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Femtosecond laser induced phenomena in active ion-doped glasses and their applications

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Femtosecond laser is a perfect laser source for materials processing when high accuracy and small structure size are required. Due to the ultra short interaction time and the high peak power, the process is generally characterized by the absence of heat diffusion and, consequently molten layers. Various induced structures have been observed in glasses after the femtosecond laser irradiation. Here, we report space-selective valence state manipulation of active ions, long-lasting phosphorescence and photostimulated long-lasting phosphorescence phenomena and recipitation control of gold nanoparticles inside transparent materials by a femtoscecond laser and heat-treatment in the femtosecond laser-irradiated glasses. The mechanisms of the observed phenomena were also discussed.

Key words: Femtosecond laser, Glass, Nanotechnology

1. INTRODUCTION

It is well known that laser light can be pulsed and focused to a spot of wavelength order. Ultrashort pulsed lasers have been used as powerful tools to clarify elementary processes, such as excitation-energy relaxation and both electron and proton transfer on nanosecond and picosecond time scales that occur in a micrometer-sized area. Chemical-reaction mechanisms have also been elucidated for hydrogen atom transfer, isomerization reaction, and consecutive bond breaking by means of time-resolved laser spectroscopy. In addition, ultrashort pulsed laser can be used to make microscopic modifications to transparent materials. [1-10] The reason for using this laser is that the strength of its electric field can reach 100 TW/cm^2, which is sufficient for inducing nonlinear optical effects in materials by 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 multiphoton processes.

On the other hand, considerable research has been carried out on the writing of Bragg gratings inside optical fibers. The reaction between light and glass is usually induced by irradiating an area in a glass to achieve various types of light-induced structural changes. It is difficult to produce an interaction effect between glass and light by a one-photon process when the wavelength of excitation light differs from the resonant absorption wavelength of the glass. However, as shown in Fig. 1, various structures can be produced inside a glass sample by using pulsed laser operating at the non-resonant wavelength with pulse widths of the order of femtoseconds: colored line due to the formation of color center, refractive index spot due to densification and defect formation, microvoid due to remelting and shock wave, microcrack due to destructive breakdown etc. A regeneratively amplified 800-nm Ti sapphire laser that emits 120 fs, 1 kHz, mode-locked pulses was used in our experiments. The laser beam was focused by an objective lens on the interior of the glass sample with the help of an XYZ stage. An increase in refractive index has been observed in an irradiated area in silica or germanium-doped silica glass samples with focused femtosecond laser pulses.[1, 3] It was found that the irradiated region could function as an optical waveguide. We have demonstrated the observed induced microstructures can be used for 3D marking, fabrication of 3D optical memory with ultrahigh storage density, optical circuit, micro-optical elements and photonic crystal.[1-10]

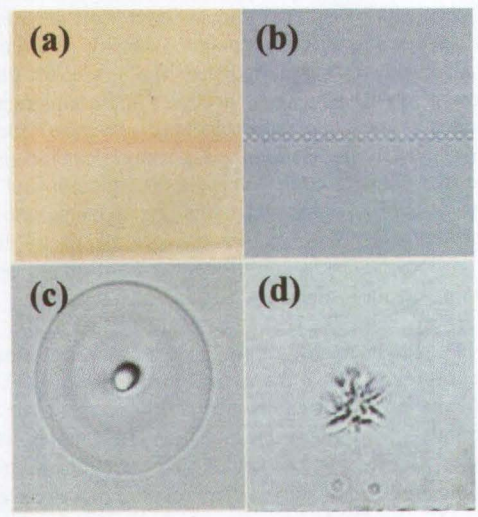

Fig. 1. Various structures induced by the infrared femtosecond laser pulses.

