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Three-Dimensional Micro- and Nano-Fabrication in Transparent Materials by Femtosecond Laser

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Femtosecond pulsed lasers have been widely used for materials microprocessing. Due to their ultrashort pulse width and ultrahigh light intensity, the process is generally characterized by the nonthermal diffusion process. We observed various induced microstructures such as refractive-index-changed structures, color center defects, microvoids and microcracks in transparent materials (e.g., glasses after the femtosecond laser irradiation), and discussed the possible applications of the microstructures in the fabrication of various micro optical devices [e.g., optical waveguides, microgratings, microlenses, fiber attenuators, and three-dimensional (3D) optical memory]. In this paper, we review our recent research developments on single femtosecond-laser-induced nanostructures. We introduce the space-selective valence state manipulation of active ions, precipitation and control of metal nanoparticles and light polarization-dependent permanent nanostructures, and discuss the mechanisms and possible applications of the observed phenomena. [DOI: 10.1143/JJAP.44.4735]

KEYWORDS: femtosecond laser, nanofabrication, valence state manipulation, nanoparticle precipitation, nanograting

1. Introduction

Progress in high-power ultrashort pulse lasers has opened new frontiers in the physics and technology of light-matter interactions. Recent discoveries span from coherent X-ray generation^{1,2)} and nonlinear Thomson scattering^{3,4)} to directly writable three-dimensional (3D) photonic structures inside transparent materials, such as glasses.^{5–7)} A critical advantage of using femtosecond pulses instead of longer pulses is that the femtosecond pulse width is shorter than the electron–phonon coupling time (picosecond order), and it is sufficiently shorter than the thermal diffusion time; as a result, the energy of the pulses can be efficiently and precisely deposited into a material without heat transformation.^{8–10)} In addition, focused femtosecond laser pulses can induce various nonlinear processes by high localization of photons in both the temporal and spatial domains. The nature of the interaction between femtosecond laser pulses and matter makes it possible to overcome the diffraction limit of light.¹¹⁾ Misawa *et al.* observed the picosecond-pulsed YAG laser-induced refractive-index-changed microspot in silicate glass in 1995, and suggested that the observed phenomenon can be used for 3D optical memory.^{12,13)} We began systematic investigations in the femtosecond-laser-induced microstructures in glass and applications in microoptics at the end of 1994. In the early stages of research on micromachining using ultrashort laser pulses, Mazur *et al.* demonstrated a method for high-density 3D optical data storage using femtosecond laser pulses in 1996.⁶⁾ They recorded submicron-diameter bits consisting of a void surrounded by a densified region by focusing a femtosecond laser inside fused silica. When femtosecond laser pulses are tightly focused in glass by a focusing lens, the strength of the electric field at the focal point of the laser beam can reach $\sim 10\text{ TW/cm}^2$, which is sufficient for inducing various

nonlinear physicochemical reactions in materials. The photoinduced reactions are expected to occur only near the focused part of the laser pulses due to multiphoton processes. In the past several years, many research efforts have been devoted to the field of 3D microscopic modifications to transparent materials by using femtosecond lasers. Promising applications have been demonstrated for the formation of 3D optical memory^{6,14–16)} and multicolor images,¹⁷⁾ and the fabrication of optical waveguides,^{5,18)} couplers^{7,19)} and photonic crystals.²⁰⁾ In the latest an applied research, Hosono *et al.* fabricated fine-pitched micrograting structures in an amorphous SiO₂ thin film with a single femtosecond laser pulse,²¹⁾ and demonstrated that simultaneous formation of a color center and waveguide with femtosecond laser-induced microgratings produced an oscillating DFB color laser inside a LiF crystal by the femtosecond laser pulses interference technique.²²⁾ In addition, Itoh *et al.* observed that one can seize and translate voids formed by femtosecond laser irradiation inside silica glass and also merge two voids into one,²³⁾ and fabricated high-aspect-ratio 3D microchannels from the rear surface of silica glass in contact with water. They suggested that the observed phenomenon can be used for a micro-total-analysis system (μ -TAS).²⁴⁾

Although the structural changes caused by the intense femtosecond pulse irradiation have been evaluated using spectrometry, fluorescence, ESR, and other methods,^{25,26)} the mechanism of induced modifications in transparent material is still not fully understood. Moreover, unexpected anisotropic light scattering has been observed along the plane of the light polarization in a Ge-doped silica²⁷⁾ and other glass materials.²⁸⁾ This anisotropic phenomenon has been interpreted in terms of the light scattering of the polarization-dependent permanent subwavelength-size nanostructure induced by the polarized ultrashort-pulsed laser beam. Recently, strong reflection within a fused silica plate only in the direction parallel to the polarization axis of the writing femtosecond laser has been observed.²⁹⁾ Self-organized subwavelength gratings with a negative refractive index

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change $\Delta n \sim 10^{-1}$ and a characteristic period $\Lambda \sim 150$ nm over a spot size ~ 1.5 μm have been proposed to explain this reflection as well as the form birefringence of directly written structures.³⁰⁾ Surface ripples with a period equal to the wavelength of the incident laser radiation and that are likewise aligned in a direction perpendicular to the electric field of the light wave have been observed in many experiments involving laser deposition³¹⁾ and laser ablation.³²⁾ Such gratings are generated as a result of interference between the light field and the surface plasmon–polariton wave launched because of initial random surface inhomogeneities. Positive feedback leads to exponential growth of the periodic surface structures which become frozen within the material. It was suggested that the mechanism based on the interference between the light field and the generated electron plasma wave was responsible for the embedded nanogratings formation.³³⁾ In this paper, we review our recent investigations on the femtosecond laser-induced micro- and nanostructures. The mechanisms and possible applications of the observed phenomena are also discussed.

2. Various Microstructures Induced in Glass by Femtosecond Laser Irradiation

It is difficult to develop the interaction between light and glass by a one-photon process when the wavelength of the excitation light differs from the resonant absorption wavelength of the glass. However, as shown in Fig. 1, various localized structural changes can be induced inside a glass sample by focusing a femtosecond laser operating at a nonresonant wavelength. There are four examples of induced structural change: (a) coloration due to the color center formation and valence state change of active ions such as rare-earth and transition metal ions, (b) refractive index change due to local densification and atomic defect generation, (c) microvoid formation due to localized remelting and shock wave propagation, and (d) microcrack formation due to destructive breakdown or other phenomena. We know that usually glass has no absorption at 800 nm

(the wavelength of the common femtosecond laser). In other words, linear absorption of the laser radiation does not occur when the glass is irradiated by a femtosecond laser with no absorption wavelength. This is because the energy gap between the valence and conduction bands is larger than the energy of the single photon. Thus, the single photon does not contain sufficient energy to free a bound electron. However, when laser intensities are sufficiently high, an electron can simultaneously absorb the energy from the multiple photons to exceed the band gap. This nonlinear process is termed multiphoton absorption. It is a highly intensity-dependent process, with the rate $P(I) = \sigma_k I^k$, where σ_k is the multiphoton absorption coefficient for k -photon absorption. Once an electron is excited to the conduction band, it serves as a seed to a process called avalanche ionization.⁸⁾ Seeds can also arise from other process, such as electron tunneling and thermal excitation from impurity states.³⁴⁾ An electron in the conduction band can absorb sufficient energy from photons, $kh\nu \geq E_g$, where k is the number of photons absorbed sequentially and E_g is the band gap energy of glass; it can then use the excess energy to ionize another electron via direct collision, also known as impact ionization. The resultant two electrons in the conduction band can continue the process of linear absorption and impact ionization to achieve an exponential growth of free electrons. Such avalanche ionization produces highly absorptive and dense plasma, facilitating the transfer of energy from the laser pulses to the glass. The resulting melting, material displacement due to plasma expansion, and possible chemical restructuring develop in various induced structures.

3. Valence State Manipulation of Active Ions

3.1 Photooxidation of transition metal ions

We observed space-selective, persistent photooxidation of Mn^{2+} to Mn^{3+} in a silicate glass by focusing femtosecond laser pulses through a microscope objective lens.¹⁶⁾ The glass composition of the Mn- and Fe-ion codoped silicate glass sample used in this experiment was $0.05\text{Fe}_2\text{O}_3$ – 0.1MnO – 70SiO_2 – 10CaO – $20\text{Na}_2\text{O}$ (mol %). A $4\text{ }\mu\text{m}$ spot was formed in the focused area of the laser beam in the Mn- and Fe-ion codoped glass sample after irradiation by 120 fs laser pulses operated at a wavelength of 800 nm (repetition rate: 1 kHz, pulse energy: 0.4 mJ) on each spot for $1/63$ s (i.e., 16 pulses) via a $10\times$ objective lens with a numerical aperture of 0.30 inside the glass sample. A purple area with a diameter of about $30\text{ }\mu\text{m}$ was observed. The length of the induced structure along the laser beam propagation path was about 1.5 mm. To measure the absorption spectrum of the glass sample after the laser irradiation, we wrote a “damaged” plane of $3.0 \times 3.0\text{ mm}^2$ inside the glass sample, which consisted of a “damaged” line at an interval of $10\text{ }\mu\text{m}$ by scanning the laser beam at a rate of 1 mm/s. The distance of the “damaged” plane from the surface of the glass sample was about 0.5 mm. No apparent absorption was observed for the unirradiated glass sample in the wavelength region from 400 to 1000 nm, while there was an apparent increase in the absorbance in the wavelength region from 300 to 1000 nm in the irradiated area (Fig. 2). There was a peak ranging from 400 to 800 nm, peaking at 520 nm, which can be assigned to the absorption of Mn^{3+} ions.^{35,36)} In addition, a peak was observed at 320 nm, which can be assigned to the absorption

