Laser-controlled precipitation of gold nanoparticles in silicate glasses

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(Received 13 February 2003; accepted 9 June 2003)

We report on the observation of space-selective precipitation of gold nanoparticles in Au_2O-doped silicate glass by a method of irradiation with an 800-nm femtosecond laser and further heat treatment. The irradiated region of the glass first became gray in color after irradiation with the femtosecond laser and then turned red after further heat treatment at around 520 °C, indicating that gold nanoparticles have precipitated in the irradiated region of the glass. A possible mechanism has been suggested that the Au^+ ions in the region irradiated are reduced to Au^0 atoms by the femtosecond laser, and then the Au^0 atoms accumulate to form gold nanoparticles with the glass sample heat treated. The observed phenomenon should have potential applications in the fabrication of ultrafast all-optical switches.

I. INTRODUCTION

Gold nanoparticles, used for more than 300 years in the coloration of glass to obtain so-called gold ruby glass,[1] have again aroused the interests of scientists because of their unique optical properties,[2–4] such as nonlinear optical properties and ultrafast nonlinear response, which are different from those of bulk gold as well as those of individual gold atoms or ions. Materials doped with gold nanoparticles have a large optical absorption coefficient due to the surface plasmon resonance of gold nanoparticles in wavelengths from 500 to 560 nm, and consequently strong enhancement of the third-order nonlinear optical susceptibility ($\chi^{(3)}$) has been observed around the peak of the absorption band.

Glasses, with the advantages of being transparent and able to be made in bulk materials, have been used as base materials to dope gold nanoparticles. Extensive studies have been made on the fabrication of the glass doped with gold nanoparticles.[5,6] Conventional methods used to obtain glasses containing gold nanoparticles fabricate Au^+-doped glasses through traditional melting or ion-exchange techniques, combined with heat treatment or ionizing radiation of the glasses to precipitate gold nanoparticles. Other techniques, such as sol-gel, chemical vapor deposition, sputtering, and ion implantation,[7–10] are also widely used in the fabrication of the glass doped with gold nanoparticles. However, it is not easy to space-selectively control the precipitation of gold nanoparticles in glasses by using these methods. Recently, we first used a new method combining the irradiation of a femtosecond laser and successive heat treatment to produce silver nanoparticles and succeeded in the space-selective precipitation of silver nanoparticles inside glass.[11] Nice butterflies, yellow in color, composed of silver nanoparticles, were drawn inside the glass sample. In the end of the paper of Ref. 11, it is mentioned that gold nanoparticles can also be induced to space-selectively precipitate inside glass, but no details were provided.

In this paper, we report in detail on the space-selective precipitation of gold nanoparticles in Au^+ doped silicate glasses using a method identical to that in Ref. 11. We observed that gold nanoparticles, red in color, could be precipitated anywhere inside the glass with the help of a femtosecond laser. Other interesting phenomena have been observed in the Au^+ doped glass, such as the variation of the color of gold nanoparticles with the intensity of the laser and laser-induced dissolution of gold nanoparticles preformed in the glass, which are now being studied and will be reported latter.

II. EXPERIMENTAL

The composition of the glass sample studied was $70SiO_2 \cdot 20Na_2O \cdot 10CaO$ doped with $0.01Au_2O$ (mol%). Regent-grade SiO_2, Na_2CO_3, $CaCO_3$, and $AuCl_3 \cdot HCl \cdot 4H_2O$ were used as starting materials. The batch was melted in a platinum crucible at 1500 °C for 2 h under the ambient atmosphere. Then the melt was poured onto a stainless module kept at room temperature, and quenched into transparent and colorless glass. The glass was annealed at 500 °C for 1 h. Glass samples were obtained by cutting and polishing the glass to a thickness of 3 mm.

A Ti:sapphire laser (800 nm, 120 fs, 1 KHz) was used in our experiments. The maximum average output power was 700 mW. The laser beam with an average power of 130 mW was focused by a 5× objective lens with a numerical aperture of 0.13 into the interior of the glass sample, which was put on an XYZ stage. The XYZ stage was controlled by a computer and could move in three dimensions with a precision of 100 nm at different speeds. A spectrophotometer (JASCO V-570, Japan) was used to measure the absorption spectra of the glass samples. Electron spin resonance (ESR) was recorded with a spectrometer (Bruker ESP 300E, Germany), which was operated at X-band microwave frequency (~9.68 GHz).

For the convenience of the following measures, an irradiated area of 4 × 10 mm was obtained by focusing the laser into the glasses and translating the glasses to-and-fro at a speed of 2.5 mm/s and with a line interval of 20 μm along the direction perpendicular to the incident laser beam.