2. EXPERIMENTAL AND RESULTS

2.1 Space selective valence state manipulation of rare earth ions inside glasses

Here, we have also observed space-selective room-temperature permanent photoreduction of rare-earth ions of Eu^{3+} to Eu^{2+}, and Sm^{3+} to Sm^{2+} in glasses by an infrared femtosecond laser. ESR spectra of

an Eu^{3+}-doped fluorozirconate glass sample before and after laser irradiation showed that no apparent signals were observed in the spectrum of the non-laser-irradiated glass sample, whereas apparent signals due to Eu^{2+} and two signals at approximately 330 mT due to hole-trapped V-type centers and to electrons trapped by Zr^{4+} ions were observed in the spectrum of the laser-irradiated glass sample. Therefore, some of the Eu^{3+} ions were reduced to Eu^{2+} in the Eu^{3+}-doped fluorozirconate glass after laser irradiation.

Room-temperature permanent photoreduction of Sm^{3+} to Sm^{2+} was also observed in borate and other glass samples. The photoluminescence spectra of the Sm^{3+}-doped glass sample before (a) and after (b) laser irradiation show that only emissions at 560, 600, 645, and 705 nm were observed in the unirradiated glass sample due to the 4f–4f transitions of Sm^{3+}. Four new peaks at 683, 700, 724, and 760 nm were observed in the photoluminescence spectrum of the laser-irradiated glass sample due to the 4f–4f transitions of Sm^{2+}. Therefore, a part of Sm^{3+} was converted to Sm^{2+} after the laser irradiation.

We observed room-temperature hole burning phenomenon in femtosecond laser-reduced Sm^{2+}-doped glass sample. The results demonstrated the possibility of selectively inducing a change of valence state of Eu^{3+} (Sm^{3+}) ions on the micrometer scale inside a glass sample by use of a focused nonresonant femtosecond pulsed laser. Whereas a three-dimensional optical memory has approximately 10^{13} bits/cm^3 storage density, which means that data information can be stored in the form of a change in refractive index in a spot, optical memory using a valence-state change of rare-earth-ions in a spot may have the same storage density and may allow one to read out data in the form of luminescence, thus providing the advantage of a high signal-to-noise ratio. Therefore, the present technique will be useful in the fabrication of three-dimensional optical memory devices with high storage density. Moreover, femtosecond laser-photoreduced Sm^{3+} -doped glasses exhibited a photochemical spectral hole burning memory property. The microspot induced by the focused femtosecond laser inside a glass sample can be further used to store data information via the irradiation of laser light with different wavelengths. As a result, the data information can be read out in the form of spectral holes. Sm^{2+} -doped glasses could become an ultimate optical memory device with an ultrahigh storage density.

2.2 Space selective valence state manipulation of transition and heavy metal ions inside glasses

We have also observed the permanent valence state manipulation of transition and heavy metal ions inside glasses after the femtosecond laser irradiation. An purple colored area with diameter of about 30 μ m was observed in a Mn and Fe ions co-doped glass sample after the femtosecond laser irradiation. Absorption spectra of the glass sample before (a) and after (b) the femtosecond laser irradiation exhibit that a part of Mn^{2+} was oxidized to Mn^{3+} after the femtosecond laser irradiation. Mn and Fe co-doped silicate glass sample has no absorption in the wavelength region near 800 nm. Therefore, photo-oxidation of Mn^{2+} to Mn^{3+} should be a nonlinear optical process. We suggest that multiphoton absorption be one of the mechanisms of the observed phenomenon. Free electrons are generated by the multiphoton absorption of the incident photon and consequent avalanche ionization. Mn^{2+} captures a hole to form Mn^{3+}, while Fe^{3+} as well as active sites in glass matrix may act as electron trapping centers, resulting in the formation of Mn^{3+}. However, the length of the induced structure (1.5 mm) is far longer than that of the Rayleigh length of the focused beam (200 μ m). Therefore, other mechanisms also should be taken into consideration. Since the power density is larger than 10^{12}W/cm^2, nonlinear refractive index largely contributes to the refractive index of the glass during the laser irradiation. The refractive index increases with the intensity of the laser and self-focusing of the laser beam takes place. On the other hand, formation of electron plasma due to electric field, causes a decrease in the real part of the refractive index and induce self-defocusing of the beam. The balance between the self-focusing due to the increase of refractive index and self-defocusing due to the plasma formation results in a phenomenon called self-trapping or filamentation. In the filaments, white light supercontinuum containing Strokes and anti-Strokes wave is generated due to self-phase modulation. The single or two-photon absorption of short wavelength component of the white light supercontinuum causes photoionization of transition ions as well as glass matrix, leading to the formation of Mn^{3+}. We confirmed that the length of the induced structure was directly proportional to the square root of the average power of the laser beam. If we assume that the length of the induced structure is directly proportional to the length of the filament, the result is in a good agreement with the theory of Zverev et al.[11] Therefore, filamentation due to the balance of self-focusing arose from increase in refractive index and self-defocusing arose from plasma formation takes an important role in the oxidation of Mn^{2+} to Mn^{3+}. The trap levels of defect centers may be deep, thus resulting into the stable Mn^{3+} at room temperature. The structural difference among the cross section of the induced structure may be resulted from the high temperature and high pressure at the center part due to the strong plasma formation, and ionization of transition metal ion as well as glass matrix due to the multiphoton absorption of the incident laser and single or two photoabosrption of the white light supercontinuum.