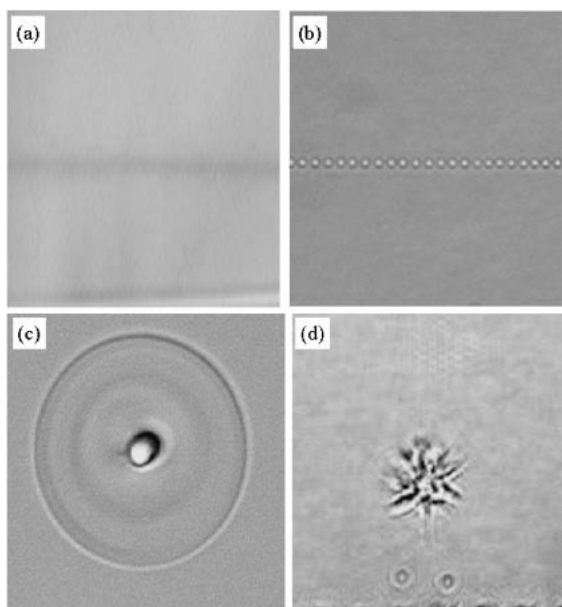


Fig. 1. Various femtosecond-laser-induced localized microstructures.

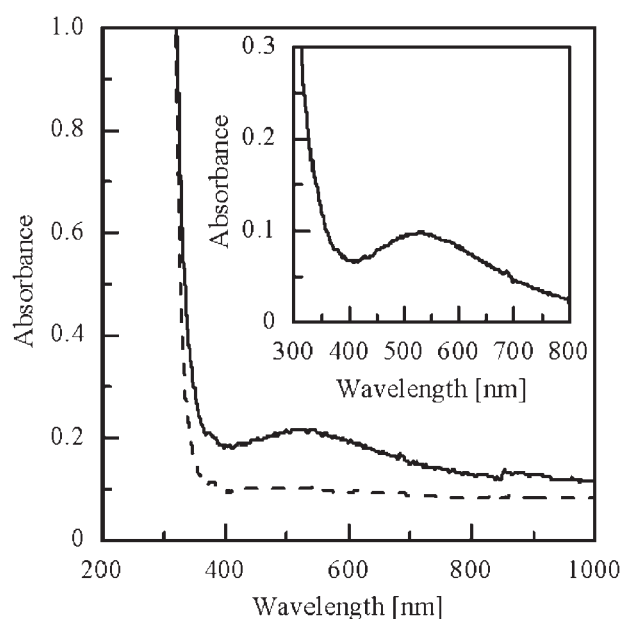


Fig. 2. Absorption spectra of the Mn- and Fe-ion codoped silicate glass before (dashed line) and after (solid line) the femtosecond laser irradiation. The inset shows the difference spectrum between absorptions of the glass sample after and before the femtosecond laser irradiation.

of hole-trapped centers as observed in the X-ray irradiated silicate glass.³⁷⁾ The electron spin resonance (ESR) spectrum of the unirradiated glass sample indicates resolved hyperfine structures of six lines spread over a range of about 500 G in width centered at 3350 G (splitting coefficient $g \sim 2.0$). The spectrum showed a pattern similar to those observed for various glasses containing Mn^{2+} ions [Fig. 3(a)].³⁸⁾ The low resolution of the hyperfine lines is due to the dipolar broadening. No apparent absorption due to Mn^{3+} was observed in unirradiated glass (Fig. 2). Therefore, most Mn ions are present in the divalent state in glass. Two new

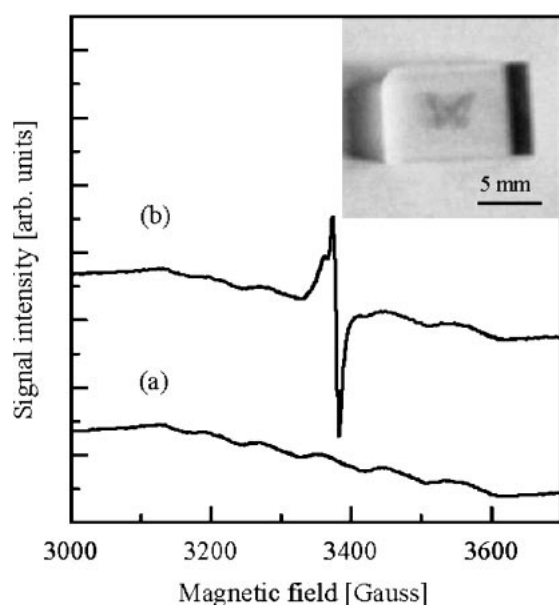


Fig. 3. Electron spin resonance spectra of the Mn and Fe codoped silicate glass before (a) and after (b) the femtosecond laser irradiation. The inset photograph shows an image of a butterfly in purple color written inside the glass by femtosecond laser irradiation.

signals at g values of 2.010 and 2.000 were observed in the glass sample after laser irradiation. The signals can be assigned to hole-trapped centers in the glass matrix [Fig. 3(b)].³⁹⁾

From the above results, we can see that a part of Mn^{2+} was oxidized to Mn^{3+} after the femtosecond laser irradiation. The Mn- and Fe-ion codoped silicate glass sample has no absorption in the wavelength region near 800 nm. Therefore, photooxidation of Mn^{2+} to Mn^{3+} should be a nonlinear optical process. We suggest that multiphoton absorption is one of the mechanisms of the observed phenomenon.⁸⁾ 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 the glass matrix may act as electron trapping centers, resulting in the formation of Mn^{3+} . Since the trap levels of defect centers may be deep, the induced Mn^{3+} ions are thermally stable. Based on the above results, since only the focal spot is colored purple, it is possible to write a 3D colored image inside the transparent and colorless glass as shown in Fig. 3 inset.

3.2 Photoreduction of rare-earth ions

We also observed photoinduced reduction of rare-earth ions by irradiation with the femtosecond laser.⁴⁰⁾ The composition of the Eu^{3+} -doped fluorozirconate glass sample used in this experiment was $0.1\text{EuF}_3\text{-}53\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}3.9\text{LaF}_3\text{-}3\text{AlF}_3\text{-}20\text{NaF}$ (mol %). For comparison, we prepared a Eu^{2+} -doped fluoroaluminate glass sample with a composition of $0.1\text{EuF}_2\text{-}14.9\text{YF}_4\text{-}10\text{MgF}_2\text{-}20\text{CaF}_3\text{-}10\text{SrF}_3\text{-}10\text{BaF}_2\text{-}35\text{AlF}_3$ (mol %). A $10\text{ }\mu\text{m}$ bright spot was formed at the focal point of the laser beam in the Eu^{3+} -doped fluorozirconate glass sample after irradiation by 120 fs laser pulses operating at a wavelength of 800 nm (repetition rate: 200 kHz, pulse energy: $1\text{ }\mu\text{J}$) for 1 s (i.e., 2×10^5 pulses) via a $10\times$ objective lens with a numerical aperture of 0.30 inside the glass sample. To measure the absorption spectrum of the glass sample after the laser irradiation, we wrote a “damaged” plane of $4.0 \times 4.0\text{ mm}^2$ inside the Eu^{3+} -doped fluorozirconate glass sample that consisted of “damage” lines at an interval of $10\text{ }\mu\text{m}$ by scanning the laser beam at a rate of 1 mm/s. The distance of the plane from the surface of the glass sample was about 1 mm. A small peak at 394 nm and a strong broad peak at 250 nm can be assigned to the $4f\text{-}4f$ transition and the charge transfer state of Eu^{3+} , respectively (Fig. 4).⁴¹⁾ No apparent increase in the absorbance was observed in the 400 nm to $1\text{ }\mu\text{m}$ region, whereas absorption in the 200 to 400 nm region increased after laser irradiation. From comparison of the difference absorption spectrum of Eu^{3+} -doped fluorozirconate glass before and after the femtosecond laser irradiation and the absorption spectrum of Eu^{2+} -doped fluoroaluminate glass (Fig. 4 inset), the broad peak at about 260 nm can be assigned mainly to the absorption that is due to the $5d\text{-}4f$ transition of Eu^{2+} .⁴²⁾

In addition, we observed emission spectra of the Eu^{3+} -doped fluorozirconate glass sample before and after the femtosecond laser irradiation (Fig. 5). All emission peaks observed in the unirradiated glass sample can be assigned to the $4f^6 \rightarrow 4f^6$ transition of Eu^{3+} , and no emission due to Eu^{2+} was detected. Eu ions are present in the trivalent state in the unirradiated glass sample. The emission peaks at 360

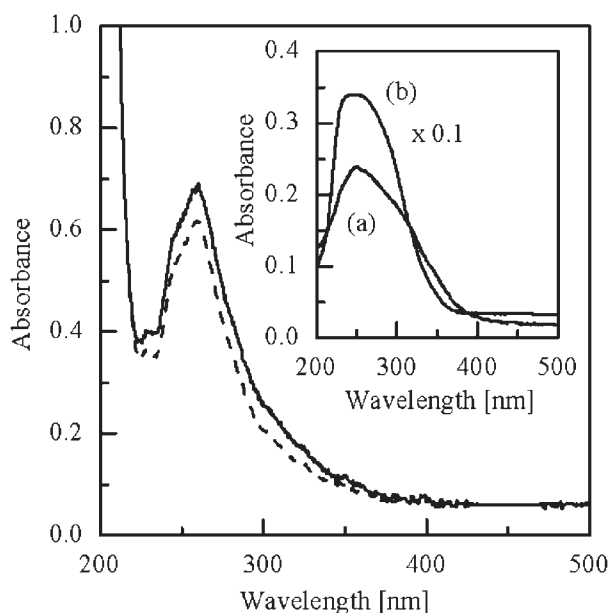


Fig. 4. Absorption spectra of Eu^{3+} -doped fluorozirconate glass before (dashed line) and after (solid line) the femtosecond laser irradiation. The inset shows (a) the difference absorption spectrum of Eu^{3+} -doped fluorozirconate glass before and after the femtosecond laser irradiation, together with (b) the absorption spectrum of a Eu^{2+} -doped fluoroaluminate glass sample fabricated in a reducing atmosphere. Note that curve (b) is scaled down by a factor of $\times 0.1$.

