

Space-selective Control of Functional Properties
in Transparent Materials
by Femtosecond Laser Irradiation

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General Introduction

Femtosecond(fs) laser processing has been recognized as a powerful tool to provide transparent materials with new functionalities. The definition of “transparent” is that the energy of a single photon of the incident laser beam is smaller than the band gap energy(E_g) of the material. The important advantages of fs laser processing “space-selective” and “damage less” modification. In 1996, K.M. Davis et al.¹. published the first paper about fs laser processing inside transparent materials. They investigated the effect of 810-nm fs laser irradiation of various glasses with the goal of being able to create optical devices for the telecommunications industry. Fs laser irradiation inside glasses results in a space-selective increase of refractive index around the laser focal spot, which suggests the possibility to write three-dimensional optical circuits in bulk glasses. The next year, Miura et al.² confirmed waveguiding in the region of high refractive index. In 1996, E.N. Glezer et al.³ reported the application of fs laser irradiation to three-dimensional optical data storage. They demonstrated data storage with modification with 2- μm in-plane bit spacing and 15- μm inter plane spacing (17 Gbits/cm³). Furthermore, they experimentally showed that the structures produced by 100-fs pulses differ drastically from those produced by 200-ps and 10-ns pulses. With the longer pulses, the structures are irregularly shaped, and cracks appear in the glasses even at energies only slightly above the threshold for structural change. On the other hand, with the 100-fs pulses, they did not observe the cracking even up to pulse energies 100 times the threshold. Such “space-selective” and “damage less” processing has been applied to fabricate various devices such as optical waveguides¹⁻², optical data storage³⁻⁴, couplers⁵⁻⁶, gratings⁷⁻⁸, and 3D channels⁹⁻¹⁰. These facts directly demonstrate the advantage of fs laser processing compared to longer pulse laser processing.

Ionization process in transparent materials by fs laser

Knowledge of the ionization process is important to understand the above characteristics of fs laser processing in transparent materials. A qualitative picture of ionization under fs laser irradiation in transparent materials is shown in Fig.1¹¹. In this section, the words “free electron” and “ionization” correspond to the electrons in the conduction band and excitation from the valence band to the conduction band, respectively.

When the fs laser pulses are tightly focused into a transparent material with an objective lens, the first stage of ionization begins with two processes: multiphoton ionization(MPI) and tunneling ionization. MPI is ionization in which more than one photon are simultaneously absorbed by a single electron. The probability of MPI is expressed by the rate $P(I)_{MPI} = \sigma_n I^n$, where σ_n is the multiphoton absorption coefficient for absorption of n photons and I is the intensity of the electric field¹². When the number of the photons n meets the condition $n h \nu > E_g$, where h is Planck's constant and ν is the frequency of the photon, an electron in the valence band can be excited to the conduction band. On the other hand, tunneling ionization is ionization in which the energy barrier of coulomb potential is suppressed by the intense electromagnetic field and an electron in the valence band can tunnel to the conduction band. In order to distinguish MPI and tunneling in photoionization, Keldysh introduced a parameter¹²,

$$\gamma = \frac{\omega}{e} \sqrt{\frac{m c n \varepsilon_0 E_g}{I}}$$

where ω is the laser frequency, m and e are the reduced mass and charge of the electron, c is the velocity of light, n is the refractive index of the material, and ε_0 is the permittivity of free space. For values $\gamma \ll 1$ as obtained with low frequency and large field strength, tunneling is responsible for the initial ionization. On the other hand, for values $\gamma \gg 1$, the probability of MPI

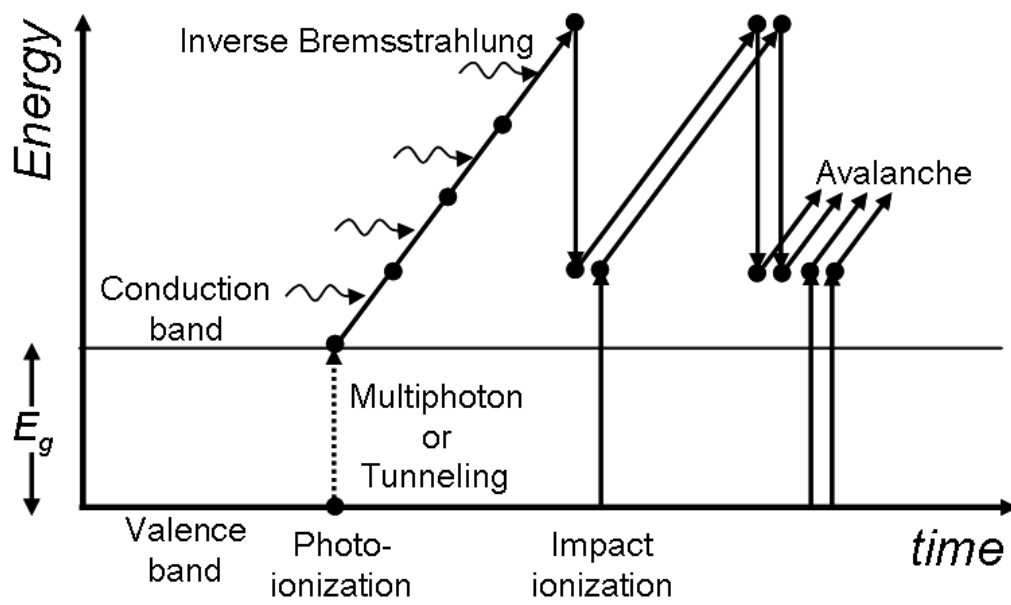


Fig. 1. Schematic view of ionization process

is much higher than that of tunneling.

Once a free electron is produced in the medium, it can absorb photons through an inverse Bremsstrahlung process. In this process, the incident electric field of laser light oscillates a free electron, which gains kinetic energy during absorption of a photon. After a sequence of several inverse Bremsstrahlung events, the kinetic energy is enough large to produce another free electron through impact ionization. Impact ionization is induced by the collision between the free electron and an electron in the valence band. This produces two free electrons with low kinetic energies which can gain energy through inverse Bremsstrahlung absorption. The iteration of Bremsstrahlung absorption and impact ionization leads to an avalanche growth in the number of free electrons, which is called avalanche ionization.

These processes occur only around the focal volume of the objective lens because an intense electric field is necessary to generate the initial free electron which acts as a seed for the avalanche ionization. This enables the “space-selective” modification inside transparent materials. Furthermore, the shorter pulse of fs lasers means that a lower pulse energy can generate the initial free electron compared to longer pulse laser, because the peak intensity of a shorter pulse is more than that of a longer pulse with the same pulse energy. In the case of the longer pulse, when the pulse energy exceeds the absorption threshold, the temperature elevates dramatically due to the large pulse energy around the focal volume, and cracking occur because of the intense thermal stress. On the other hand, in the case of the shorter pulse, the temperature elevation around the focal volume in the vicinity of the energy threshold is not so high as to generate cracking. Such low energy threshold leads to “damage less” modification inside transparent materials.