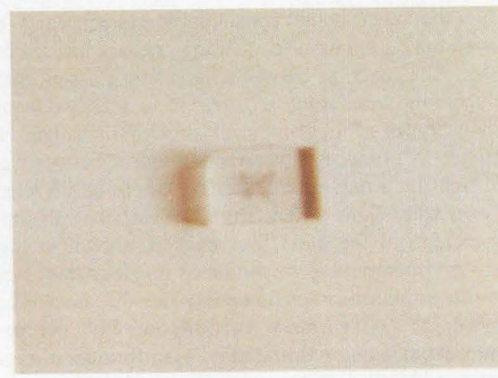

Fig. 2. A butterfly image written inside a Mn^{2+}-Fe^{3+}-doped silicate glass sample by using photo-induced valence state change of Mn ions

Since focused area becomes purple after the laser irradiation, it is possible to write a 3-dimensional colored image inside the transparent and colorless glass as shown in Fig. 2.

Since the length of the induced structure is directly proportional to the square root of the average power of the laser beam, it is possible to control the longitudinal spreading of the oxidation area from several hundred nanometers to several millimeters by selecting proper irradiation condition. This method should also be useful for the space-selective valence state manipulation of other transition metal ions inside transparent materials. Our results demonstrated a possibility to space-selectively induce change of valence state of transition metal ions in a micrometer small dimension inside a transparent material by using a focused non-resonant femtosecond pulsed laser. Therefore, the present technique will be useful in the fabrication of 3-dimensional colored industrial art object, optical memory and micro-optical devices.

2.3 Photostimulated long-lasting phosphorescence in femtosecond laser irradiated rare-earth ion-doped glasses

We observed photostimulated long-lasting phosphorescence in femtosecond laser irradiated Tb^{3+}-doped glasses. After irradiation by the focused femtosecond laser, bright and long-lasting phosphorescence was observed for the glass sample in the dark after the removal of the activating light. The appearance of the femtosecond laser-induced phosphorescence is similar to that of the photoluminescence spectrum. All emission peaks can be assigned to the $^5D_J \rightarrow {}^7F_{J'}$ (J=3, 4, J'=3-6) transitions of Tb^{3+}. Though no long-lasting phosphorescence could be detected in the non-irradiated glass sample after the irradiation of 365 nm, UV light at, apparent long-lasting phosphorescence was observed once again in the the femtosecond laser irradiated glass sample after the excitation by the 365 nm UV light when the femtosecond laser-induced long-lasting phosphorescence could not be detected. The appearance of the photostimulated long-lasting phosphorescence spectra is the same as that of the long-lasting phosphorescence spectra. A peak at 342K was observed in the thermoluminescence curve of the glass sample after irradiation by the femtosecond laser. The peak at 342K disappeared, and a peak at 405K appeared in the glass sample 24 hours after the removal of the activating light, when the femtosecond laser-induced long-lasting phosphorescence could not be detected. The peaks at both 342K and at 405K can be assigned to the traps, in which the trapped electrons can and cannot be released by heat energy at room temperature, respectively. No peak was observed in the non-irradiated glass sample, while a small peak at 342K was observed in the femtosecond laser-irradiated glass sample after the excitation by the 365 nm UV light for two minutes. Therefore, after the excitation by the 365 nm UV light some electrons trapped in deep traps were excited to high energy levels, then re-trapped by the shallow traps. The recombination of electrons released from shallow traps by heat energy with trapped holes resulted in the observation of photostimulated long-lasting phosphorescence at room temperature. The observed phenomenon may have application in the fabrication of 3D display and rewriteable 3D optical memory.