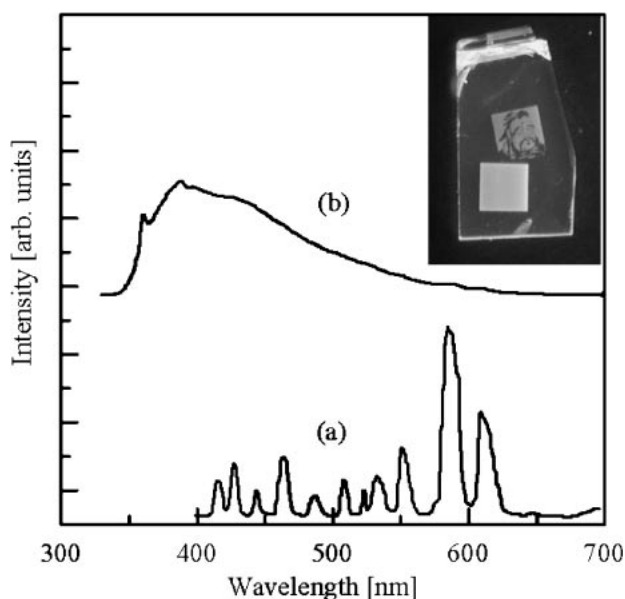


Fig. 5. Emission spectra of Eu^{3+} -doped fluorozirconate glass (a) before and (b) after the femtosecond laser irradiation. Inset image shows the photograph when the glass sample was excited by UV light at 365 nm.

and 400 nm in the irradiated glass sample can be assigned to the $6P^{7/2} \rightarrow 8S^{7/2}$ and $4f^65d^1 \rightarrow 4f^7$ transitions of Eu^{2+} , respectively. Figure 5 inset shows the photograph when the glass sample was excited by a UV light at 365 nm. The unirradiated area shows a red emission, while the femtosecond-laser-irradiated area shows a blue emission. From comparison of the ESR spectra of Eu^{3+} -doped fluorozirconate glass before and after the femtosecond laser irradiation and the ESR spectrum of Eu^{2+} -doped fluoroaluminate glass,

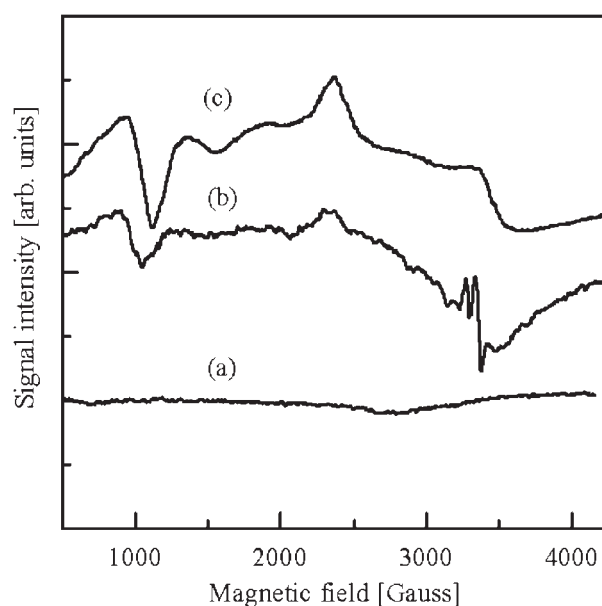


Fig. 6. Electron spin resonance spectra of Eu^{3+} -doped fluorozirconate glass (a) before and (b) after the femtosecond laser irradiation, together with (c) the spectrum of a Eu^{2+} -doped fluoroaluminate glass sample fabricated in a reducing atmosphere.

no apparent signals can be observed in the spectrum of the unirradiated Eu^{3+} -doped fluorozirconate glass sample, whereas apparent signals similar to those of the Eu^{2+} -doped fluoroaluminate glass and two signals at about 3300 G (splitting coefficient $g \sim 2.0$) can be observed in the spectrum of the laser-irradiated Eu^{3+} -doped fluorozirconate glass sample (Fig. 6). Therefore, some of the Eu^{3+} ions were reduced to Eu^{2+} in the Eu^{3+} -doped fluorozirconate glass after the femtosecond laser irradiation. In addition, the signals at $g \sim 2.0$ can be assigned to hole-trapped V-type centers and to electrons trapped by Zr^{4+} ions, as in X-ray irradiated fluorozirconate glasses.⁴³⁾

From the above results, we can see that a part of Eu^{3+} was reduced to Eu^{2+} after the femtosecond laser irradiation. The Eu^{3+} -doped fluorozirconate glass sample has no absorption in the wavelength region near 800 nm. Therefore, photo-reduction of Eu^{3+} to Eu^{2+} should be a nonlinear optical process. We suggest that the mechanism of photoreduction is that active electrons and holes are created in the glass through a multiphoton ionization process.⁸⁾ Holes are trapped in the active sites in the glass matrix, and some electrons are trapped by Eu^{3+} , leading to the formation of V-type hole-trapped defect centers and Eu^{2+} . In addition, the trap levels of defect centers can be deep, resulting in stable Eu^{2+} at room temperature. We have also observed space-selective permanent photoreduction of Sm^{3+} to Sm^{2+} in various glasses and crystals by femtosecond laser irradiation and demonstrated 3D optical data storage by using the femtosecond-laser-induced valence-state change of Sm ions in glasses.⁴⁴⁻⁴⁶⁾ Based on the above results, the present technique will be useful in the fabrication of 3D optical memory devices with high storage density. Optical memory using a valence-state change of rare-earth ions at a spot allow data to be read out in the form of luminescence, thus providing the advantage of a high signal-to-noise ratio.

4. Precipitation and Control of Nanoparticles

Noble-metal-nanoparticle-doped glasses exhibit a large third-order nonlinear susceptibility and an ultrafast nonlinear response.^{47,48)} They are expected to be promising materials for an ultrafast all-optical switch in the THz region.⁴⁹⁾ Stookey⁵⁰⁾ developed photosensitive glasses in the early 1950's. These glasses contain noble metal photosensitive ions such as Ag^+ and Au^+ together with Ce^{3+} , which act as a sensitizer. After the irradiation by UV light, Ce^{3+} releases an electron to form Ce^{4+} , while Ag^+ or Au^+ captures the electron to form an Ag or Au atom. After subsequent heat treatment, crystallites, *e.g.*, LiF and Li_2SiO_5 , precipitate in the UV-irradiated area due to the nucleation by the metal cluster or colloids. Although it is possible to fabricate a 3D designed structure using UV laser pulses with a resonant absorption wavelength of glass, the vertical spatial resolution is lower than in the case of femtosecond laser pulse irradiation because the UV light resonates linearly on the surface.⁵¹⁾ We have demonstrated 3D precipitation and control of noble nanoparticles due to photoreduction of the ion (Ag^+ or Au^+) to the atom (Ag or Au) in various transparent glasses by focused femtosecond laser pulses and successive annealing.^{52–57)} A typical glass composition of $77\text{SiO}_2\text{--}5\text{CaO--}18\text{Na}_2\text{O}$ (mol %) and doped with 0.01 mol % Ag_2O was used in this experiment.⁵³⁾ A plane of $4.0 \times 4.0 \text{ mm}^2$ that consisted of lines at an interval of $20 \mu\text{m}$ was written inside the Ag^+ -doped glass sample by scanning the laser beam at $2500 \mu\text{m/s}$ with the focused 120 fs laser pulses operated at a wavelength of 800 nm (repetition rate: 1 kHz, pulse energy: 80 mJ) via a $10\times$ objective lens with a numerical aperture of 0.30 inside the glass sample. The position of the focal spot was about 1 mm beneath the sample surface. The irradiated sample was annealed at 500°C for 10 min in air. After irradiation by the focused femtosecond laser, a gray spot was formed near the focal spot in the Ag^+ -doped silicate glass sample. Absorption peaks at 430 and 620 nm can be observed and assigned to the hole trap centers (HC) at the nonbridging oxygen in the SiO_4 polyhedron with two and three nonbridging oxygen atoms, *e.g.*, HC_1 and HC_2 , respectively [Fig. 7(b)].⁵⁸⁾ After annealing at 500°C for 10 min, the laser-irradiated area became yellow, and a peak at 408 nm due to the surface plasmon absorption of the silver nanoparticles was observed [Fig. 7(c)].⁵⁹⁾ The inset image in Fig. 7 shows the transmission electron microscopy (TEM) observation of the yellow area. Composition analysis using energy-dispersive spectroscopy (EDS) in TEM confirmed that the spherical nanoparticle is metallic Ag. Spherical silver nanoparticles with sizes ranging from 1 to 4 nm were observed in the femtosecond-laser-irradiated area after annealing at 500°C for 10 min. On the basis of absorption and ESR spectra, we suggest that the Ag^+ ion is reduced to an Ag atom by capturing an electron from a nonbridging oxygen during the femtosecond laser irradiation, and silver atoms migrate and aggregate to form nanoparticles after the heat treatment.⁵²⁾

