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2004 J. Phys.: Condens. Matter 16 2901

(http://iopscience.iop.org/0953-8984/16/16/014)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 2901–2906 PII: S0953-8984(04)68079-9

The effect of femtosecond laser irradiation conditions on precipitation of silver nanoparticles in silicate glasses

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Received 28 August 2003, in final form 2 December 2003
Published 8 April 2004
Online at stacks.iop.org/JPhysCM/16/2901
DOI: 10.1088/0953-8984/16/16/014

Abstract

We report the effect of femtosecond laser irradiation conditions on precipitation of silver nanoparticles in silicate glasses. Absorption spectra show that the intensity of the absorption peak due to the surface plasmon resonance of silver nanoparticles increases with increase of the light intensity of the laser beam, beam diameter in the focal plane, Rayleigh length of the focusing lens and shot number of the laser pulse. The position of the surface plasmon resonance peak remains constant regardless of the variation of the irradiation conditions. The influences of laser irradiation conditions on the size and spatial distribution of silver nanoparticles are discussed.

1. Introduction

Femtosecond pulsed lasers have been widely used in microscopic structure modification of transparent materials since its development. When a femtosecond laser beam is focused onto a transparent material, the high peak power of the laser pulse induces multiphoton absorption and ionization processes near the focal point of the laser beam inside the transparent materials. The diameter of the induced microstructure can be less than 1 μm, and can be controlled by the laser irradiation conditions [1–5]. Several groups have demonstrated promising applications of femtosecond induced three-dimensional (3D) microstructures in the formation of optical waveguides, optical memory with ultrahigh storage density and micro-optical components, etc [6–8]. Recently, we reported that metallic nanoparticles could be precipitated near the focal point of the femtosecond laser beam inside transparent glasses by irradiation with the femtosecond laser and subsequent annealing [9]. We suggest the mechanism of the

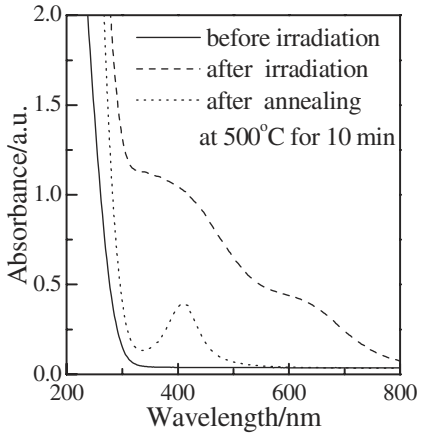

Figure 1. Absorption spectra of the Ag^+-doped glass sample before and after laser irradiation, and further annealing at 500 °C for 10 min.

precipitation of silver nanoparticles is that laser irradiation induces the reduction of silver ions to silver atoms, and subsequent annealing results in the aggregation of silver atoms to form silver nanoparticles.

In this paper, we investigate the effect of femtosecond laser irradiation conditions on the precipitation of silver nanoparticles within glass.

2. Experiments

Ag^+-doped silicate glass with the composition of $77SiO_2{\cdot}18Na_2O{\cdot}5CaO{\cdot}0.01Ag_2O$ (mol%) was prepared by a melt-quenching process. A mixed batch was melted at 1550 °C for 4 h under an ambient atmosphere. The resultant transparent and colourless glass sample was polished to 3 mm thick plates. Glass samples were then irradiated with a regeneratively amplified 800 nm, 120 fs, 1 kHz Ti:sapphire laser (Spectra-Physics Company) through a focusing lens in an optical microscope. The position of the focal point was 1 mm beneath the glass surface. A plane of 4.0 mm $\times$ 4.0 mm was written inside the glass sample that consisted of lines at an interval of 20 μm by scanning the laser beam at a constant rate. Irradiated samples were then annealed in an electric furnace at 500 °C for 10 min in air. Optical absorption and fluorescence spectra were measured with JASCO V-570 absorption and FP-6500 fluorescence spectrophotometers, respectively, at room temperature. TEM (transmission electron microscope) observation was carried out with a JEM-2010 electron microscope (JEOL).