2.4 Precipitation control of gold nanoparticles inside transparent materials by a femtoscecond laser and heat-treatment

Nanoparticles exhibit a wide range of electrical and optical properties due to the quantum size effect, surface effect and conjoint effect of the nanostructures. Noble metal nanoparticles doped into materials exhibit large third-order nonlinear susceptibility and ultrafast nonlinear response. They are expected to be promising materials for ultrafast all-optical switches in the THz region. Nanoparticles need to be arranged into well-defined configurations or to be distributed space-selectively in materials in order to built integrated systems. Up to now, many studies have been carried out on the fabrication of nanoparticle-doped materials.[12-14] However, there are no effective methods of preparation so that the distribution of nanoparticles are space-selectively well controlled.

In this section, we demonstrate three-dimensional precipitation and control of nanoparticles in materials by using focused femtosecond laser irradiation and successive annealing in detail. We also demonstrate that the size distribution of nanoparticles can be controlled by the laser irradiation conditions. This method should be useful not only for practical applications such as three-dimensional optical memory and fabrication of integrative all-optical switches, but also for controlling nucleation and crystal growth processes.

We selected a typical silicate glass composed of $70SiO_2 \cdot 10CaO \cdot 20Na_2O$ (mol%) and doped with $0.1mol\%Au_2O$. Reagent grade SiO_2, $CaCO_3$, Na_2CO_3, and $AuCl_3 \cdot HCl \cdot 4H_2O$ were used as starting materials. An approximately 40 g batch was mixed and placed into a platinum crucible. Melting was carried out in an electronic furnace at 1550°C for 1 hour under the ambient atmosphere. The glass sample was obtained by quenching the melt to room temperature. The glass sample thus obtained was transparent and colorless. The glass sample was cut, polished, and subjected to experiments.

After irradiation by the focused infrared femtosecond laser with an average power of 300 mW and focused by a 10X objective lens with a numerical aperture of 0.30 on each spot for 1/63 s, a gray-colored spot with a diameter of about 40 μ m was formed near the focused area of the laser beam. Then, the glass sample was annealed at 550°C for 1 hour. The laser-irradiated part became red after the heat treatment. By using these phenomena, we drew a red-colored butterfly and then a gray-colored image inside the glass sample, as shown in Fig. 3. Absorption spectra of the glass samples were measured by a spectrophotometer (JASCO V-570). Direct observation of precipitated gold nanoparticles was carried out with a JEM-2010FEF transmission electron microscope operated at 300 kV. All of the experiments were carried out at room temperature.

An absorption spectra of the glass sample before, after the femtosecond laser irradiation and successive annealing at various temperatures for 1 hour show there was an apparent increase in absorbance in the

wavelength region from 300 to 800 nm in the irradiated region due to hole trap centers, e.g., HC1 and HC2 at nonbridging oxygen near Au^+ ions.[15] After annealing at temperatures below 400°C, the induced absorption decreased as the temperature increased, and the femtosecond laser induced gray color disappeared at 400°C and become colorless and transparent. Annealing at temperatures above 450℃ resulted in the appearance of a new peak at 530 nm due to the surface plasmon absorption of gold nanoparticles and the color of the laser-irradiated part of the glass sample became red. The absorption peak increased with an increase in both temperature and annealing time. We suggest that a gold ion was reduced to a gold atom by capturing an electron from nonbridging oxygen during the femtosecond laser irradiation and gold atoms aggregated to form nanoparticles after the heat treatment.