We also succeeded in the space-selective precipitation and control of gold nanoparticles in glass.⁵⁷⁾ An Au^{3+} -doped silicate glass sample with the composition of $70\text{SiO}_2\text{--}10\text{CaO--}20\text{Na}_2\text{O}$ and doped with 0.01 mol % Au_2O_3 was irradiated inside the glass sample on each spot with focused

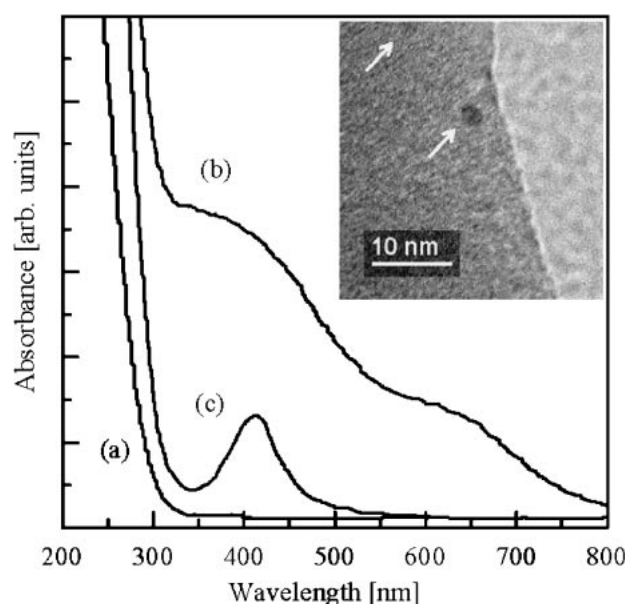


Fig. 7. Absorption spectra of the Ag^+ -doped silicate glass sample (a) before and (b) after the femtosecond laser irradiation, together with (c) the spectrum of the laser-irradiated sample after annealing at 500°C for 10 min. The inset shows a TEM image of the femtosecond-laser-irradiated area of the Ag^+ -doped silicate glass after annealing at 500°C for 10 min.

120 fs laser pulses operating at a wavelength of 800 nm (repetition rate: 1 kHz, pulse energy: $0.8 \mu\text{J}$) for $1/63 \text{ s}$ (*i.e.*, 16 pulses) via a $10\times$ objective lens with a numerical aperture of 0.30. Gray spots of about $40 \mu\text{m}$ were observed in the focused laser-irradiated area through an optical microscope. No microcracks were observed in the glass samples. After the samples were annealed at 550°C for 30 min, the gray spots became red. Absorption spectra showed that there was an apparent increase in absorption in the wavelength range from 300 to 800 nm in the irradiated area (Fig. 8). From the difference absorption spectrum of the Au^{3+} -doped glass sample before and after the femtosecond laser irradiation (Fig. 8 inset), the peaks at 245, 306, 430, and 620 nm can be assigned to E' centers ($\text{E}' = \text{Si}$), which include an electron trapped in an sp^3 orbital of silicon at the site of an oxygen vacancy, a hole trapped by an oxygen vacancy that neighbors alkali-metal ions, and nonbridging oxygen hole centers, respectively.

The absorption spectra of the Au^{3+} -doped silicate glass samples, which were annealed at various temperatures for 30 min after the femtosecond laser irradiation, are also plotted in Fig. 8. When the annealing temperature is below 300°C , the absorption (300–800 nm) intensities induced by laser irradiation decrease as the annealing temperature increases, and completely disappear when the temperatures reaches 300°C . The gray spots induced by the femtosecond laser irradiation disappear at 300°C and become colorless and transparent. Annealing at 450°C results in the appearance of a new peak at 506 nm, and the laser-irradiated areas turn red. This peak can be assigned to the surface plasmon resonance absorption of Au nanoparticles.⁶⁰⁾ The wavelength of the absorption peak increases from 506 to 548 nm with increasing annealing temperature at the same time that its intensity significantly increases. Based on the Mie theory, the average radii of the embedded metal nanoparticles R are

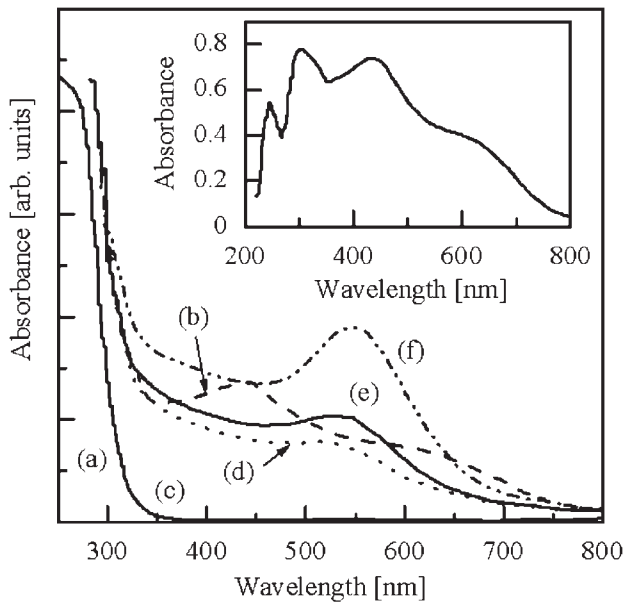


Fig. 8. Absorption spectra of Au^{3+} -doped silicate glass (a: solid line) before and (b: dashed line) after the femtosecond laser irradiation, together with (c: dashed line), (d: dotted line), (e: solid line), and (f: double-dashed line) the absorption spectra of the laser-irradiated sample after annealing at 300, 450, 500, and 550°C for 30 min, respectively. The inset shows the difference spectrum between the absorption of the glass sample after and before the femtosecond laser irradiation.

Table I. Experimental results of the wavelength and FWHM of surface plasmon resonance for the various annealing temperatures.

Annealing temperature (°C)	λ_p (nm)	$\Delta\lambda$ (nm)	$\lambda_p^2/\Delta\lambda$ (nm)
300	—	—	—
450	506	196	1306
500	526	156	1774
550	548	136	2208

proportional to the value of $\lambda_p^2/\Delta\lambda$, where λ_p is the characteristic wavelength of surface plasmon resonance and $\Delta\lambda$ is the full-width at half-maximum (FWHM) of the absorption band.^{61,62)} The value of $\lambda_p^2/\Delta\lambda$ increases from 1306 to 2208 nm when the annealing temperature is increased from 450 to 550°C (Table I). Note that no absorption peak due to the surface plasmon resonance of Au nanoparticles is observed in the femtosecond-laser-irradiated Au^{3+} -doped glass sample after annealing at 300°C. Therefore, the average size of the Au nanoparticles increases with increasing annealing temperature. We directly observed the precipitation of Au nanoparticles in the femtosecond-laser-irradiated Au^{3+} -doped glass sample after annealing at 550°C for 30 min by TEM and confirmed that these spherical nanoparticles are metallic Au. The size of the Au nanoparticles ranges from 6 to 8 nm (Fig. 9).

We studied the effect of the femtosecond laser fluence on the size of the precipitated nanoparticles. With increasing laser intensity from 6.5×10^{13} to 2.3×10^{14} to 5.0×10^{16} W/cm², the color of the femtosecond-laser-irradiated areas became violet, red and yellow, respectively (Fig. 10 inset). The absorption peak that can be assigned to the surface plasmon resonance absorption of Au nanoparticles shifts to

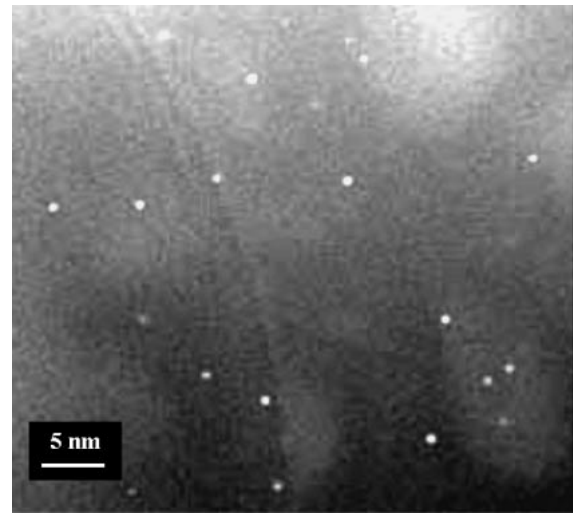


Fig. 9. TEM image of Au nanoparticles (small white dots) in the femtosecond-laser-irradiated area of the Au^{3+} -doped silicate glass after annealing at 550°C for 30 min.