Time scale of the various phenomena induced by fs laser irradiation

The timescale of the physical phenomena involved in the interaction between a single fs pulse and a transparent material is indicated in the Fig.2¹³. Although the time demonstrated in Fig.2 depends on the material, the order of magnitude of the time is meaningful. The initial photoionization process (multiphoton absorption and tunneling ionization) starts 1 fs after pulse irradiation. Avalanche ionization occurs after 50 fs because it does not occur before the density of free electrons exceeds a certain value. The next process is energy transfer from electrons to the lattice, which starts after 1 ps. After this process, the system reaches an equilibrium state and the temperature can be defined. Especially, in this thesis, the timescale of thermal diffusion is important. When the time interval of the pulse train is less than that of the thermal diffusion time, the thermal energies by every irradiation are accumulated around the focal spot, and temperature elevates. For example, in the case of silicate glass, it takes approximately 10 μ s until the heat diffuse out from the laser focal volume, which means heat accumulation occurs at repetition rates above 100 kHz. In this thesis, the irradiation protocol above 100 kHz is referred as “high repetition laser irradiation”. High repetition laser irradiation has been used to fabricate low-loss optical wave guides¹⁴⁻¹⁵ and laser welding¹⁶.

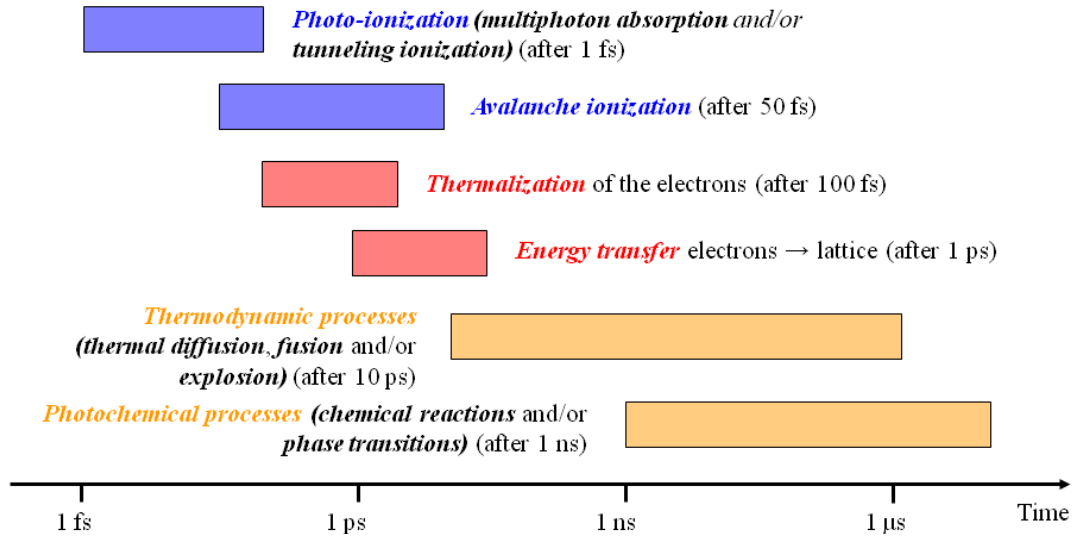


Fig. 2. Timescale of the physical phenomena involved in the interaction between a fs pulse and transparent material

Summary of each chapter

Chapter 1: One of the most important factors to understand and control the modification induced by fs laser irradiation is temperature distribution. I experimentally elucidated the three-dimensional temperature distribution and the modification mechanism in a soda-lime-silicate glass under irradiation of ultrafast laser pulses at high repetition rates by analyzing the relationship between morphology of the modification and ambient temperature. In the analysis, I considered temperature dependence of the thermophysical properties and nonlinear effect on the absorbed energy distribution along the beam propagation axis. The results indicate that the visco-elastic deformation and material flow play an important role in the laser-induced modification inside a glass.

Chapter 2: Element migration in multicomponent glass is a phenomenon induced by high-repetition femtosecond laser irradiation and enables spatially selective modification of glass composition. Since the composition of a glass affects its material properties such as refractive index, luminescence, etching rate, viscosity, crystallization temperature, and phase-separation property, element migration is of great interest for practical applications. However, the mechanisms underlying migration have not been elucidated. In this study, we succeeded in identifying its driving force. In an experimental study, we simultaneously focused two beams of femtosecond laser pulses into two spatially-separated spots inside silicate glass. We observed the formation of characteristically shaped element distributions by electron probe microanalysis. In addition, we performed numerical simulations in which we considered concentration- and temperature-gradient-driven diffusions. The simulation results were in excellent qualitative agreement with the experimental results, indicating that element migration

can be explained by thermodiffusion.

Chapter 3: As application of the formation of the element distribution, I demonstrate the space-selective modification of optical and chemical properties such as refractive index, phase separation property, and luminescence property.

Chapter 4: I demonstrate that intense ultrashort light pulses induces localized phase transformation of diamond. Photoinduced amorphous structures have electrical conducting properties of a maximum of 64 S/m based on a localized transition from sp^3 to sp^2 in diamond. The laser parameters of fluence and scanning speed affect the resultant electrical conductivities due to recrystallization and multi-filamentation phenomena. The laser-processed diamond with periodic cylinder arrays has the characteristic transmission properties in terahertz region, which are in good agreement with theoretical calculations. The fabricated periodic structures act as metallo-dielectric photonic crystal

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Chapter 1

Temperature distribution and heat modification mechanism in glasses under ultrafast laser irradiation

1.1 Introduction

Nonlinear photoexcitation by femtosecond fs laser has been utilized to provide transparent materials, especially glasses, with various kinds of functionalities¹⁻¹² such as optical waveguides¹⁻⁶, diffractive optics⁷⁻⁹, and three dimensional optical data storages¹⁰⁻¹². Because of low threshold of nonlinear absorption by an ultrashort pulse, thermal damage can be made minimal in fs laser processing. In general, thermal energy is regarded as a negative factor for precise laser processing, because the diffusion of heat enlarges the modified volume and sometimes induces thermal damage. Nevertheless, heat accumulation by fs laser irradiation at a high-repetition rate 100 kHz has been recognized as a useful effect for the processing of glasses in recent years^{3-6,13-19}. For example, optical waveguides with symmetric guiding cross sections can be formed by isotropic thermal diffusion³⁻⁶. For other examples, heat accumulation inside a glass induces the precipitation of crystals¹⁵⁻¹⁶ and the modification of composition distribution around the laser focal volume¹⁷⁻¹⁸ which make it possible to control three-dimensional properties in glasses.