3. Results

3.1. Precipitation of silver nanoparticles

Figure 1 shows the absorption spectra of the Ag^+-doped glass sample before and after laser irradiation, and further annealing at 500 °C for 10 min. The laser beam with average power of 80 mW was focused by a 10$\times$ objective lens with a numerical aperture (NA) of 0.30. The scanning rate was 2500 μm s^{-1}. The light intensity of the laser beam is estimated to be 7.8×10^{15} W cm^{-2}. The Ag^+-doped silicate glass sample became grey after irradiation of the focused femtosecond laser. Absorption peaks at 430 and 620 nm can be observed in figure 1. The peaks can be assigned to the nonbridging oxygen hole centres HC1 and HC2,

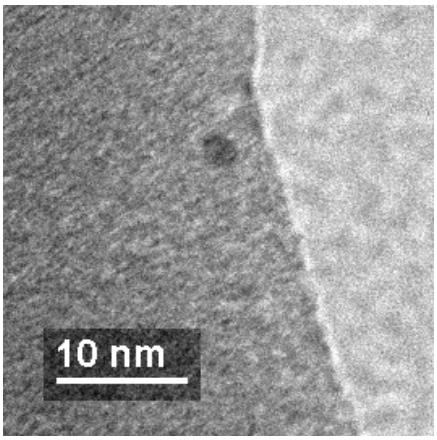

Figure 2. A TEM image of a femtosecond laser-irradiated Ag^+-doped glass sample after further annealing at 500 °C for 10 min.

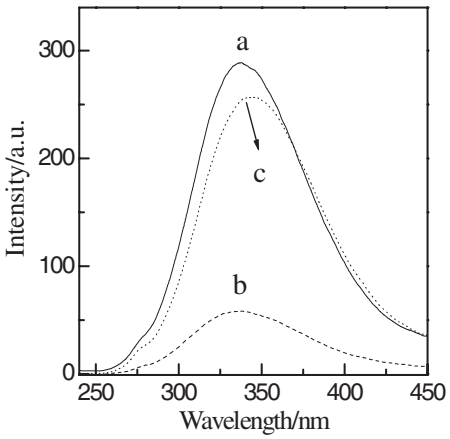

Figure 3. Fluorescence spectra of the Ag^+-doped glass sample before (a) and after (b) femtosecond laser irradiation and further annealing at 500 °C for 10 min (c). The excitation wavelength is 227 nm.

respectively [10]. After annealing at 500 °C for 10 min, the sample became yellow, and a peak at 408 nm due to the surface plasmon absorption of the silver nanoparticles was observed [11].

Figure 2 is a TEM image showing the precipitation of nanoparticles in the femtosecond laser-irradiated Ag^+-doped glass sample after annealing at 500 °C for 10 min. Compositional analysis using energy dispersive spectroscopy (EDS) in TEM confirms that the spherical nanoparticle is metallic Ag. The diameter of the silver nanoparticle is about 2 nm. Statistical observation showed that the sizes of the precipitated nanoparticles were about 1–4 nm. No silver nanoparticles were observed in the unirradiated glass.

Figure 3 shows the fluorescence spectra of the Ag^+-doped silicate glass before and after femtosecond laser irradiation and further annealing at 500 °C for 10 min. The emission peak at 350 nm can be attributed to the transition of isolated Ag^+ centres [12]. Compared to that for unirradiated glass, the relative intensity of the emission peak decreased due to the reduction of free Ag^+ ions to Ag^0 atoms after the femtosecond laser irradiation. After subsequent annealing, the intensity of the emission increased. We suggest that during the annealing process, a portion of silver atoms combined with released free electrons to form Ag^+ ions, while a portion of the silver atoms aggregated to form silver nanoparticles.

3.2. Effect of light intensity

We irradiated the Ag^+-doped glass sample with the femtosecond laser under different conditions. The absorption spectra of the Ag^+-doped glass sample after irradiation with different light intensities and further annealing at 500 °C for 10 min are shown in figure 4. The scanning rate was 2500 μm s^{-1}. A 10× microscope objective lens with a numerical aperture of 0.30 was used to focus the laser beam. With increasing power density, the absorbance increased but the position of the absorption peak remained at 408 nm.