III. RESULTS AND DISCUSSION

With the glass irradiated by the laser, an obvious change in color from colorless to gray was observed in the irradiated area of the glass. Figure 1 shows the difference in absorption between the original and irradiated glass. The absorption of the glass in the irradiated area increases greatly in the wavelength range of 260–800 nm, arising from the color-center generation induced by the laser.[12,13] Three absorption bands, with peaks at 320, 430, and 620 nm, respectively, can be observed in Fig. 1. The absorption bands at 620 nm, and at 430 and 320 nm can be ascribed to electron-trapped color centers and hole-trapped color centers, respectively.[14]

After the irradiation of the laser, the glass sample was heat treated at different temperatures between room temperature and 600 °C, resulting in further changes in the color of the glass with the temperature. The changes fall into two major steps, which are the disappearance of the color centers with temperatures lower than 300 °C and the appearance of red color with annealing temperatures higher than 500 °C.

Figure 2 shows the variation of the absorption of the irradiated glass with the temperature between room temperature and 300 °C. The absorption bands at 430 and 620 nm gradually decrease as the temperature increases from room temperature, and totally disappear at the temperature of 300 °C. The disappearance of the absorption bands at 430 and 620 nm results from the decomposition of the color centers, which are thermally unstable at several hundred degrees centigrade.

Further heat treatment at a higher temperature can result in another change in the color of the glass. A color of red starts to appear in the irradiated area of the glass with the temperature reaching 500 °C, and the intensity of the color increases with the increase of annealing temperature until 600 °C. Figure 3 shows the change of the absorption of the glass in the irradiated area corresponding to the change in the color of the glass. Since the gold nanoparticles have a characteristic absorption band in the wavelength range of 500–560 nm due to the surface plasmon absorption of gold nanoparticles,[15] the appearance of the

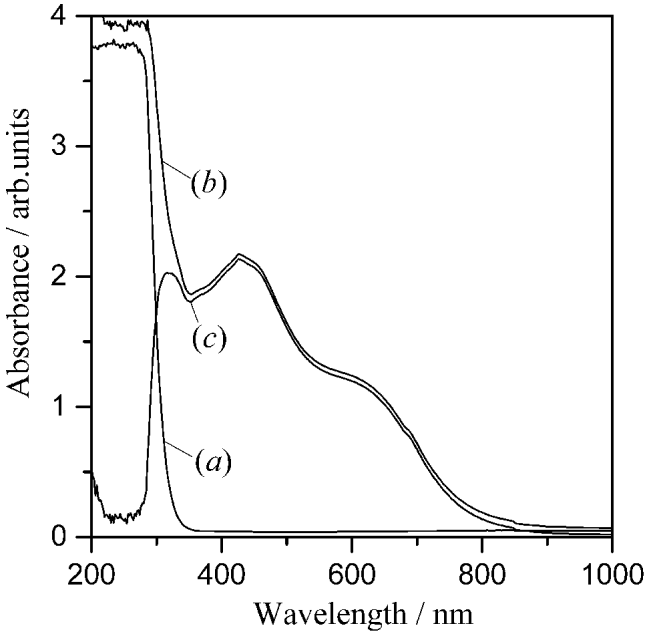

FIG. 1. Absorption spectra and induced absorption spectra of Au^+-doped silicate glass: curve (a) original glass; curve (b) irradiated by femtosecond laser; and curve (c) difference between curves (a) and (b).

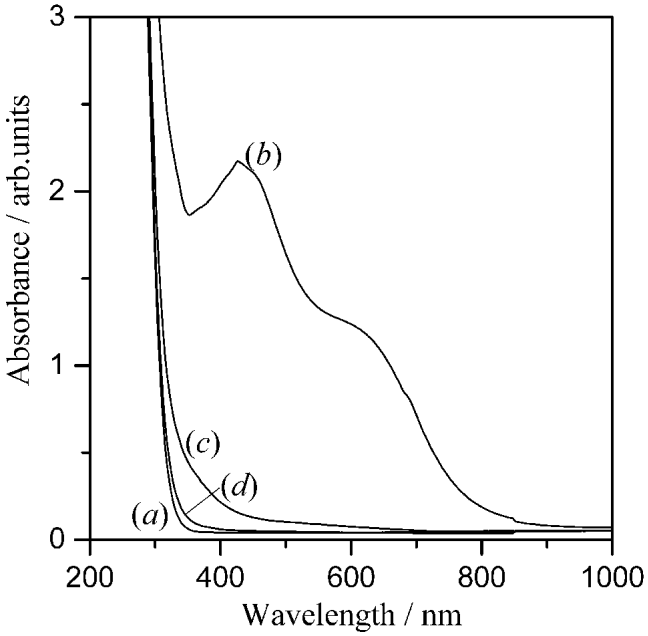

FIG. 2. Absorption spectra of Au^+ doped silicate glass (a) before and (b) after femtosecond laser irradiation, and after further heat treatment at (c) 200 °C and (d) 300 °C for 30 min.

absorption band peaking at 500 nm, which is observed in Fig. 3 [curve (c)], is indicative of the precipitation of gold nanoparticles in the glass irradiated by the laser.