The modifications with and without heat accumulation differ in morphology completely. In the case of laser irradiation at 1 kHz (Fig. 1(a)), in which heat accumulation does not occur, the structural change is localized only in a laser focal region in spite of temperature elevation of more than several thousand degrees at the focus²⁰⁻²⁴. The localization of the structural change is because the thermal energy diffuses out of the photoexcited region almost completely before the next pulse comes (Fig. 1(b))^{23,25}. On the other hand, the modification volume is much larger

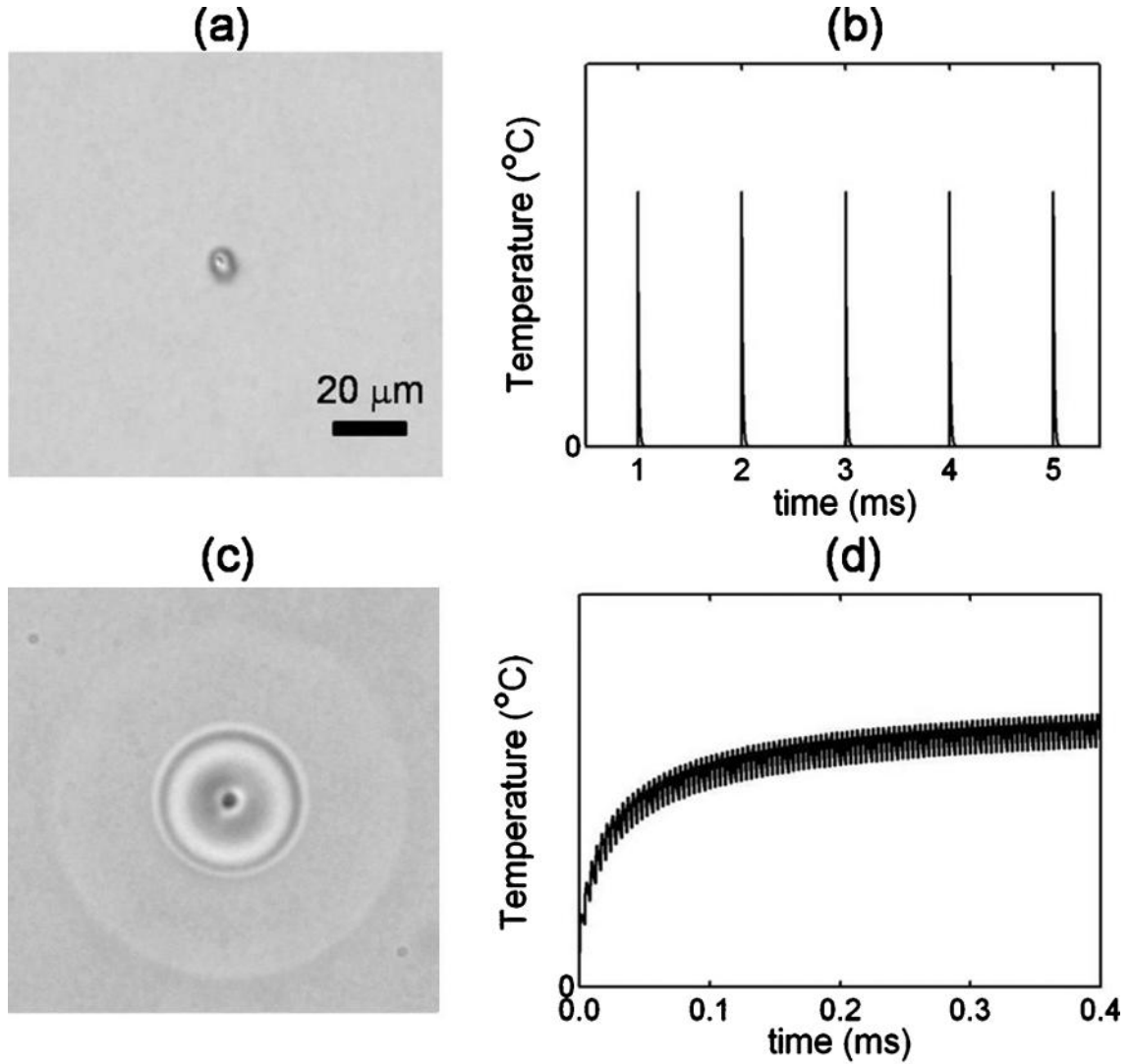


Fig. 1. Optical microscope images of modifications by laser irradiation at (a) 1 kHz and (c) 250 kHz and typical temperature change at the focus at (b) 1 kHz and (d) 250 kHz. The pulse energy was 2.0 μJ in the both cases. The observation is performed from the laser propagation direction.

when heat accumulation occurs by irradiation at 250 kHz (Fig. 1(c))^{3-6,15-18}. When fs pulses are focused at a high repetition rate, the photoexcitation by the following pulses occurs before the heat generated by the previous pulses diffuses out of the photoexcited region; as the result, the temperature increases due to cumulate heat and the modification volume becomes larger because of the temperature elevation in a larger volume (Fig. 1(d)).

Two circular boundaries are observed in the modification by photoexcitation at a high-repetition rate (Fig. 1(c))⁴⁻⁶. In the region inside the inner boundary, flowing of material is observed during the exposure of laser pulses. As the result of material flowing, precipitation of crystals¹⁵⁻¹⁶ and material composition change¹⁷⁻¹⁸ occur in the region. In this thesis, this region is referred to as an “inner-modified region.” According to the plastoelastic simulation with a comprehensive photoexcitation model by Mermillod-Blondin *et al.*²⁴, the boundary of the inner-modified region has been attributed to the generation of stress wave after photoexcitation. On the other hand, in the ring-shaped region between the inner and outermost boundaries, any change in composition or crystal precipitation has not been observed, although there is a well-defined refractive index variation at the outermost boundary. In this thesis, the region between the inner boundary and outer boundary is referred as “outer-modified region”.

Several researchers have proposed the mechanism of the heat modification^{5-6,13,19}. Schaffer *et al.*¹³ and Miyamoto *et al.*¹⁹ assumed that the heat-modification should be due to melting of a glass. On the other hand, Eaton *et al.*⁵⁻⁶ assumed that the heat-modification should occur in a region in which the temperature exceeded softening or working temperatures of borosilicate glasses 1000 °C and 1225 °C, respectively. Although the radiuses of the heat-modification under various irradiation conditions have been explained partially based on their assumption of the threshold temperatures, they did not explain why a clear outermost boundary appears at which the temperature reaches the threshold temperatures. In other words,

they do not have any definite reasons for the threshold temperatures. It must be taken into consideration that the softening and working temperatures of a glass are not the temperatures at which the property of the glass changes drastically²⁶. In fact, these temperatures are defined based on the viscosity. For example, the working point is defined the temperature at which the viscosity is equal to 10^3 Pas. Therefore, we need to reconsider the physical meaning of the threshold temperature in order to understand the mechanism of the heat-modification.

To elucidate the heat modification mechanism, the temperature distribution during laser irradiation is important, because it can affect the main factors of modification such as stress, material flow, crystallization, and glass transition²⁶. In this chapter, we determine the three-dimensional temperature distribution and discuss the modification mechanism based on it.