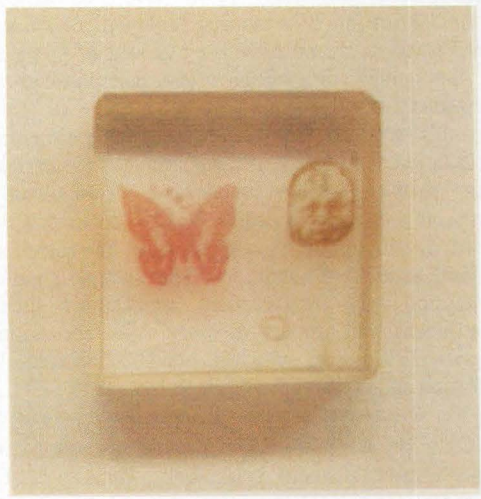

Figure 3. Photograph of images drawn inside the glass sample by using a femtosecond laser: gray-colored image (after femtosecond laser irradiation) and red-colored butterfly (after femtosecond laser irradiation and further heat treatment at 550℃ for 1 hour).

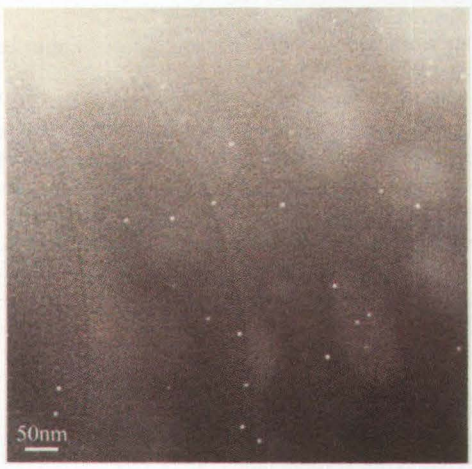

Figure 4. TEM image of gold nanoparticles in the femtosecond laser-irradiated glass sample after annealing at 550℃ for 1 hour.

Figure 4 shows a TEM observation of precipitated gold nanoparticles in the femtosecond laser-irradiated part after successive annealing at 550℃ for 1 hour. We observed spherical gold nanoparticles with sizes ranging from 5 to 8 nm. We carried out several experiments to clarify the mechanism of the formation of induced structures after femtosecond laser irradiation. We observed that the space of the nanoparticle-precipitated area is the same as the area in which supercontinuum white light was observed during femtosecond laser irradiation and that it is also the same as the gray-colored area induced by femtosecond laser irradiation. There is now a consensus that multiphoton absorption due to the fundamental wave and supercontinuum white light, which arises from self-phase modulation of the laser beam, plays an important role in the formation of induced structures. [16-18] In the present case, electrons are driven out from the 2p orbital of the nonbridging oxygen in the SiO_4 polyhedron via the multiphoton absorption of the incident photon. Au^+ captures the electron to form an Au atom. We confirmed that the length of the femtosecond laser induced structure is directly proportional to the square root of the average power of the laser beam. This result is in good agreement with the theory of Zverev et al., if we assume that the length of the induced structure is directly proportional to the length of the filament, which is due to the balance between self-focusing arising from an increase in the refractive index and self-defocusing arising from plasma formation.[11] We also confirmed that no change occurs in the absorption spectrum of the nanoparticle-precipitated glass sample after heat treatment at room temperature even over a period of 6 months, indicating that the precipitated nanoparticles are stable at room temperature. We did not observe precipitation of gold nanoparticles for the unirradiated glass sample even after annealing at 600°C for more than 2 hours. However, we did observe the precipitation of gold nanoparticles in the laser-irradiated part after annealing at 450℃ for 10 min. Therefore, femtosecond laser irradiation induces the reduction of a gold ion to form a gold atom, and the gold atom acts as crystal nucleus in the crystal growth process.

We performed a femtosecond optical Kerr shutter (OKS) experiment for a 2-mm long gold nanoparticle-precipitated sample annealed at 550℃ for 1 hour. The full-width at half-maximum of the incident pulse was estimated as 500 fs at the position of the sample. The photo energy of the pulse was set to the surface-plasmon resonance peak (2.3 eV). The Kerr signal raised and decayed suddenly at around t = 0. The FWHM of the signal is 240 fs and no slow decay component was observed. This is a very fast nonlinear response time for a gold nanoparticle system. The $\chi^{(3)}$ of the gold nanoparticle-precipitated part is estimated to be 0.93×10^{-11}, which is 300 times the magnitude of that for SiO_2 glass (2.8×10^{-14}esu).