Figure 4 shows the ESR spectra of the Au^+-doped silicate glass irradiated by the femtosecond laser as well as the variation of ESR spectra with the temperature of the heat treatment. A strong signal, which is due to the hole trap centers induced by femtosecond laser,[11,16] was observed after the glass irradiated by the femtosecond laser [curve (a)]. The hole-trap centers are the same as those induced in the soda-lime-silicate glasses by ultraviolet light or x-ray.[14] The signal of ESR centers becomes weaker as temperature increases, and no signal is observed in the glass sample with the annealing temperature higher than 300 °C. Therefore, the variation of ESR spectra with annealing temperature demonstrates that the radiation defects of hole-trap centers are decomposed in the heat treatment of the glass at a temperature of several hundred degrees centigrade. This result is in good agreement with the decomposition of the color centers upon heat treatment, concluded from the measurement of absorption spectra of the glass.

Here are some considerations on the mechanism of the precipitation of gold nanoparticles. On the irradiation of the Au^+-doped silicate glass by the focused femtosecond laser, nonlinear absorption occurs near the focus point of the laser with an ultrahigh power density,[12] resulting in the generation of free electrons from $2p$ orbital of nonbridging oxygen. The free electrons, while they travel in the glass matrix, will be trapped by structural defects to form color centers, and more importantly, will be trapped by Au^+ ions to form Au^0 atoms. Therefore, we believe that the Au^+ ions near the focus point of the laser have been reduced to Au^0 atoms with the irradiation of the laser.

$$\text{glass matrix} \xrightarrow{\text{laser}} h^+ + e^- \quad , \tag{1}$$

$$h^+ \text{ or } e^- + \text{structural defects} \rightarrow \text{color-centers} \quad , \tag{2}$$

$$e^- + Au^+ \rightarrow Au^0 \quad . \tag{3}$$

In heat treating the glass sample irradiated by the laser, the electron-trapped color centers were stimulated thermally and released to free electrons again. These electrons may also be trapped by Au^+ ions, but most of them recombined with holes and then disappeared. This results in the bleaching of the glass at 300 °C because of the decomposition of color centers. As the temperature increases, the mobility of pre-formed Au^0 atoms increases, which will lead to the increase of the diffusion of the atoms as well as the final aggregation of them. As to this case, when the temperature of the heat treatment reaches 500 °C, gold nanoparticles red in color begin to appear in the irradiated area of the glass. Since the diffusion of Au^0 atoms relates with the time and the temperature of the heat treatment, more gold nanoparticles form when the irradiated glass is heat treated at a higher temperature or for a longer time at the temperature range from 500 to 600 °C. However, there are still some questions left unclear. For example, according to our explanations of the mechanism of the gold nanoparticles formation process, there should be a lot of hole-trapped color-center left in the glass matrix for the trapping of electrons by Au^+. However, no signal corresponding to

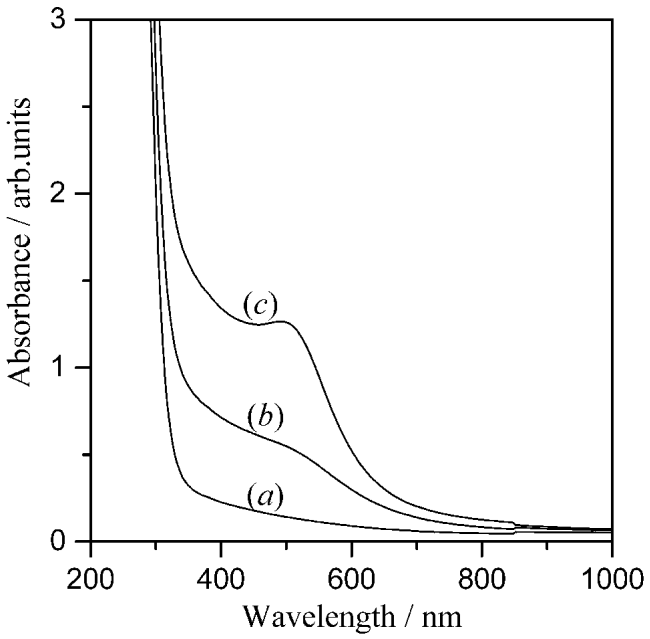

FIG. 3. Absorption spectra of Au^+-doped silicate glass after femtosecond laser irradiation and further heat treatment at (a) 500 °C, (b) 520 °C, and (c) 540 °C for 30 min.