1.2 Experiment

Fs laser pulses, which were regeneratively amplified pulses from a mode-locked Ti:sapphire laser (Coherent; Mira-RegA9000; 800 nm wavelength) were focused inside a soda-lime-silicate glass plate (Schott; B-270 Superwite²⁷) with a 20x microscope objective lens (Nikon; LU Plan ELWD 20x, NA=0.40). The repetition rate of the pulses was 250 kHz and the pulse duration was 80 fs in all the experiments. The glass plate was placed on a temperature-controllable stage (Yonekura; MS-TPS), in which the ambient temperature can be controlled by heating the container of the glass with an infrared radiation from a halogen lamp. The ambient temperature was measured with a thermocouple. Because the glass plate did not contact the thermocouple, the measured temperature was calibrated by the observations of the fusing of several metals (Sn, Zn, and Al; melting points are 232 °C, 417 °C, and 648 °C, respectively, they were measured by the differential scanning calorimetry). In this paper, the ambient temperature was denoted by T_a . The energy of laser pulses was controlled with a neutral density filter. The exposure time of laser pulses (t_{ex}) were controlled by selecting the number of pulses from RegA9000 by inputting electric trigger pulses into the controller of RegA9000. The irradiation of a glass with fs laser pulses was performed with different pulse energies 1.0, 1.5, and 2.0 μ J under different ambient temperatures 25–446 °C. After the laser irradiation, the modifications inside a glass were observed with an optical microscope (Olympus, BX51). To examine the strain distribution in the modified region, we observed the birefringence with a polarization microscope with a liquid crystal (LC) compensator (CRI, Inc. LCPolscope). In the microscope, a sample is illuminated by a nearly monochromatic (wavelength = 550 nm, band width = 30 nm) circular polarized light and the transmitted light, which becomes ellipsoidally polarized by birefringence in a sample, was detected by a CCD camera after passing through a LC compensator and an analyzer²⁷. By analyzing the images obtained under

several setups of the LC compensator, we can obtain two-dimensional distribution of birefringence; both the axis of slower polarization (slow axis) and phase differences between two polarizations of transmitted light in the slow and fast axes (retardance).

1.3 Experimental results

Figures 2(a)-(c) show the optical microscope images of the modified regions after irradiation of 2.0 μJ pulses. The images are obtained from the direction normal to the laser propagation direction. Because absorbed energy along the laser propagation axis is not symmetric due to plasma dispersion and Kerr effect¹⁸, these images have more information than the image in Fig.1. Two boundaries are also observed in the images. The volume of the outer boundary becomes larger at higher ambient temperature. As shown in Figs.2 (d)-(f), the ambient temperature-dependent volume of the outer modified region can be understood by assuming that the modification occurs above the characteristic temperature (T_{out}). We quantify the size of the outer-modified region by employing the R_r and R_z , which are defined in the Fig.2(a). Figure 2(g) shows the ambient temperature dependence of R_r and R_z .

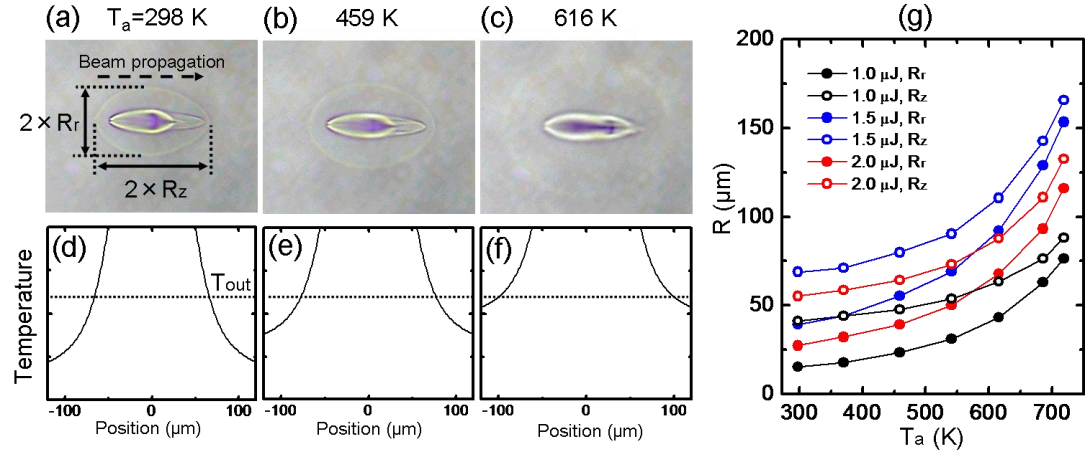


Fig. 2. (a)-(c) Optical microscope images of the modifications induced at various ambient temperature T_a . The broken arrow indicates the direction of the excitation laser beam propagation. (d)-(f) The schematic explanation of the size change of the outer boundary. T_{out} is the temperature threshold of the modification. (g) The ambient temperature dependence of the size of modification.

1.4 Discussion

We simulated the thermal energy distribution during laser irradiation to obtain the temperature distribution. The starting equation is Fourier's law:

$$\mathbf{J}(t, \mathbf{r}) = -\lambda(T(t, \mathbf{r})) \nabla T(t, \mathbf{r}) \quad (1.1)$$

, where $\mathbf{J}(t, \mathbf{r})$ is the flux of thermal energy, $\lambda(T)$ is the thermal conductivity, and $T(t, \mathbf{r})$ is the temperature distribution, ∇ is nabla, t is the time after the photoexcitation by the first pulse, and $\mathbf{r}$ is the Cartesian coordinates. From the definition of the specific heat,

$$q(t, \mathbf{r}) = \rho \int_{T_a}^{T(t, \mathbf{r})} C_p(T) dT \quad (1.2)$$

, where $q(t, \mathbf{r})$ is the thermal energy per unit volume, ρ is the density (weight per unit volume), $C_p(T)$ is the specific heat under constant pressure, and T_a is the ambient temperature.

By the equation of continuity, the eqs. (1.1) and (1.2), and the heat source by laser irradiation, we obtain the following equation,

$$\frac{\partial q(t, \mathbf{r})}{\partial t} = \nabla (D \nabla q(t, \mathbf{r})) + \frac{\partial q_{laser}(t, \mathbf{r})}{\partial t} \quad (1.3)$$

, where $D = \lambda(T(t, \mathbf{r})) / (\rho C_p(T(t, \mathbf{r})))$, which corresponds to the thermal diffusivity.