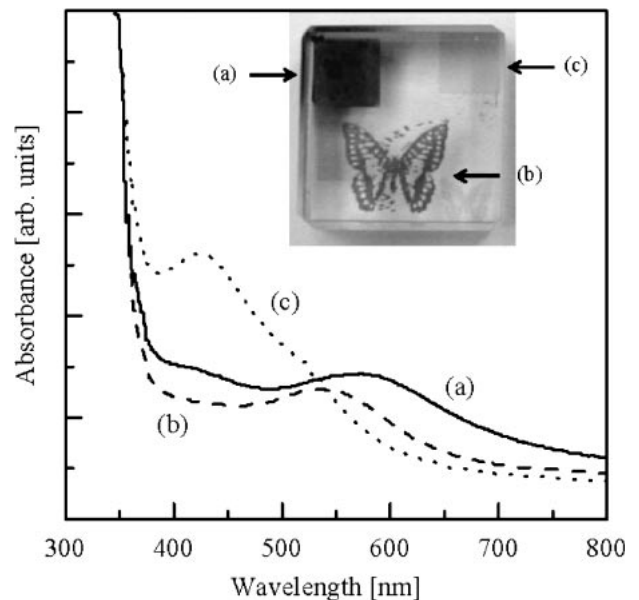


Fig. 10. Absorption spectra of Au^{3+} -doped silicate glass irradiated with different laser intensities: (a: solid line) 6.5×10^{13} W/cm², (b: dashed line) 2.3×10^{14} W/cm², (c: dotted line) 5.0×10^{16} W/cm². All samples were annealed at 550°C for 1 hour. The inset shows the photograph of images drawn inside the Au^{3+} -doped (0.1 mol %) glass sample.

shorter wavelengths from 568 to 534 to 422 nm with the increase of the laser intensity (Fig. 10). The apparent blue shift of the peak from 568 to 422 nm is due to the decrease in the average size of the Au nanoparticles. This is probably because the high irradiation intensity produces a high concentration of reduced Au atoms per unit volume, and thus a high concentration of nucleation centers. As a result, under the same annealing process, the higher the light intensity, the smaller but denser the precipitated particles. However, the wavelength of surface plasmon resonance is not only determined by the size of nanoparticles, but also the concentration of nanoparticles. Further investigation is needed to verify the above mechanism.

5. Polarization-Dependent Nanostructure Induced by Single Femtosecond Laser Beam

5.1 Anisotropic polarization-dependent phenomena

It is well known that a glass structure is optically isotropic to visible light and other wavelengths. When the linear polarized light propagates within glass, the scattering of polarized light in the plane of the light polarization in the glass is always weak compared with that of the orthogonal plane, since a dipole does not radiate in the direction of its axis. We have observed a new phenomenon in glass pumped by intense femtosecond laser radiation: the scattering of light, in particular, luminescence, which peaks in the plane of light polarization (anomalous anisotropic light scattering).²⁷⁾ In our experiment, we used a commercial Ge-doped silicate glass which has an interesting property, strong photosensitivity, associated with defects in glass such as germanium oxygen-deficient centers (Ge-ODC or Ge-Si wrong bonds).^{63,64)} These centers produce a strong absorption band at 5 eV (240 nm, singlet-singlet transition), a weak absorption band at 3.7 eV (330 nm, forbidden singlet-triplet transition), and blue triplet luminescence at 3.1 eV with a decay time of about 100 μ s.^{65,66)} A strong blue luminescence with a center wavelength at 410 nm due to the oxygen defect state (Ge-ODC) was observed during the 120 fs laser pulses operated at a wavelength of 800 nm (repetition rate: 200 kHz, pulse energy: 50 nJ) via a 20 $\times$ objective lens inside Ge-doped (GeO₂ $\sim$ 8 mol %) silicate glass. When the laser was focused slightly ($\sim$ 50 μ m) above the surface of the sample, the shape of the spot of the blue luminescence imaged via a microscope and a CCD camera was circular [Fig. 11(a)]. Unexpectedly, it was discovered that when the laser was focused inside the sample the spatial isotropy of the blue luminescence can be broken [Fig. 11(b)]. The luminescence scattering increases along the direction of laser polarization, while the circular shape of the laser beam remains unchanged. If we rotate the direction of the laser polarization by using a half-wave plate, the elongated pattern of the blue luminescence follows this rotation [Figs. 11(c)–11(e)]. It should be noted that the blue luminescence was not polarized and that self-focusing was not observed at the peak powers used in these experiments. We called this phenomenon the “propeller effect” due to the propeller-like shape of the luminescence spot in the focus of the laser beam. The observed phenomenon represents the first evidence of anisotropic light scattering that peaks in the plane of laser polarization in isotropic media.

The fact that the blue luminescence is elongated along the laser polarization indicates that some additional momentum is acquired by the photons in this direction. We believe that such transformation of the momentum can be caused by the photoelectrons moving along the direction of laser polarization. Photoelectrons with anisotropic momentum distribution can be created via the multiphoton ionization of defects (two-photon ionization of Ge-ODC from the long-lived triplet state) by the linearly polarized femtosecond laser pulses (Fig. 12). Indeed, it is well known that the angular distribution of photoelectrons can be elongated in the direction of the light polarization: $d\sigma/d\Omega \propto 1 + \cos^2\theta$, where $d\sigma/d\Omega$ is the differential scattering cross section of electrons and θ is the angle between the field amplitude

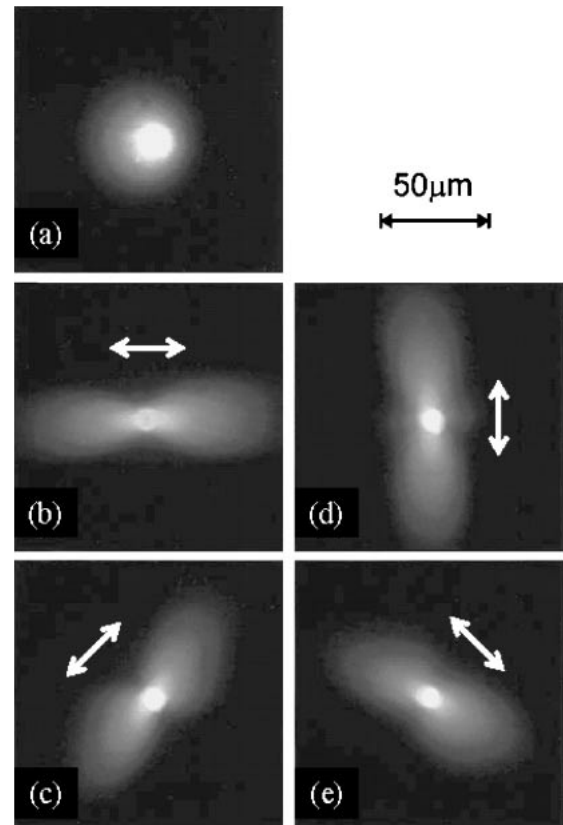


Fig. 11. Photographs of the blue luminescence spots in the focus of the linearly polarized femtosecond laser pulses. Laser light is focused above the sample (a). Laser light with four different orientations of polarization indicated by arrows is focused inside the sample (b)–(e). Notice that the blue luminescence spot is elongated along the laser light polarization. The pink spot is produced by the laser light leaking through the dichroic mirror.

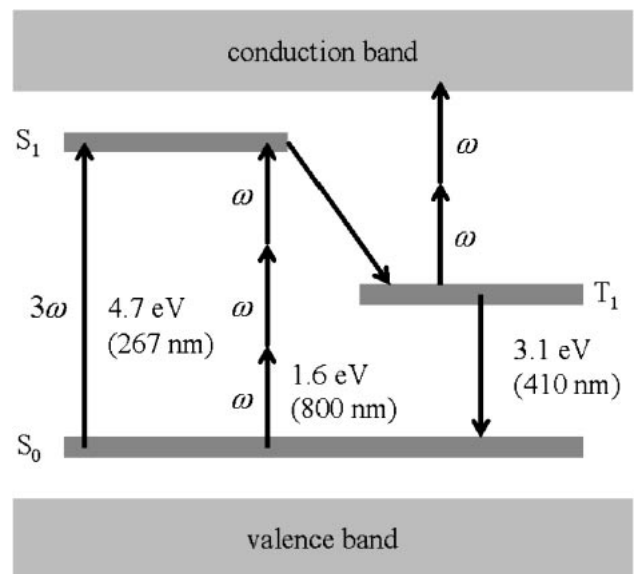


Fig. 12. Energy-level diagram of a Ge-Si defect in silicate glass with the possible channels of excitation.

vector E and the electron momentum vector k_e .^{67,68)} It is clear that the photoelectrons can be involved in a microscopic movement (with displacement on the order of 10 nm) in the direction of the laser polarization. Microscopic

displacements (much less than a laser wavelength) of the photoelectrons in the direction of laser polarization can lead to anisotropic fluctuations of dielectric constant. Such fluctuations are obviously stronger in the direction of laser polarization (the direction of electron movement) than in the perpendicular direction. The fluctuations of the dielectric constant in the direction of laser polarization induce index inhomogeneities which are elongated in the direction perpendicular to the laser polarization and which have k vectors of spatial harmonics parallel to the direction of polarization. The anisotropic inhomogeneities scatter photons (*e.g.*, the ultraviolet photons of the third harmonic of the laser light) in the plane of laser polarization.