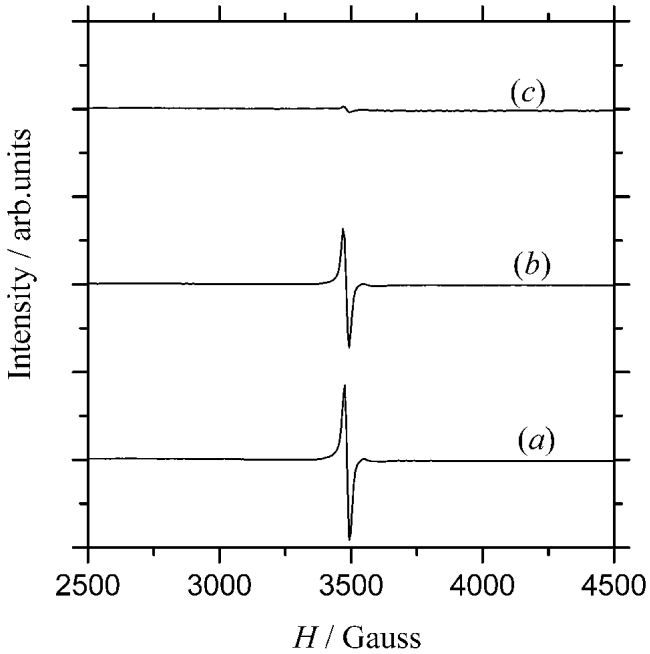

FIG. 4. ESR spectra of Au^+ doped silicate glass (a) after irradiation of femtosecond laser and after further heat treatment at (b) 100 °C and (c) 200 °C for 30 min.

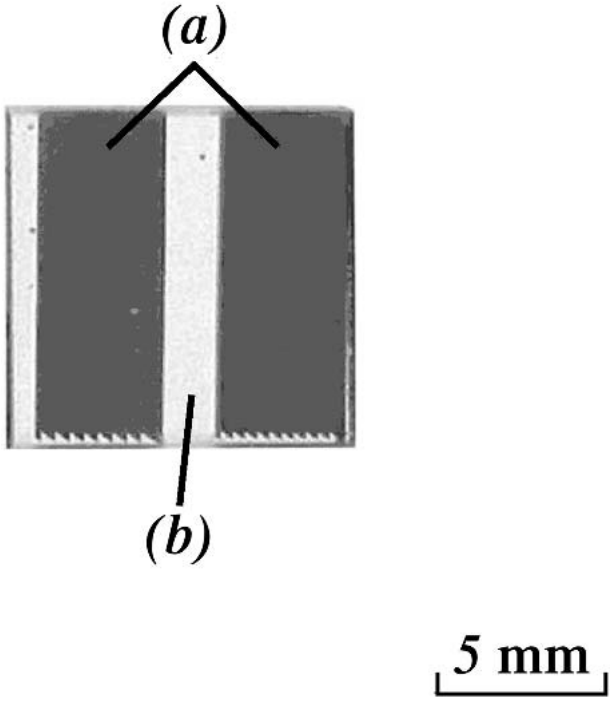

FIG. 5. Photograph of Au^+ doped glass after irradiation of femtosecond laser and heat treatment at 540 °C for 30 min.: (a) irradiated area, (b) unirradiated area.

such radiation defects was observed in the ESR spectra of gold-nanoparticle-precipitated glass. Therefore, further experiments are needed to clarify the mechanism.

As the heat-treatment temperature increased further, it was observed that the glass sample begins to turn red at 600 °C with a treatment time of 30 min, and the whole sample become uniformly dark red. On this case, gold nanoparticles precipitate in the whole glass due to the thermally driven reduction of the Au^+ ions and the consequent aggregation of the Au^0 atoms.

Based on the discussion above, a reasonable conclusion can be made that it is possible to space-selectively induce the precipitation of gold nanoparticles in glass by using a femtosecond laser since the temperature for the precipitation of the gold nanoparticles in the irradiated area is considerably lowered, compared with the temperature for purely thermal-induced precipitation of gold nanoparticles. Figure 5 shows two rectangular areas of red color, which contain gold nanoparticles inside, formed in one glass sample. Moreover, it is possible to induce any graphics as well as arrays of red dots inside the glass, which can be used in the fabrication of three-dimensional colored industrial art objects and optical memory.

IV. CONCLUSIONS

Gold nanoparticles have successfully been space-selectively precipitated in Au^+ doped silicate glass. The precipitation of gold nanoparticles is considered to be due to the femtosecond laser-induced reduction of Au^+ ions and consequent thermally driven aggregation of Au^0 atoms upon heat treating. This method provides us a new chance to obtain functional microstructures with a high third-order nonlinear optical susceptibility inside glass.

ACKNOWLEDGMENT

This work was partially supported by National Natural Science Foundation of China under Grant Nos. 50125258 and 50072037.

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