In the first step of the analysis, we assumed the heat source for the single pulse is expressed as following:

$$\frac{\partial q_{laser}(t, \mathbf{r})}{\partial t} = \delta(t - nt_L) q_0 \exp \left[-\frac{r^2}{(w_r/2)^2} - \frac{z^2}{(l_z/2)^2} \right] \quad (1.4)$$

, where n is the pulse number, Δt_L is the interval between pulses ($=4\mu s$), q_0 is the maximum absorbed energy, $r = \{(x^2 + y^2)^{1/2}\}$ and z are the radial distance and the position along the beam propagation axis, respectively, and w_r and l_z are the width of absorbed energy in the radial direction ($=1.1 \mu m$, which is determined by the diffraction limit) and that in the beam propagation direction (fig. 3(a)). We used the room-temperature value $(4.6 \times 10^{-7} \text{ m}^2/\text{s})^{28}$ of D for

all temperature range because there are experimental report that the change of D is small from 300 K to 1650 K in soda-lime-silicate glasses²⁹⁻³⁰. Under initial condition of eq. (1.4), we can solve the eq. (1.3) analytically and obtain the time evolution of the energy distribution for one pulse:

$$\Delta q_1(t', \mathbf{r}) = q_0 \frac{(w_r/2)^2}{(w_r/2)^2 + 4Dt'} \cdot \left[\frac{(l_z/2)^2}{(l_z/2)^2 + 4Dt'} \right]^{1/2} \exp \left[-\frac{r^2}{(w_r/2)^2 + 4Dt'} - \frac{z^2}{(l_z/2)^2 + 4Dt'} \right] \quad (1.5)$$

, where t' is the time after the photoexcitation of a certain pulse. After the irradiation with N_{th} pulse, the thermal energy distribution is expressed by

$$q_N(t, \mathbf{r}) = \sum_{n=0}^{N-1} \Delta q_1(t - n\Delta t_L, \mathbf{r}) \quad (1.6)$$

, where n is integer. The thermal energy distribution can be exchanged to temperature distribution by the eq. (1.2).

We used the temperature dependence of the specific heat shown in Fig. 3(b), which is obtained by only shifting the position of the T_g in the reported data on soda-lime-silicate glass³¹. We neglected the temperature dependence of the density³² and used the room-temperature value ($2.55 \times 10^3 \text{ kg/m}^3$)²⁸. Therefore, the temperature-dependent material parameter considered in this study is only the specific heat.

Since we assumed that the temperature at the outer boundary reaches the characteristic temperature T_{out} during laser irradiation, the following relation is obtained at the outer boundary

$\mathbf{r} = \mathbf{r}_{boundary}$:

$$q_N(t_{ex}, \mathbf{r}_{boundary}) = \int_{T_a}^{T_{out}} C_p(T) dT \quad (1.7)$$

where t_{ex} is the exposure time of 250 kHz laser pulses (=1 s). When $\mathbf{r} = (R_r, 0, 0)$ {or $\mathbf{r} = (0, 0, R_z)$ } is substituted into eq. (1.7), the R_r (or R_z) function of T_a can be obtained. By fitting the relationship between R_r (or R_z) and T_a by the function, q_0 , l_z , and T_{outs} can be determined.

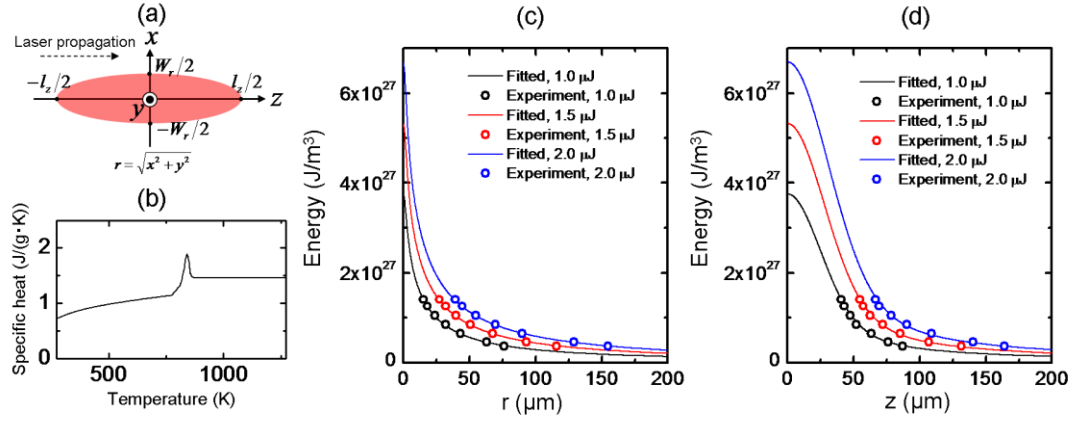


Fig. 3. (a) Heat source in Cartesian coordinates. (b) Specific heat for the simulation. (c) Fitted results for the radial direction. (d) Fitted results for the beam propagation direction. The curves in (c) and (d) are the thermal energy distribution under room temperature irradiation, which were calculated by Eq. (6) with the determined fitting parameter. The plots show the experimental data corresponding to the right-hand side of Eq. (7) with T_{out} determined.

We summarize the best fit parameter in Tabel 1 and show the energy distribution curve in Fig. 3(c) and (d). The opened circles in Fig. 3(c) and (d) are the thermal energies after 1s laser irradiation at the positions of $\mathbf{r}=(R_r, 0, 0)$ {or $\mathbf{r}=(0, 0, R_z)$ }, which were calculated by the right-hand side of eq. (7) with T_a and determined T_{out} .

The absorbed energy (Q_a) for one pulse can be obtained by integrating eq. (7) over all space:

$$Q_a = \pi^{3/2} q_0 (w_r / 2)^2 (l_z / 2) \quad (1.8)$$

The optical absorptivity calculated by dividing the Q_a by the pulse energy is shown in Fig. 4(a). As the reference, we also show the absorptivity determined with the transmission loss measurement (shown in the inset the Fig. 4(a)). The optical absorptivity determined by Q_a corresponds to the lower limit of the absorptivity, since photoluminescence, thermal radiation, and stress energies should include the absorbed light energy. On the other hand, transmission loss measurement can not exclude these contributions. Figure 3 (a) shows that the absorptivity calculated using Q_a is smaller by 3.5 % than that evaluated by the transmission loss measurement. This difference indicates that the contribution of photoluminescence, thermal radiation, and stress energies should be less than 3.5 % of absorbed light energy.

Here, we discuss the formation mechanism of the outer boundary. The determined characteristic temperatures (T_{out}) are shown in the Fig.4(b). Since the T_{out} is near the T_g (=806 K) of this glass and the intense stress generates under sharp temperature gradient during laser irradiation, the formation of the outer boundary should be attributed to the visco-elastic deformation. According to the most simple viscoelastic model (Voigt-Kelvin element, Fig. 5(a)), after the application of a constant stress S , the temporal evolution of strain $\varepsilon(t)$ can be described by

$$\varepsilon(t) = (S / 2G) [1 - \exp(-Gt / \eta)] \quad (1.9)$$

,where G and η are the shear modulus and viscosity of the glass. Because the viscosity of a glass varies drastically in the temperature range from the glass transformation temperature to the softening temperature (from 10^{12} to 10^7 Pa·s) as shown in Fig. 5(b), the response time to the stress [$\tau = \eta(T)/G$] also varies in the temperature range. We assumed that G is constant (=29.3 GPa), because the temperature dependence is much smaller than that of η . The relaxation ratio [$P_{relax} = 100\%(\varepsilon(t_{ex})/\varepsilon(\infty))$], which indicates the degree of deformation, during the laser exposure (t_{ex}) was evaluated by

$$P_{relax} = 100\% \times \varepsilon(t_{ex}) / \varepsilon(\infty) \quad (1.10)$$

The gray band indicates the temperature range where the estimated percentage of the stress relaxation after 1s laser irradiation changed from 1 % to 99 %. This means that the stress relaxation is almost completed when the temperature reached above the gray band during the exposure time (=1 s).