We have also observed the memorized polarization-dependent light scattering in a Eu^{2+} -doped fluoroaluminate glass sample.²⁸⁾ Anisotropic blue luminescence, which peaked in the plane of the light polarization, was observed in the glass sample by the focused 150 fs laser pulses operating at a wavelength of 800 nm with a repetition rate of 200 kHz. When we changed the direction of the laser light polarization and irradiated the same location, we observed an anisotropic blue-luminescence pattern identical to the original one at the beginning, but then observed a new pattern in the new direction of light polarization while the original light-scattering pattern disappeared gradually with the passage of time. This observed phenomenon was considered to be due to the light scattering of the polarization-dependent permanent microstructure induced by the polarized ultrashort-pulsed laser itself (Fig. 13).

5.2 Self-organized nanostructure induced by single femtosecond laser beam

The structure induced by focused femtosecond laser irradiation depends on the level of laser intensity. One can

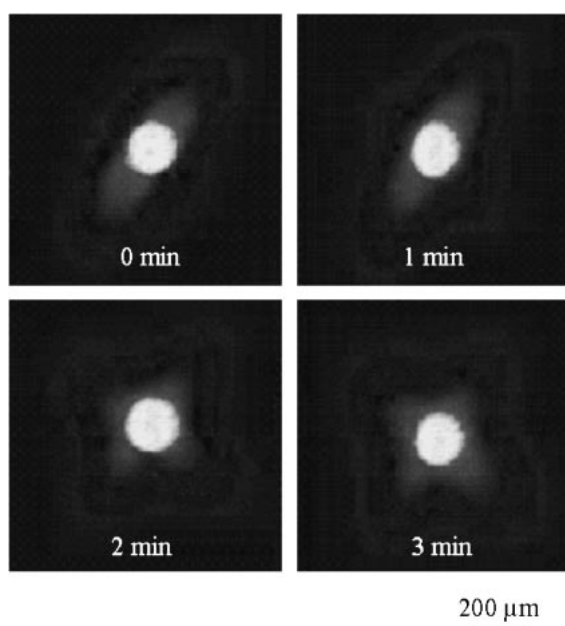


Fig. 13. Photographs of blue luminescence patterns near the focus of a linearly polarized femtosecond laser beam. The time shown in the figure is the duration after changing the polarization direction of the laser beam and irradiating the same location that was irradiated using the previous polarized laser beam.

induce any of three qualitatively different types of modification or damage:^{26,69)} low intensity induces a smooth positive refractive-index change relative to the unprocessed material (type I); an intermediate intensity results in birefringent regions (type II); and at a high intensity the damage consists of voids embedded into the glass (type III). Type II modification can develop not only the above-mentioned anisotropic light scattering phenomenon but also the birefringence effect.^{30,69–72)} Recently Mysyrowicz *et al.* observed uniaxial birefringence imprinted in structures written within fused silica plates by focused femtosecond laser irradiation.⁶⁹⁾ We discovered anisotropic reflection, which we explained in terms of the formation of a self-organized nanograting within the focal volume,²⁹⁾ and more recently the existence of self-induced nanograting was proven by direct imaging.³³⁾ In our experiments, we used commercially available synthetic silica glass, ED-H (Tosoh Quartz Corp., wet silica with OH $\sim$ 50 ppm) and a tellurium dioxide (TeO_2) single crystal [Oxide Corp., z-cut with an orientation of (0,0,1)]. The absorption spectra of samples were observed and the absorbances of SiO_2 glass and TeO_2 crystal at a wavelength of 800 nm were about 0.04 and 0.1, respectively. The 150 fs femtosecond laser pulses operating at a wavelength of 800 nm with a repetition rate of 200 kHz were focused via a 100 $\times$ objective lens with a numerical aperture of 0.95 towards the interior of the samples. The beam was focused at about 100 μm below the sample surface and the beam waist diameter was estimated to be $\sim$ 1 μm . The irradiated spot was imaged in the visible spectral range via an optical microscope using a colored charge-coupled device (CCD) camera. The irradiation parameters were controlled by an electronic shutter, a variable neutral density filter, and a half-wave plate placed in the optical path of the laser beam. After laser irradiation, the sample was observed using an optical microscope (Fig. 14) and polished to the depth of the beam waist location.

The polished sample surface was analyzed by scanning electron microscopy (SEM). The secondary electron images (SEIs) are shown in Fig. 15. In addition, backscattering electron images (BEIs) of the same surface of the SiO_2 glass sample are shown Fig. 16. It is well known that the SEI reveals the surface morphology of a surface, while the BEI is sensitive to the atomic weight of the elements or the density of the material constituting the observation surface. The SEI of the polished SiO_2 glass sample indicates that the

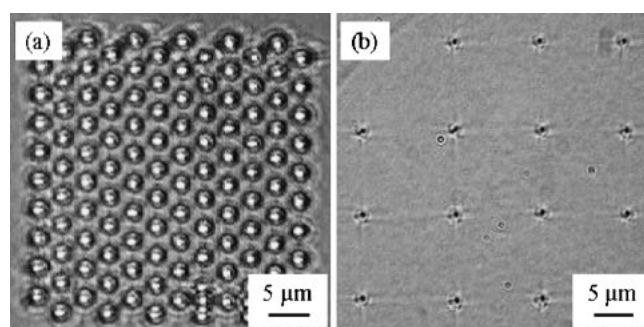


Fig. 14. Optical microphotograph of the array of written dots within (a) silica glass and (b) a tellurium dioxide single crystal. The pulse energies of the femtosecond laser irradiation are (a) 1.0 μJ and (b) 0.8 μJ , respectively.

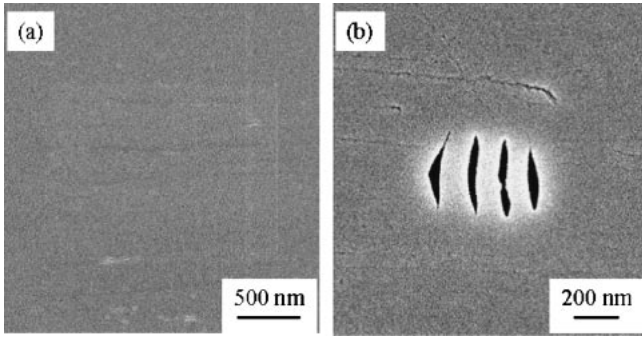


Fig. 15. Secondary electron images of the polished sample surface of (a) silica glass and (b) a tellurite dioxide single crystal after being polished close to the depth of the focal spot location.

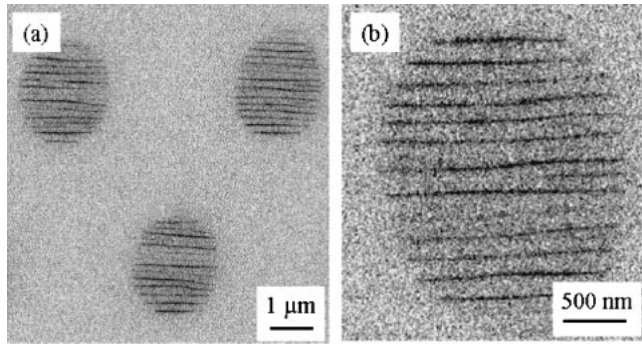


Fig. 16. Backscattering electron images of the polished silicate glass sample after being polished close to the depth of the focal spot location. The magnifications of (a) and (b) are 10000 $\times$ and 30000 $\times$, respectively.

morphology at the focal point does not change; namely, a void does not exist. On the other hand, in the case of the TeO_2 crystal, stripelike voids of nanoscale pitch and width exist within the focal point. The SEI of TeO_2 crystal shows that periodic voids ~ 30 nm wide are aligned perpendicular to the polarization direction of the laser beam. Furthermore, as with the SEI of the TeO_2 crystal, the BEI of SiO_2 glass shows a periodic structure of stripelike dark regions ~ 20 nm wide consisting of material with a low density, which are aligned perpendicular to the laser polarization direction. In the case of SiO_2 glass, we speculate, on the basis of the fact that the elements constituting the sample are silicon and oxygen (average molecular weight of SiO_2 glass ~ 60.1), that the oxygen defects were formed in the regions corresponding to the dark domains of the BEI, which reduce the average molecular weight in these regions ($\text{SiO}_{2-x} \sim 60.1 - 16x$).

To test this suggestion we carried out Auger spectra mapping of silicon and oxygen on the same surface by Auger electron spectroscopy (AES). The Auger electron intensity is proportional to the concentration of the element on the surface and the spatial resolution of AES was about 10 nm. The Auger signal of the oxygen in the regions corresponding to dark domains in the BEI is low compared with other regions, indicating low oxygen concentrations in these domains [Fig. 17(a)]. Furthermore, the intensity of the oxygen signal is stronger in the regions between the dark domains of the BEI. On the other hand, the intensity of the silicon signal is the same in the whole imaged region

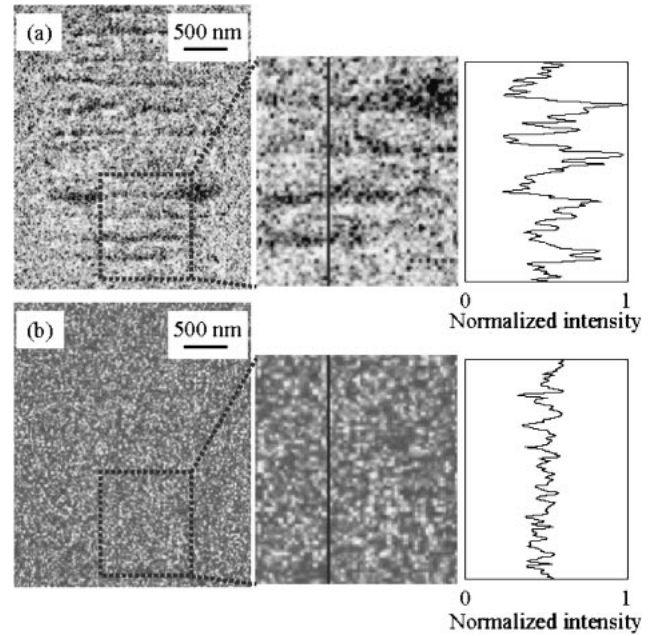


Fig. 17. Auger spectra mapping and corresponding line scans of (a) oxygen and (b) silicon on the same silicate glass sample surface polished close to the depth of the focal spot location.