3.3. Effect of beam diameter and Rayleigh length of the focusing lens

Figure 5 shows absorption spectra of the Ag^+-doped glass sample after laser irradiation with different diameters and Rayleigh lengths of the focusing lens and further annealing at 500 °C for 10 min. The average laser power was 80 mW and the scanning rate was 2500 μm s^{-1}. The

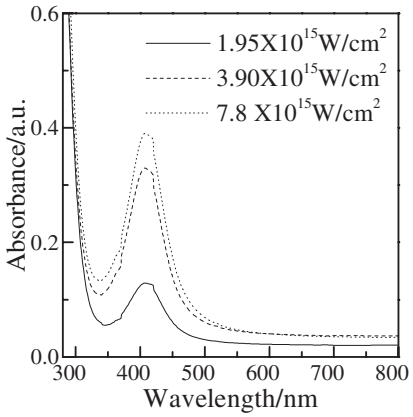

Figure 4. Absorption spectra of the Ag^+-doped glass sample after laser irradiation with different light intensities and further annealing at 500 °C for 10 min.

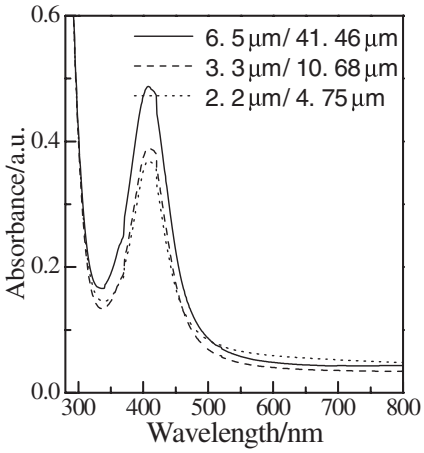

Figure 5. Absorption spectra of the Ag^+-doped glass sample after laser irradiation with different beam diameters (D) and Rayleigh lengths (L) of the focusing lens and further annealing at 500 °C for 10 min.

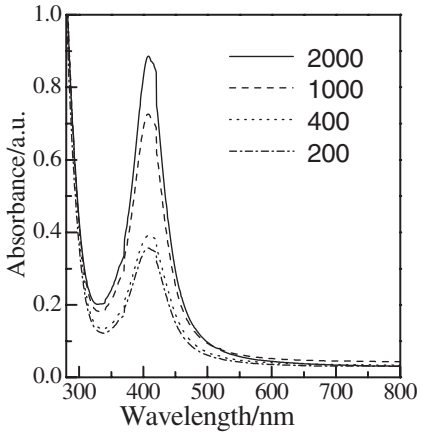

Figure 6. Absorption spectra of the Ag^+-doped glass sample after laser irradiation with different shot numbers of laser pulses per millimetre and further annealing at 500 °C for 10 min.

laser beam was focused by the objective lens with magnification/NA of 5×/0.15, 10×/0.30 and 20×/0.45. The calculated beam diameter and Rayleigh length are 6.5 μm/41.46 μm, 3.3 μm/10.68 μm and 2.2 μm/4.75 μm, respectively. The intensity of the absorption peak due to surface plasmon resonance of silver nanoparticles increased with increase of the beam diameter and Rayleigh length of the focusing lens. No apparent peak shift was observed.

3.4. Effect of shot number of the laser pulse

Figure 6 shows the absorption spectra of the glass sample after laser irradiation with different numbers of shots and further annealing at 500 °C for 10 min. The average laser power was 80 mW and a 10× microscope objective was used to focus the laser beam. The scanning rate was 500 μm s^{-1}, 1000 μm s^{-1}, 2500 μm s^{-1} and 5000 μm s^{-1} and the shot number of the

laser pulse per millimetre was 2000, 1000, 400 and 200 shots, respectively. It is observed that the intensity of the absorption peak increased with increase of the shot number of the laser pulse. The wavelength of the absorption peak remained constant.