The T_{out} for three pulse energies are located in the gray band, which indicates that, inside the outer boundary, the viscoelastic stress relaxation had occurred during the exposure time. On the other hand, out of the outer boundary, viscoelastic relaxation had not started during the exposure time. Therefore, the material out of the boundary served as a wall to the materials inside the boundary. As the result, the clear boundary appeared.

Since the absorbed energy of one pulse has been determined, we will evaluate the detailed temperature distribution with the absorbed energy fixed. Although we assumed an elliptically symmetric heat distribution to obtain the optical absorptivity and the characteristic temperature, the actual heat distribution should be asymmetry in the beam propagation direction because of plasma dispersion and Kerr effect³³. In order to obtain more plausible temperature

Table1. Parameters determined by fitting R_z , R_r vs. T_a by Eq. (7). The fitting was conducted by minimizing the mean squared error.

	1.0 μJ	1.5 μJ	2.0 μJ
q_0 (J/m^3)	1.34×10^{28}	1.84×10^{28}	2.25×10^{28}
l_z (μm)	65.0	72.8	80.8
T_{out} (K)	834	831	831

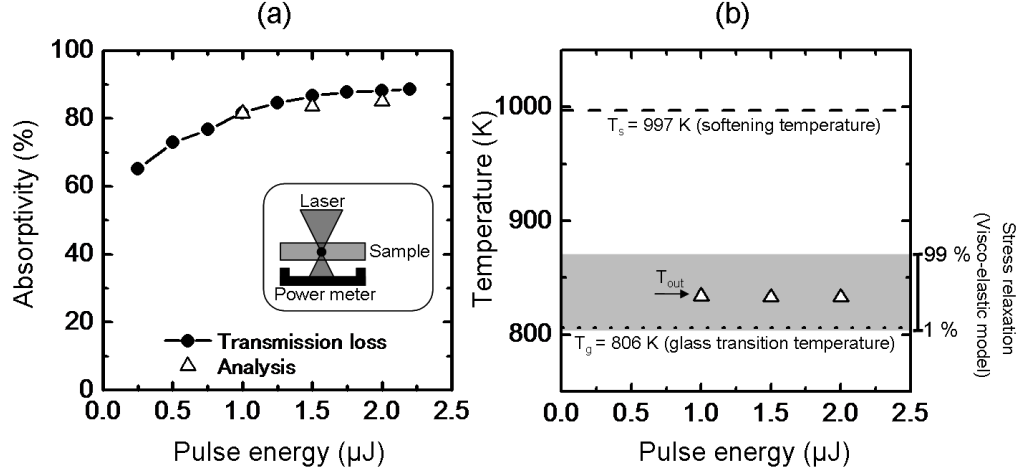


Fig. 4. (a)Optical absorptivity determined by the analysis and transmission loss measurement. (b)The comparison between the determined characteristic temperature (T_{out}) and other important transformation temperature. The gray band indicates the temperature range where the estimated percentage of the stress relaxation after 1s laser irradiation changed from 1 % to 99 %.

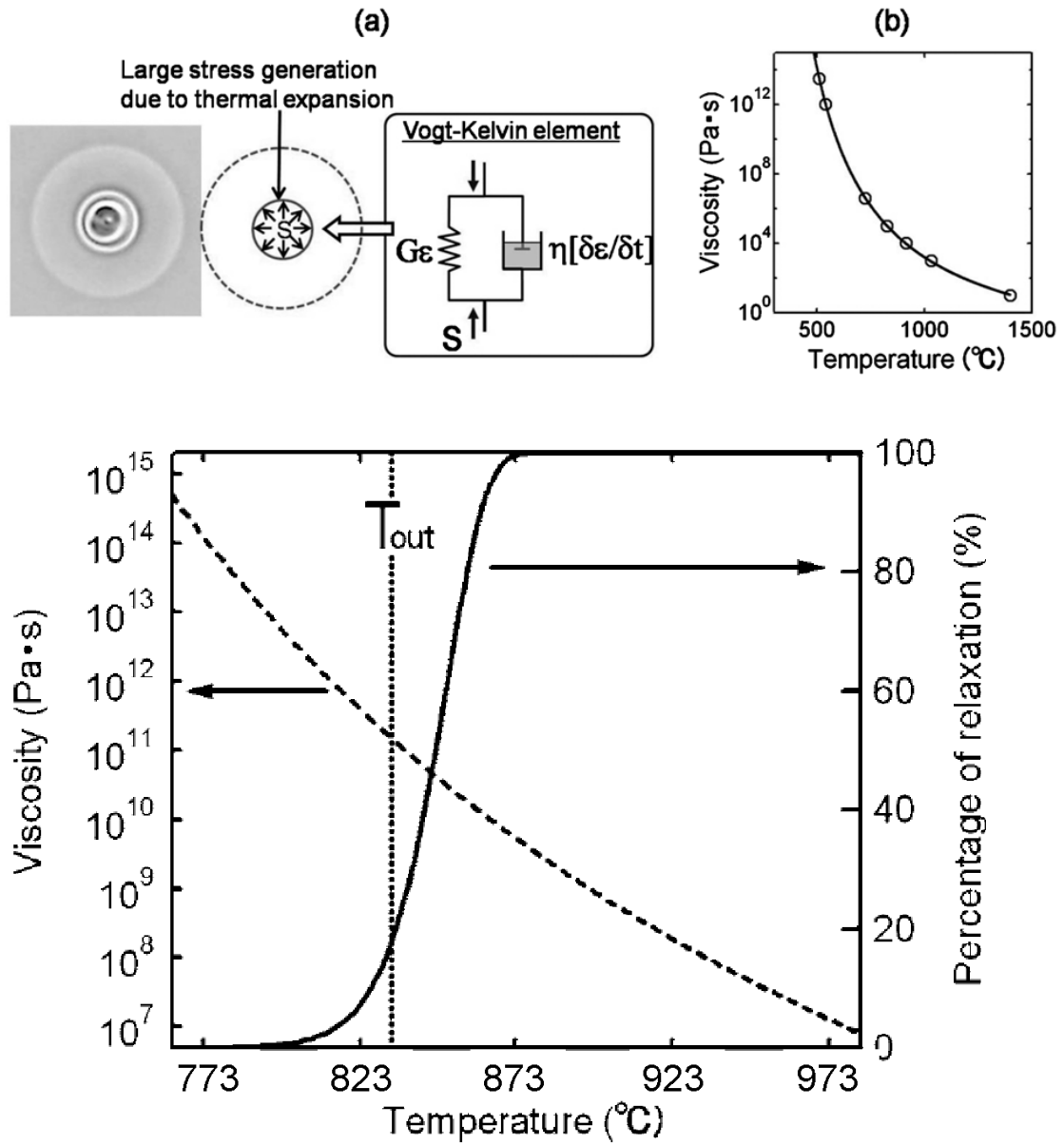


Fig. 5. (a) Vogt-Kelvin model. (b) Temperature dependence of the viscosity of B270 glass. Flucher's equation was used to interpolate the viscosity data. (c) Percentage of relaxation for 1 s exposure calculated by the Voigt-Kelvin model.