[Fig. 17(b)]. These results indicate that the periodic structures observed in the BEI consist of periodically distributed oxygen-deficient regions (SiO_{2-x}). The Auger signal intensity is proportional to the concentration of element constituting the surface, which gives an estimated value of $x \sim 0.4$. Furthermore, in the SiO_2 glass experiment, we observed a decrease of the grating period with an increase of the exposure time. With a pulse energy of 1 μJ , the grating periods were about 240, 180 and 140 nm for the number of light pulses of 5×10^4 , 20×10^4 and 80×10^4 , respectively. The pulse energy of 1 μJ corresponds to an intensity of about $2 \times 10^{14} \text{ W/cm}^2$ in our experiments. This indicates a logarithmic dependence of the grating period Λ on the number of light pulses N_{pulse} .

The dependence of the observed periodic nanostructures on pulse energy for a fixed exposure time was also investigated, and an increase of the period with increase in the pulse energy was observed. For the number of light pulses of 20×10^4 , grating periods of 180, 240 and 320 nm were measured at pulse energies of 1, 2 and 2.8 μJ , respectively. The diameters of the induced structures of the SiO_2 glass and TeO_2 crystal were about 1.5 μm and 460 nm, respectively [Figs. 15(b) and 16]. We attribute this difference to the self-focusing effect. It is well known that nonlinear self-focusing is initiated by the positive lens created by the intensity-dependent refractive index via the Kerr effect. The intensity-dependent refractive index is defined as⁷³⁾

$$n = n_0 + n_2 I, \quad (1)$$

where n_0 is the ordinary refractive index and I is the intensity of the laser. The nonlinear refractive index (n_2) is given by⁷⁴⁾

$$n_2 \text{ (esu)} = \frac{12\pi^2}{n_0^2 c} \chi^{(3)} \text{ (esu)}, \quad (2)$$

Table II. The irradiated condition, the structural changing size, the refractive index n_0 , and nonlinear susceptibility $\chi^{(3)}$ from the literature for SiO₂ glass and TeO₂ crystal.

Material	Pulse energy (μJ)	Number of light pulses	Size (μm)	n_0	$\chi^{(3)}$ (esu)	Reference
SiO ₂ glass	1.0	20×10^4	~ 1.5	1.45	$\sim 3 \times 10^{-14}$	75
TeO ₂ crystal	0.8	16×10^2	~ 0.46	2.26	$\sim 1 \times 10^{-12}$	76

where c is the speed of light and $\chi^{(3)}$ is the nonlinear susceptibility. When self-focusing occurs,⁷⁵⁾ the size of the structurally changed area is inversely proportional to the refractive index and the nonlinear index of change Δn :

$$d \propto \frac{1.22\lambda_0}{\sqrt{8n_0\Delta n}}, \quad (3)$$

where λ_0 is the laser wavelength. The irradiated conditions, the size of the structurally changed area, the refractive index, and the nonlinear susceptibility for SiO₂ glass and TeO₂ crystal are shown in Table II.

5.3 Formation mechanism of self-organized nanograting

When the intense femtosecond laser pulses are focused inside a transparent media, the ionization of the material takes place. Apparently, the energy of a single laser photon with a wavelength of 800 nm ($E = 1.55$ eV) is small for ionization of a material with a large band-gap energy (the E_g values of SiO₂ glass and TeO₂ crystal are ~ 7.5 and ~ 3.6 eV, respectively). Since the intensity of the light at the beam focus is sufficiently high (i.e., $\sim 10^{14}$ W/cm²), the multiphoton ionization process is dominant.⁷⁸⁾ A high free-electron density is produced at the focal point by multiphoton ionization, and the material has the properties of plasma. Here, only the movement of the electrons is considered because ions are almost immobile at high frequencies. Free electrons cannot absorb energy directly from the photons, but they oscillate in the electric field of the light wave. In plasma, this oscillation is damped, through electron-ion collisions.^{79,80)} The electrons are accelerated and their oscillatory energy is converted into the thermal energy of the plasma by collisions with ions by the linear damping mechanism (*inverse Bremsstrahlung heating*). The temperature of the plasma increases. Thus, the generated plasma will absorb the laser energy via one-photon absorption. A light wave traveling in plasma causes electrons to move, exciting an electron plasma density wave (*Langmuir wave*). The light can propagate through the plasma only at frequencies $\omega_{ph} > \omega_p$, where ω_p is the plasma frequency:

$$\omega_p = \sqrt{\frac{e^2 n_e}{\epsilon_0 m_e}}. \quad (4)$$

Where, e is the electron charge, n_e is the electron density, and ϵ_0 is the permittivity of free space. The critical density n_{crit} ($\omega_p = \omega_{ph}$) from eq. (4) is

$$n_{crit} = \frac{\omega_{ph}^2 \epsilon_0 m_e}{e^2} = \frac{4\pi^2 \epsilon_0 m_e c^2}{e^2} \cdot \frac{1}{\lambda_0^2}, \quad (5)$$

where c is the speed of light in vacuum, which gives $n_{crit} = 1.74 \times 10^{-21}$ cm⁻³ for $\lambda_0 = 800$ nm. The electron plasma density waves are longitudinal acoustic waves with the electric field component parallel to the direction of propagation. The dispersion relation for the electron plasma

wave is

$$\omega_{pl}^2 = \omega_p^2 + \frac{3}{2} v_e^2 k_{pl}^2, \quad (6)$$

where ω_p is the plasma frequency, $v_e (= 2\kappa_B T_e / m_e)$ is the thermal speed of electrons, k_{pl} is the electron plasma wave vector, κ_B is the Boltzmann constant, and T_e is the electron temperature. This is known as the *Bohm–Gross* dispersion relation. Similarly, the dispersion relation for a light wave propagating in electron plasma is

$$\omega_{ph}^2 = \omega_p^2 + \frac{c^2}{n^2} k_{ph}^2, \quad (7)$$

where k_{ph} is the light wave vector. Figure 18 shows the dispersion relationship of the light field and the electron plasma waves of SiO₂ glass. The dispersion for an electron plasma wave changes slightly. Since light waves cannot propagate inside plasma below the plasma frequency (ω_p), the dispersion relation for light waves in plasma is asymptotic to the curve of the electron plasma wave. An electron plasma wave could couple with the incident light wave only if it propagates in the plane of light polarization. Initial coupling is produced by inhomogeneities induced by electrons moving in the plane of light polarization.²⁷⁾ The coupling is increased by a periodic structure created via a pattern of interference between the incident light field and

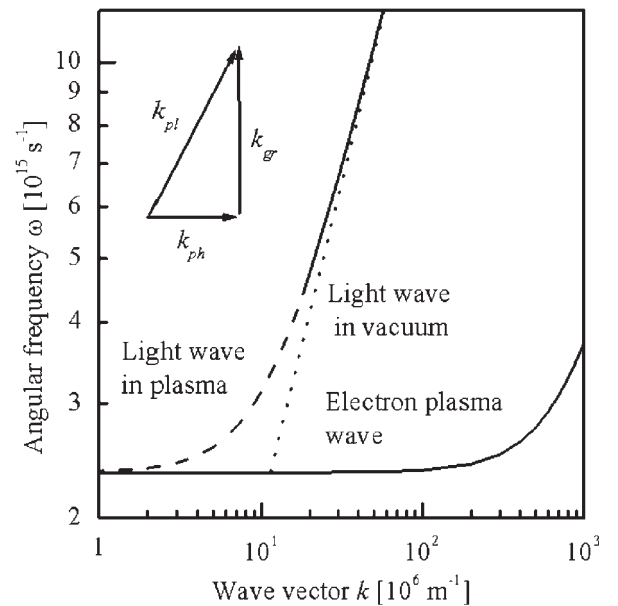


Fig. 18. Dispersion relations (double logarithmic plot) for a light wave and an electron plasma wave of silica glass. Note that the dispersion for the electron plasma wave slightly changes below $k = 1.0 \times 10^8$ m⁻¹. The dispersion relation for the light wave in plasma is asymptotic to the curve of the electron plasma wave, because light waves cannot propagate inside plasma below the plasma frequency (ω_p).

the electric field of the bulk electron plasma wave, resulting in the periodic modulation of the electron plasma concentration and the structural changes in glass. A positive gain coefficient for the electron plasma wave will lead to an exponential growth of the periodic structures oriented perpendicular to the light polarization, which become frozen within the material. Such behavior is common for self-organized structures in light-matter interactions.³¹⁾ The electron plasma wave is efficiently generated only with the wave vector k_{pl} in the plane of light polarization and only in the direction defined by the conservation of the longitudinal component of the momentum (Fig. 18 inset).

