Precipitation of Silver Particles by Femtosecond Laser Pulses inside Silver-ion Doped Glass

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The following is a report on the photosensitivity of Ag-doped glasses. Success was achieved in the precipitation of silver particles into glasses by the irradiation of femtosecond laser pulses. A condensation area of silver particles was observed at a bottom of the irradiated area. The condensation area was approximately 5 microns in diameter, measured by Electron Probe Micro Analyzer (EPMA). A diffraction grating was also fabricated inside the Ag-doped glass by the irradiation of femtosecond laser pulses. This grating shows high diffraction efficiency. We also demonstrated the possibility of an electrical wiring in the glass precipitated with silver particles. These results will be applicable to three-dimensional (3D) wiring and functional optical devices such as optical memory, optical switches, and 3D photonic crystal devices.

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Introduction

Recently, microprocessing by irradiation of ultrashort laser pulses into optical materials has attracted much interest. An Advantage of focused ultrashort-pulsed laser microprocessing is very large electric field intensity over GW/cm². Therefore, the ultrashort laser pulses can induce nonlinear optical effects. Materials, irradiated with very large energy absorb the energy, resulting in rapid transfer into the plasma. The plasma then disappears very rapidly. Therefore, ultrashort-pulsed laser can induce the effects in a very small area with little thermal effects. This technique can be used for micro-fabrication in many materials and is applicable to realize functional optical devices.

In general, it is difficult to form interactions using an infrared (IR) laser inside transparent materials. However, various interactions between an IR laser and transparent materials can occur when intense ultrashort laser pulses are focused inside them. It is reported that photosensitivity associated with the ultrashort laser pulses is advantageous for introducing a variety of chemical or physical modifications into transparent materials. However, the exact mechanisms responsible for IR photosensitivity are still unclear. These phenomena are considered to be related closely with nonlinear optical processes, such as multiphoton absorption or ionization, because of the extremely high electric field intensity of the ultrashort laser pulses.

Functional optical devices have been fabricated by irradiation of femtosecond laser pulses in transparent materials. For instance, an optical waveguide and a 3D optical storage device were formed by the irradiation of femtosecond laser pulses into glasses. Many researchers have investigated areas relevant to the precipitation of functional materials into glasses. Formations of β-BBO crystal and Ag color center have been reported. Metallic particles were also formed by femtosecond laser irradiation and successive heat treatment.

Silver ions and particles in glasses have functional characteristics such as photochromism, nonlinear optical properties like the Kerr effect, and the highest electrical conductivity in metals. These properties are advantageous in realizing an optical storage, mirror reflectors, and nonlinear optical devices such as ultrafast all-optical switches. Furthermore, opto-electronics devices and 3D optical devices with these properties can be realized by the precipitation control of silver particles.

In this paper, we will report on photosensitivity by the irradiation of femtosecond laser pulses in the Ag-doped glasses. We also demonstrated applications of 3D precipitation and control of nanoparticles.

Experimental

(1) Sample preparation

Sample glasses, whose compositions were 46SiO₂–27CaO–25Na₂O–2P₂O₅–xAgO (x = 0.01, 0.1, 1) mol%, were prepared from reagent grade SiO₂, CaCO₃, Na₂CO₃, and AgNO₃ powder. A mixture of the raw materials was melted in a platinum crucible under an atmosphere for 2 hours. The melt was poured to a carbon plate and annealed at 400°C for 30 minutes. The obtained glass was cut and polished into a plate of 1 to 3 mm in thickness.

(2) Precipitation of silver particles

The glass samples were irradiated with femtosecond laser pulses. We used a regenerative amplified Ti:Sapphire laser. The pulse duration was adjusted from 100 to 1500 fs by tuning a pulse compressor. The repetition rate was 250 kHz. The averaged maximum power was 600 mW (2.4 µJ/pulse). At that time, the pulse duration was 200 fs. A laser beam of 6 mm in diameter was focused onto a spot of approximately a few microns by a 100× objective (NA = 1.4). The beam was focused at 40 to 100 µm deep from the sample surface. The average power on the sample was adjusted from 10 to 350 mW using an attenuator, which was inserted before the objective. Using an air bearing XY stage, the sample was translated in a range of 1 × 1 mm at a speed of 100 to 1000 µm/sec. After irradiation, the glass samples were observed using a microscope. Mapping images of elements in the irradiated area were observed using an Electron Probe Micro Analyzer (EPMA-1600, SHIMAZU, Japan).

(3) Optical property measurement

The optical absorption coefficient of the sample was measured by a conventional spectrometer (U-4100, HITACHI, Japan). We also fabricated a diffraction grating inside the sample by the irradiation of femtosecond laser pulses. The grating period was 10 µm. We measured a diffraction pattern using an He–Ne laser. The refractive index of the irradiated
area at 675 nm was measured by Beam Profile Reflectometry (BPR: Opti Probe-2000, TORAY Research Center, Japan).

(4) Electrical property measurement

The glasses were dielectric materials. SEM images of the glasses couldn’t be observed clearly without a conductive surface coating because of charge-up. On the other hand, silver is a conductive material. When silver particles form a conductive wire, some difference in the electric conductivity between the matrix glass and the area precipitated with silver particles should be observed by SEM. Therefore we compared the SEM images of the matrix glass and the area precipitated with silver particles without a surface coating. An accelerated voltage electron beam was set up at a range of 20 to 25 kV.