distribution, we changed the shape of heat distribution only in the z direction to reproduce the outer boundary in all the region with fixed absorbed energy for one pulse. We show the determined three-dimensional temperature distribution for 2.0 μJ in the Fig. 6(a)-(c). We show the temperature distribution of 0, 1, and 4 μs after 1 s irradiation at 2.0 μJ of pulse energy in Fig. 6(b), (c) and (d), respectively, and the contour lines of the characteristic temperatures of the outer boundary and inner boundary are drawn in the figures. The sharp edge near the beam propagation axis in the contour lines of T_{out} at 0 μs disappear after 1 μs due to the thermal diffusion, and the difference between the 1 μs and 4 μs is small. Such cycle had repeated per 4 μs before the exposure of laser pulses is stopped. In contrast, such a sharp edge is not observed in the optical microscope image. This implies that the modification is slow enough that the sharp edge of the temperature distribution cannot affect the modification.

Miyamoto et al³⁴. indicates that the characteristic temperature of outer boundary (T_{out}) in Schott D263 glass is 1324 K and that of the inner boundary (T_{in}) is 3873 K. The estimated T_{out} in our analysis are much lower than theirs although the glass transition temperature ($T_g=830$ K) and the softening temperature ($T_s=1009$ K) of D263²⁸ are close to those ($T_g = 806$ K and $T_s=997$ K) of the B270²⁸. The difference of T_{out} is because their assumption in the analysis is not valid. They assumed that T_{out} is glass-forming temperature (at viscosity of 4.0 dPas) since welding between two glass plates occur inside the outer boundary. However, there is no evidence for the fact that the welding does not occur below this temperature. In addition, the difference between T_{out} and T_{in} in our analysis is smaller than theirs. This is because we take into account the temperature dependence of the specific heat in the analysis. In our result, the T_{in} is 1220 K, which is close to the glass-forming temperature (=1306 K, viscosity of 4.0 dPas) of B270. However, it is difficult to explain the formation of the boundary according to this

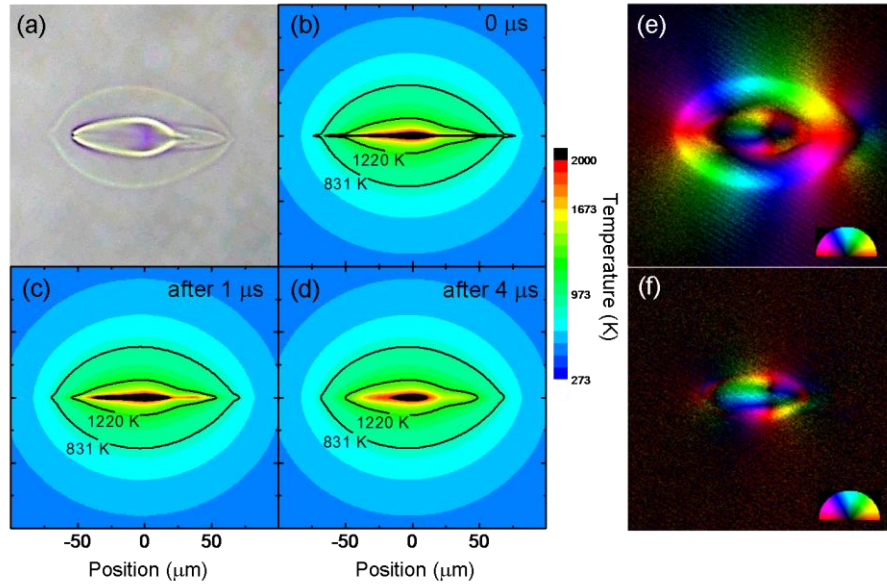


Fig. 6. (a)Optical microscope images and (b)(c)(d)three-dimensional temperature distribution under pulse energy of 2.0 μJ at ambient temperature of 298K. (b)Just after final pulse irradiation. (c) 0.1 μs after final pulse irradiation. (d)4 μs after final pulse irradiation. (e) Residual strain distribution after laser irradiation (f) Residual strain distribution after heat treatment. In the (e)(f), the brightness indicates the relative intensity of birefringence. The colors express the direction of the slow axis of the index ellipsoid. The direction corresponds to that in the inset of semicircular shape. The scale of the all figures are the same as the (c)(d).

temperature. To investigate the formation mechanism of inner boundary, we heat-treated the glass sample at T_g ($=806$ K) for one hour after laser irradiation. In the Figs. 6(e) and (f), we show the residual strain distribution before and after the heat treatment, measured with the polarization microscope with a liquid crystal compensator²⁷. Before the heat treatment, the direction of the slow axis in Fig. 6(e) indicates that the strain was directed in the radial direction in the outer-modified region. This implies that the outer-modified region is compressed owing to thermal expansion in the central high-temperature region during laser exposure. After the heat treatment, as is shown in Fig. 6(f), the strain in the inner-modified region still remained, whereas that in the outer modified region disappeared. Given that the strain cannot be removed by heat treatment at T_g , formation of the inner-modified region is likely to include the flow of glass elements. In addition, the changes cannot be reversed to the original state unless the temperature of the heat-treatment is so high that the elements in the glass can move freely. Blondin et al. suggested that the change in the refractive index distribution near the focal spot under high-repetition fs laser irradiation is likely related to the flow of glass elements²⁴. Our experimental result supports their suggestion.

1.5 Conclusion

In conclusion, I determined three-dimensional temperature distributions and considered the modification mechanism in a glass exposed to laser irradiation. The optical absorptivity evaluated with the temperature distribution is approximately 80 % and at most 3.5 % smaller than that evaluated by the transmission loss measurement. Based on the temperature distribution and the strain distribution, we conclude that the formation of the outer-modified region is due to visco-elastic deformation, and that of the inner-modified region is due to the flow of glass elements.