$$k_{pl} = \frac{\omega_{pl}}{v_{pl}}. \quad (8)$$

Where, v_{pl} is the speed and ω_{pl} is the angular frequency of the electron plasma wave. The period of the observed grating is defined by the momentum conservation condition:

$$k_{gr} = \frac{2\pi}{\Lambda} = \sqrt{k_{pl}^2 - k_{ph}^2}. \quad (9)$$

Taking into account the energy conservation condition $\omega_{pl} = \omega_{ph}$, the electron density (N_e) is obviously below the critical density (n_{crit}) in the boundary between underdense and overdense plasma.

$$N_e = n_{crit} - \frac{3\varepsilon_0\kappa_B T_e}{e^2} k_{pl}^2 \leq n_{crit}. \quad (10)$$

It is possible to obtain an analytical expression for the grating period (Λ) versus electron temperature and density:

$$\Lambda = \frac{1}{\sqrt{A(N_e)B(T_e)}}, \quad (11)$$

$$A(N_e) = \frac{c^2}{\lambda_0^2} - \frac{e^2}{4\pi^2\varepsilon_0 m_e} N_e, \quad (12)$$

$$B(T_e) = \frac{m_e}{3\kappa_B T_e} - \frac{(n_0 + n_2 I)^2}{c^2}. \quad (13)$$

This formula has been considered to explain both the decrease of the refractive index due to the dispersion for light wave propagation inside plasma and the increase of the nonlinear index due to the high intensity of the laser. This dependence shows that the grating period increases with the increase of electron density and electron temperature. The electron density increases steeply when the electron density approaches the critical density [$A(N_e) \rightarrow 0$, $N_e \sim n_{crit} = 1.74 \times 10^{21} \text{ cm}^{-3}$ at $\lambda_0 = 800 \text{ nm}$]. Similarly, the electron temperatures of SiO₂ glass and TeO₂ crystal have critical values of 9.34×10^8 and $3.67 \times 10^8 \text{ K}$ with a pulse energy of $1.0 \mu\text{J}$, respectively [$B(T_e) \rightarrow 0$]. It also follows from the above that for a given grating period the electron temperature decreases with the increase of the electron density:

$$\frac{1}{T_e} = \frac{3\kappa_B n^2}{m_e c^2} \left(1 + \frac{\lambda_0^2}{n^2} \cdot \frac{1}{\Lambda^2} \cdot \frac{n_{crit}}{n_{crit} - N_e} \right). \quad (14)$$

This gives a wide range of realistic electron densities and temperatures^{8,15,81)} which could identify a certain grating period, including the periods observed in our experiments.

For comparison of the theory and experiment, it is useful to define the dependence of the grating period on a measurable value, such as pulse energy. Then, the depend-

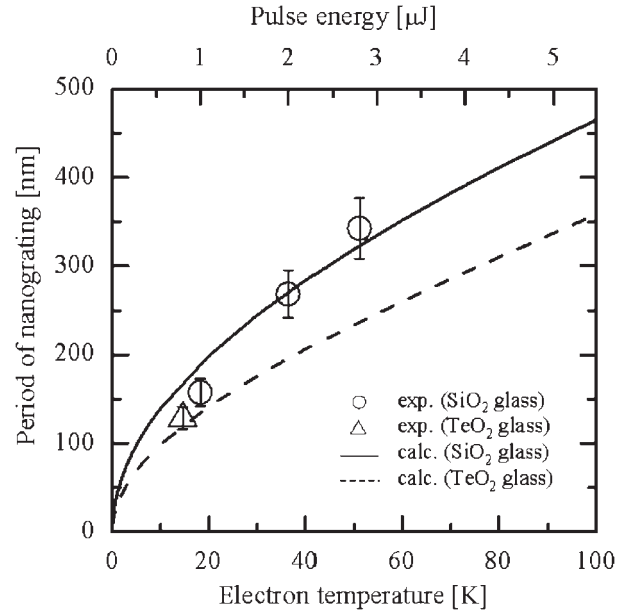


Fig. 19. Pulse energy dependence of the experimental nanograting period of silica glass (○) and tellurium dioxide single crystal (△). Theoretical curves of nanograting period versus electron temperature are also shown.

ences of electron temperature and density on light intensity should be clarified. These dependences are complicated and are not very well established in bulk silica.^{8,82)} However, it is certain that the electron temperature will increase and the plasma electron density will not decrease with the increase in light intensity. Therefore, we assume that the electron thermal energy is proportional to the absorbed pulse energy in a focal point volume:⁸³⁾

$$\eta E_p \propto C_e V T_e, \quad (15)$$

$$T_e \propto \frac{2\eta}{3V\kappa_B N_e} E_p, \quad (16)$$

where E_p is the pulse energy of the laser, η is the absorption coefficient, and V is the focal volume. The experimental period of the nanograting versus pulse energy is shown in Fig. 19. The observed increase of the grating period with the pulse energy is in agreement with this theoretical prediction. Moreover, we evaluated the electron density of SiO₂ glass and TeO₂ crystal by fitting of the experimental data using eqs. (11)–(13), (15), and (16), assuming an absorption of 30% ($\eta = 0.3$) of the energy of the laser pulse.¹⁵⁾ This gives electron densities for SiO₂ glass and TeO₂ crystal of $N_e^{\text{SiO}_2} \sim 1.45 \times 10^{21} \text{ cm}^{-3}$ and $N_e^{\text{TeO}_2} \sim 1.15 \times 10^{21} \text{ cm}^{-3}$, respectively.

Based on the above mechanism of nanograting formation, it is possible to give the following explanation of the observed formation of striplike regions with atomic defects. Here structural defects represent regions of low oxygen concentration in the case of SiO₂ glass and voids in the case of TeO₂ crystals. The interference between the light wave and the electron plasma wave will lead to modulation of the electron plasma concentration. The plasma electrons are created in the process of breaking R–O–R (R is Si or Te) bonds via the multiphoton absorption of light which is accompanied by the generation of R–R bonds, nonbridging oxygen-hole centers (NBOHC, $\equiv \text{R–O}^-$), and interstitial oxygen atoms (O_i). Such oxygen atoms are mobile and can

diffuse from the regions of high concentration, possibly via the Coulomb explosion mechanism.⁸⁴⁾ Negatively charged oxygen ions can be also repelled from the regions of high electron concentration. Thus, since the binding energy of Si–O is approximately 2.5 eV higher than that of Te–O from X-ray photoelectron spectroscopy (XPS) measurements, the Te–O bond could be broken more easily than the Si–O bond. In the case of SiO₂ glass, we measured photoluminescence and Electron spin resonance (ESR) spectra, which confirmed the presence of nonbridging oxygen defects and E' centers in the irradiated samples. The small thickness of the low oxygen concentration regions compared with the period of the grating could be explained by a highly nonlinear dependence of the structural changes on the electron concentration. Major changes in composition take place after the attainment of thermal equilibrium. The interference between the light wave and the electron plasma wave leads to an interference pattern, *e.g.*, periodic modulation of the electron plasma concentration. Hot electrons are almost instantaneously excited by ultrashort laser pulses and subsequently decay into the lattice. Realistic lattice temperatures are about two orders of magnitude lower than electron temperatures due to the difference in heat capacity of electrons and ions. Our view is that electrons are locally interfered with the light first, and then the resultant periodic structure remains throughout the subsequent interactions. Structural changes involve formation and decay of defect states such as oxygen vacancies, which is a prominent feature in silica.⁸⁵⁾ On the other hand, in the case of a TeO₂ crystal, periodic voids are formed and aligned in the plane perpendicular to the polarization of the light field. Single void formation has been observed in other experiments.^{15,86)} A void formation is caused by an explosive expansion of the ionized material in the focal volume into the surrounding area by densified matrix, *i.e.* a microexplosion. In the microexplosion, an increase in pressure is caused by a rise in temperature at a constant volume. We speculate that the periodic void formation mechanism is as follows. In the early stages of the interaction between the light field and the electron plasma wave, a periodic pattern of electron density arises in common with SiO₂ glass. Due to the weaker binding energy of Te–O and its lower melting point of 730°C, a void is formed in the region where the electron plasma density distribution is maximum. The detailed mechanism of the structural changes responsible for the nanograting formation is under investigation.

Apart from the fundamental importance of the observed phenomenon as the first direct evidence of interference between light and electron density waves, the observed self-organized nanostructures are the smallest embedded structures ever created by light, which could be useful not only for optics such as optical recording, polarizer and photonic crystal fabrication, but also for hepafilters in biology.

6. Conclusion

We have observed various femtosecond-laser-induced nanostructures in glasses. We demonstrated the possibility of space-selective control of the valence state of active ions (rare-earth, transition metal ions) for the 3D optical memory with an ultrahigh storage density. We have also observed single femtosecond laser beam-induced polarization-depend-

ent nanostructures inside glasses. The mechanism of the nanograting formation is suggested to be due to the interaction between the coherent field of the femtosecond laser and laser-induced electron plasma, and matter. Recently, we have also observed the formation of a periodical nanohole array in the propagation direction of the femtosecond lasers beam and other interesting phenomena. We are convinced that femtosecond laser will open new possibilities in microoptics, material sciences, physics, chemistry, and the bioscience fields.

Acknowledgments

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