4. Discussion

The light intensity of the focused laser beam used in this study is of the order of 10^{15} W cm^{-2}, which is high enough for multiphoton ionization of the glass matrix, resulting in generation of free electrons and holes. It should be pointed out that we did not observe any apparent micro-cracks in the irradiated area, which may affect the resulting absorption spectrum due to the precipitation of silver nanoparticles. Besides the trapping of electrons and holes by active sites to form colour centres, some of the free electrons are trapped by Ag^+ ions, resulting in the formation of Ag^0 atoms during the femtosecond laser irradiation. These Ag^0 atoms diffuse and aggregate to form silver nanoparticles during the annealing process [9].

Different laser irradiation conditions result in different intensities of the peak due to the surface plasmon resonance of silver nanoparticles, but the position of the absorption peak remains at 408 nm regardless of the laser irradiation conditions. Usually, the resonance peak becomes sharp and exhibits a red-shift with increasing size of the nanoparticles [13–15]. When the approximate size of the nanoparticles is smaller than 20 nm, the following formula can be used to calculate the average size of the nanoparticles [16]:

$$R = \frac{V_f \lambda_p^2}{2\pi C \Delta\lambda}. \tag{1}$$

V_f is the Fermi velocity of the electrons in bulk metal (silver: 1.39×10^8 cm s^{-1}), $\Delta\lambda$ is the full width at half-maximum of the absorption band and λ_p is the characteristic wavelength at which surface plasmon resonance occurs. Both λ_p and $\Delta\lambda$ depend on the glass matrix and the size of the metal nanoparticles. From the formula, the diameter of the silver nanoparticles is around 2 nm, which is in good agreement with the TEM observation. Both λ_p and $\Delta\lambda$ remain almost constant; therefore, the size distribution of silver nanoparticles is insensitive to laser irradiation conditions.

However, the laser irradiation conditions affect the spatial distribution of silver nanoparticles. From the optical images observed through the optical microscope, both the size and the depth of the nanoparticle precipitated region increased with increase of the power density. When the objective lens and scanning rate were kept constant, large light intensity means that there are a lot of photons around the focal point of the laser beam; this results in a broad and long nanoparticle precipitated region in which the light intensity exceeds the threshold for the occurrence of the multiphoton reactions. When the magnifying multiple and NA of the lens increase from $5\times/0.15$ to $20\times/0.45$, the spot size of the laser beam decreases from 6.5 to 2.2 μm; though the power density increased with increasing numerical aperture of the objective lens, the nanoparticle precipitated region decreased due to the small beam diameter and Rayleigh length of the focusing lens, and the silver nanoparticles precipitated only in a very localized area. The decrease of shot number means that the number of photons per unit volume which induce multiphoton absorption or ionization decreases; the probability for inducing reduction of Ag^+ to Ag also decreases. Therefore, the concentration of silver nanoparticles decreases with increasing scanning rate. The above results showed that it is possible to control the spatial distribution of silver nanoparticles by changing the laser irradiation conditions. However, a more quantitative analysis is needed to clarify the effect of laser irradiation conditions on the precipitation of silver nanoparticles in glasses.

5. Conclusion

We examined the effect of laser irradiation conditions on the precipitation of silver nanoparticles in silicate glasses. The experimental results show that the quantity and space distribution of silver nanoparticles increase with increase of the light intensity, beam diameter in the focal plane, Rayleigh length of the focusing lens and shot number of the laser pulse. But the average size of silver nanoparticles is insensitive to the femtosecond laser irradiation conditions. The unirradiated part, irradiated part and nanoparticle precipitated area show different absorption and emission properties. Therefore, the observed phenomenon is promising for the fabrication of three-dimensional multicoloured industrial art objects and optical storage with ultrahigh storage density. In addition, the precipitated silver nanoparticles in the present glass sample show a relatively sharp size distribution. By adjusting the composition of the glass matrix and doping concentration, we expect to obtain a glass with a broad size distribution of silver nanoparticles after femtosecond laser irradiation and successive annealing; thus the glass may find application in integrated optical switch operation over a wide wavelength region.

Acknowledgments

The authors would like to acknowledge the financial support provided by the National Natural Science Foundation of China under grant No 50125258.

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