Our results showed that femtosecond laser irradiation performed by focusing a 200 mW laser beam with a 10X objective lens (NA (numerical aperture) = 0.30), a 3-mW laser beam with a 5X objective lens (NA= 0.13), a 600 mW laser beam with a 50X objective lens (NA=0.80),

and successive annealing at 600℃ for 1 hour, resulting in the laser-irradiated part becoming red, violet and yellow in color, respectively. The different color is due to the different size distribution of gold nanoparticles. Thus, the size and space distribution of gold nanoparticles can be controlled in glass by using this technique. However, how the laser irradiation condition affects the size distribution of gold nanoparticle is not fully clear and further study is needed to clarify the mechanism of the precipitation of gold nanoparticles in the femtosecond laser-irradiated glass sample.

It is possible to control the diameter and longitudinal spread of the structurally changed area from several hundred nanometers to several millimeters by selecting an appropriate irradiation condition. Our results demonstrated that it is possible to precipitate gold nanoparticles in a small mesoscopic dimension inside a material by using a focused non-resonant femtosecond pulsed laser and successive heat treatment. It is also possible to prepare a three-dimensional image, which cannot be seen with the naked eye, but which can be detected by UV-light excitation or can be clearly seen after heat treatment at a certain temperature. Therefore, the present technique will be useful in the fabrication of three-dimensional multicolored industrial art objects, optical memory with ultrahigh storage density and ultrahigh recording speed, and integrative waveguide-type all-optical switches with ultrafast nonlinear response.

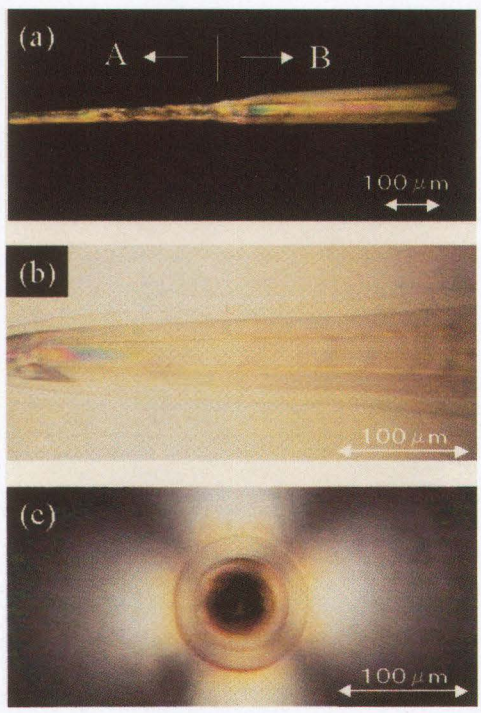

Figure 5. Polarizing-microscope photographs of the (a, b) side and (c) cross-sectional views of the crystal. (a) and (b) show polarizing-microscope photographs taken in extinction and diagonal positions, respectively. Region A in (a) shows a crystal grown while moving the melting zone at a speed of 100μm/s, and region B shows a crystal grown when this speed is 10μm/s.

2.5 Crystal growth of BBO by femtosecond laser irradiation

The production of fibrous crystalline structure in glass was obtained by a method similar to that used to produce optical waveguides. By focusing a laser beam onto a tiny region of a specially designed glass composition containing barium and boron, small, clear single crystals were produced. By moving the focal point, fibrous BaB_2O_4 (BBO) crystals could be grown (Figure5). The BBO is very effective and efficient for wavelength conversion, or second harmonic generation. Further, a variety of such crystals can be grown in addition to BBO, which cannot be obtained by conventional methods.

3. CONCLUSION

We have observed various femtosecond laser induced phenomena in glasses. We have confirmed that the femtosecond laser induced microstructure will open new possibility in the realization of novel optical functions for glass.

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