Result and discussion

(1) Precipitation of silver particles

Figure 1 shows a photograph of the sample irradiated with femtosecond laser pulses. The sample color changed from colorless to yellow by increasing the irradiating energy. Figure 2 shows microscope images of the sample in a cross sectional view. A brown area was observed at the bottom of the irradiated area, and reflectance of this area was higher than the other area. This brown area was not observed when the glass was irradiated at lower energy. Furthermore, an optical absorption peak attributed to Ag atoms was observed in the glass that exhibited no color change. On the other hand, optical absorption peaks attributed to Ag atoms and Ag particles was observed in the glass that exhibited a color change. It has been known that the color of Ag-doped glasses changed from colorless to yellow when Ag particles are formed by heat treatment. Therefore, this infers that Ag particles were formed into the glass by the irradiation of femtosecond laser pulses. Figure 3 shows SEM images and mapping images of the characteristics of radiation of Ag-Lα, O-Kα, Na-Kα, and Si-Kα. These figures indicate that silver particles or ions were condensed at the bottom of the irradiated area. The size of this condensation area was about 5 μm in diameter. From these results, it can be confirmed that the brown area in Fig. 2 is silver. We also observed an increase of the oxygen ratio at the center of the irradiated area and outside the silver condensed area. The oxygen ratio of the silver condensed area was less than the other area. For these reasons, Ag exists as particles and/or atoms. Furthermore, Na in the irradiated area was also less than the other area, and the Si distribution was unchanged. From these results, the irradiated area is changed from the original glass composition to an Si and O rich glass composition.

(2) Optical property

Figure 4 shows the differential spectra of transmittance before and after irradiation. Several absorption bands were observed at wavelengths of 300 to 700 nm. The center wavelength of these peaks is approximately 330, 420, 460, 620 nm. These peaks can be assigned to the color center, which is associated with an Ag T (trapped electron center Ag8 and trapped hole center Ag2+) , a surface plasmon of silver particles, and hole trapped center (HC1 and HC2), respectively. The HC1 and HC2 are trapped holes at non-bridging oxygen (NBO) in a SiO2 polyhedron. We observed a supercontinuum during the irradiation. This supercontinuum is considered to be plasma by extremely high electric field intensity of the femtosecond laser pulses. We were unable to observe any change in the sample when irradiated at below 0.01 μJ, where the supercontinuum wasn’t observed. Therefore, these absorption bands are formed due to electron transfer caused by extremely high electric field intensity of the femtosecond laser pulses. It is expected that the Ag T ion traps an electron from NBO by a nonlinear optical process such as multiphoton absorption. As a result, a silver atom and non-bridging oxygen hole center (NBOHC) are formed in the samples. In our study, the condensation of silver particles was observed at the bottom of the irradiated area. This result was not observed using a low repetition rate laser pulses such as 1 kHz. High repetition rate laser pulses cause a heating effect in addition to the nonlinear optical process. For this reason, we concluded that silver atoms are created by the nonlinear optical process and these silver atoms diffuse and form the condensation of silver particles by a heating effect when the laser pulses are irradiated with the high repetition rate laser.

Figure 5 shows a microscopic image of a fabricated transmission diffraction grating. Line periods are 10 μm. Figure 6 shows a diffraction pattern at a distance of 200 mm behind the
grating when a He–Ne laser beam is incident on the grating. The total measured diffraction efficiency from first to third orders was 70%. Figure 7 shows a refractive index profile measured by BPR. The refractive index decreases at the irradiated area. The refractive index increase was also observed at the edge of the irradiated area. From the results of EPMA, it is concluded that this refractive index change resulted from the change of the glass composition. A transmittance decrease of approximately 20% was also observed at the wavelength of the He–Ne laser. Therefore, high diffraction efficiency arises from the amplitude and phase grating formed by the area precipitated with silver particles.

(3) Electrical conductivity

Figure 8 shows the transmitted image, reflected image, and SEM images at the irradiated area without a conductive coating. When we dispensed the conductive coating on the surface, a flat image was observed. From this result, we observed that the irradiated area is a flat surface. We were able to observe some structures at the bottom of the irradiated area without the coating. These structures consist of the area precipitated with silver particles as shown in Figs. 2 and 3. We were unable to observe SEM images due to charge-up at the non-irradiated area. It can be concluded that the area condensed with silver particles, which was formed by the irradiation of femtosecond pulses.

Fig. 3. EPMA images of irradiated area. Irradiated pulse energy is 0.6 μJ. Stage scan speed is 1000 μm/sec.

Fig. 4. Transmittance difference of laser irradiated glasses.

Fig. 5. Microscopic view of fabricated transmission diffraction grating.

Fig. 6. Distribution of total intensity at a distance of 200 mm behind the grating.
Precipitation of Silver Particles by Femtosecond Laser Pulses inside Silver-ion Doped Glass

doped glasses. We succeeded in forming an area condensed with silver particles by irradiation of femtosecond laser pulses. It can be concluded that silver atoms are created by nonlinear optical processes such as multiphoton absorption and diffused due to the heating effect. As a result, silver particles were formed into the sample. The silver particles can be precipitated inside the glass by the control of laser irradiation.

We also fabricated a diffraction grating inside the Ag-doped glass using femtosecond laser pulses. This grating had high diffraction efficiency, which was caused by the formation of a precise periodic structure of refractive index and transmittance.

We also demonstrated that the glass precipitated with silver particles was capable of conducting electrons. These results will be applicable in the fabrication of 3D electrical wiring and functional optical devices such as optical memory, optical switches, and 3D photonic crystal devices.

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Summary

To summarize, we reported on the photosensitivity of Ag-

Fig. 7. Refractive index profile across the cross section of irradiated area.

Fig. 8. SEM images at the irradiated area without a conductive coating.

laser pulses, conducts electrons.