensity, in order of 10^{14} - 10^{17} W/cm², is high enough to generate multiphoton ionization in the glass matrix [26]. Therefore, the active electrons and holes can be created in the glass through multiphoton ionization, Joule heating, and collisional ionization [26], and form plasma. When the metal-doped silicate glass, being transparent originally, was irradiated by the focused femtosecond laser, electrons were driven out of the valence states by multiphoton absorption of the incident photon. Besides the trapping of active sites to form color centers, the free electrons were also trapped by metal ions to form metal atoms, resulting the reduction of the metal ions. At temperatures below 300 °C, only some trapped electrons and holes were excited by thermal energy and recombined with each other. When the glass sample was annealed at temperatures about 550 °C, silver or copper atoms got sufficient energy to overcome the interaction between the metal atoms and the glass network structure and started to move. The formation of the metal nanoparticles was due to the aggregation of metal atoms. It was also confirmed that no change occurred in the absorption spectrum of the nanoparticle-precipitated glass

sample after heat treatment at room temperature, even over a period of six months. This indicated that the precipitated nanoparticles were stable at room temperature. Additionally, the reduction of metal nanoparticles was not seen in the glass sample without laser irradiation, even after the sample had been annealed at 600 °C for more than 2 hours. This indicated that the temperature for precipitation of the metal nanoparticles in laser irradiated glass, compared with the temperature for purely thermal-induced precipitation of them, were considerably lowered since a higher temperature was needed to reduce the metal ions in the latter case. Thus, the reduction of a metal ion to an atom by femtosecond laser irradiation was essential in forming metal nanoparticles, and the metal atom acted as a crystal nucleus for crystal growth.

5. Conclusion

In summary, we have observed space-selective precipitation and control of silver and copper nanoparticles in transparent materials by a focused infrared femtosecond pulsed laser irradiation at room temperature and further annealing at high temperature, respectively. Nonbridging oxygen is suggested to act as HCs while the silver and copper ion acts as an electron-trapping center, thus resulting in the reduction of silver and copper ions to atoms. These metal atoms, upon thermally treating at around 550 °C, will diffuse and aggregate to form metal nanoparticles.

Our results demonstrated the possibility of space-selective precipitation of nanoparticles in a micrometer-small dimension inside a transparent material by using a focused nonresonant femtosecond pulsed laser and heat treatment. This technique will be useful in the fabrication of three-dimensional multicolored industrial art objects, optical memory, and integrative waveguidelike optical switches with ultrafast nonlinear response.

Acknowledgements

The authors would like to acknowledge the financial support provided by the Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and also by the Mitsubishi Foundation.

References

- [1] D. Ricard, P. Roussignol, and C. Flytzanis: *Opt. Lett.*, 10, (1985) 511.
- [2] F. Hache, D. Ricard, and C. Flytzanis: *J. Opt. Soc. Am. B*, 3, (1986) 1647.
- [3] H. Inouye, K. Tanaka, I. Tanahashi, and K. Hirao: *J. Phys. Soc. Jpn.*, 68, (1999) 3810.
- [4] Y. Hamana, N. Hayashi, A. Nakamura, and S. Omi: *J. Lumin.*, 87, (2000) 859.
- [5] M. Ferrari, L. M. Gratton, A. Maddalena, M. Montagna, and C. Tosello: *J. Non-Cryst. Solids*, 191, (1995) 101.
- [6] Y. Maeda: *Phys. Rev. B*, 51, (1995) 1658.

- [7] M. Dubel and G. Mosel: *Jpn. J. Appl. Phys.*, Part 1, 33, (1994) 5892.
- [8] F. Gonella, G. Mattei, P. Mazzoldi, C. Sada, G. Battaglin, and E. Cattaruzza: *Appl. Phys. Lett.*, 75, (1999) 55.
- [9] H. Hofmeister, S. Thiel, M. Dubiel, and E. Schurig: *Appl. Phys. Lett.*, 70, (1997) 1694.
- [10] S. Chen, T. Akai, K. Kadono, and T. Yazawa: *Appl. Phys. Lett.*, 79, (2001) 3687.
- [11] E. Valentin, H. Bernas, C. Ricolleau, and F. Creuzet: *Phys. Rev. Lett.*, 86, (2001) 99.
- [12] K. M. Davis, K. Miura, N. Sugimoto, and K. Hirao: *Opt. Lett.*, 21, (1996) 1729.
- [13] E. N. Glezer, M. Milosavljevic, L. Huang, R. J. Finalay, T.-H. Her, J. P. Callan, and E. Mazur: *Opt. Lett.*, 21, (1996) 2023.
- [14] K. Miura, J. Qiu, H. Inouye, T. Mitsuyu, and K. Hirao: *Appl. Phys. Lett.*, 71, (1997) 3329.
- [15] J. Qiu, K. Miura, H. Inouye, Y. Kondo, T. Mitsuyu, and K. Hirao: *Appl. Phys. Lett.*, 73, (1998) 1763.
- [16] J. Qiu, K. Miura, and K. Hirao: *Jpn. J. Appl. Phys.*, Part 1, 37, (1998) 2263.
- [17] J. Qiu, K. Miura, T. Suzuki, T. Mitsuyu, and K. Hirao: *Appl. Phys. Lett.*, 74, (1999) 10.
- [18] J. Qiu, C. Zhu, T. Nakaya, J. Si, F. Ogura, K. Kojima, and K. Hirao: *Appl. Phys. Lett.*, 79, (2001) 3567.
- [19] H. Sun, Y. Xu, S. Joudkazis, K. Sun, M. Watanabe, J. Nishii, S. Matsuo, and H. Misawa: *Opt. Lett.*, 20, (2001) 325.
- [20] B. Hua, J. Qiu, Y. Shimotsuma, K. Fujita, and K. Hirao: *J. Mater. Res.*, 20, (2005) 644.
- [21] A. Bishay: *J. Non-Cryst. Solids*, 3, (1970) 54.
- [22] I. Tanahashi, M. Yoshida, Y. Manabe, and T. Tohda: *J. Mater. Res.*, 10, (1995) 362.
- [23] H. Imagawa: *J. Non-Cryst. Solids*, 1, (1969) 262.
- [24] J. W. H. Schreurs: *J. Chem. Phys.*, 47, (1967) 818.
- [25] S. Kurbitz, J. Porstendorfer, K. -J. Berg, and G. Berg: *Appl. Phys. B*, 73, (2001) 333.
- [26] B. C. Stuart, M. D. Feit, A. M. Rubenchik, B. M. Shore, and M. D. Perry: *Phys. Rev. Lett.*, 74, (1995) 2248.

(Received: May 16, 2006, Accepted: February 1, 2007)