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Chapter 2

Formation mechanism of element distribution in multicomponent glasses under ultrafast laser irradiation at high repetition rates

2.1 Introduction

The composition of a glass affects its optical properties such as refractive index, light absorption, and luminescence property¹. Spatially selective modification of the composition in a glass would enable three-dimensional control of such properties. Femtosecond (fs) lasers have been recognized as powerful tools to modify transparent materials in a three-dimensional manner²⁻⁴. Recently, in the field of fs laser processing, element redistribution induced by irradiation with fs laser pulses at high repetition rate has attracted much attention, because it has the potential to control glass composition three-dimensionally⁵⁻¹⁰. Several researchers have reported fundamental experimental results of this phenomenon⁵⁻⁷ as well as its use in applications such as optical waveguides⁸ and microscopic control of the intensity distribution of luminescence⁹⁻¹⁰. However, no one has elucidated the mechanism of element redistribution and the dominant factor that induces migration of elements around photoexcited region inside glasses. The elucidation of them is essential for three-dimensional and effective manipulation of the glass composition. The possible factors that induce element redistribution could be high temperature and its gradient during irradiation with fs laser pulses at high repetition rate, because it has been found that the temperature around the laser focal spot inside a soda-lime glass exceeded 1500 °C and the temperature gradient was above several tens of degrees Celsius per micrometer¹¹⁻¹². In this study, to elucidate the driving force of the migration of elements, we simulated the diffusion of elements inside a CaO-SiO₂ glass and compared the results with experiment.

2.2 Experiment

I used amplified femtosecond laser pulses (250 kHz, 80 fs, 800 nm) of a mode-locked Ti-sapphire laser oscillator (Coherent; Mira and RegA). The pulses were focused inside a 50(mol%)CaO-50SiO₂ glass sample, which was prepared by a conventional glass-melting method, with a 20× objective lens (NA = 0.40; Nikon LU Plan). The exposure time of the laser pulses, which was 2.0 s, was controlled by a mechanical shutter. The pulse energy, which was 2.0 μJ, was controlled using a neutral density filter. We also performed simultaneous two-spot laser irradiation (1.0 μJ per pulse and per spot and 3.0 s exposure) to modify the spatial distribution of the temperature¹¹⁻¹². After laser irradiation, the element distributions around the modified region were analyzed with an electron probe microanalyzer (EPMA; JXA-8100, JEOL).

2.3 Experimental results

Figure 1 shows the optical microscope (OM) images and element distributions after laser irradiation. In the OM image [Fig. 1(a)], two circular boundaries are observed. During laser irradiation, the temperature increases with decreasing distance from the focal spot. According to ref.11, the temperature exceeded the glass transition temperature inside the outer boundary during the laser irradiation and visco-elastic deformation was induced by the stress due to thermal expansion around the photoexcited region. Inside the inner boundary, the element distribution is modified [right side of Fig. 1(a)]. The CaO concentration determined by a micro-Raman was more than 30 mol% at every point even after the element redistribution. The concentration means that phase separation, which occurs in approximately 0-30 mol% CaO, did not occur in this experiment. This element migration should result in decrease of refractive index in the central region according to the Appen's additive factors for refractive index, 1.730

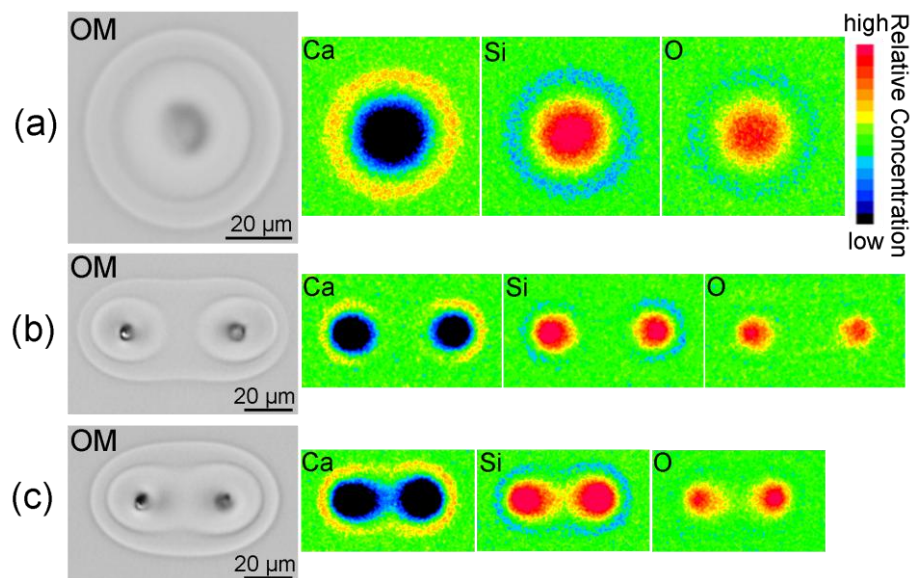


Fig. 1. (Color) Optical microscope images and element distributions after laser irradiation. (a) One-spot irradiation. (b) Two-spot irradiation with a distance of 42.7 μm between the two focal spots. (c) Two-spot irradiation with a distance of 31.9 μm between the two focal spots.

for CaO and 1.475 for SiO₂¹³.

The distributions of elements in the case of two-spot irradiation were not simple sum of those of single spot irradiation [Fig. 1(b) and (c)]. For example, the Ca concentration in Fig. 1(b) does not clearly increase between the two photoexcited points, the Ca concentration in Fig. 1(c) is lower in the region between the two points and the higher Si concentration region in Fig. 1(c) is shaped like a teardrop.

2. 4 Numerical simulation

In the numerical simulation, we assumed that the diffusing species are the simple oxide molecules CaO and SiO₂¹⁴, and that their self-diffusion coefficients are equivalent to the experimentally measured self-diffusion coefficients of Ca and Si, respectively¹⁴. The fluxes of the diffusing species under a temperature gradient are expressed by the following equations¹⁵:

$$\mathbf{J}_1 = -D_1 \nabla C_1 - \frac{D_1 Q_1 C_1}{RT^2} \nabla T(x, y) + C_1 \mathbf{v}, \quad (2.1)$$

$$\mathbf{J}_2 = -D_2 \nabla C_2 - \frac{D_2 Q_2 C_2}{RT^2} \nabla T(x, y) + C_2 \mathbf{v}, \quad (2.2)$$

where the subscripts 1 and 2 denote the diffusing species CaO and SiO₂, respectively, D_i is the self-diffusion coefficient ($i = 1$ or 2), C_i is the molar concentration, Q_i is the heat of transport, R is the gas constant ($= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$), $\mathbf{v}$ is the velocity of mass flow due to the difference in the diffusion speed between the two species, and $T(x, y)$ is the temperature. We employed the condition of a volume-fixed reference frame¹⁴, which is given by $\Omega_1 \mathbf{J}_1 + \Omega_2 \mathbf{J}_2 = 0$, where Ω_i is the partial molar volume. Based on the definitions of Ω_i and C_i , $\Omega_1 C_1 + \Omega_2 C_2 = 1$. From these equations, we obtain the following equation:

$$\begin{aligned} \frac{\partial C_1}{\partial t} = & \nabla \left[\left\{ (1 - \Omega_1 C_1) D_1 + \Omega_1 C_1 D_2 \right\} \nabla C_1 \right] \\ & - \nabla \left[C_1 (1 - \Omega_1 C_1) \frac{D_2 Q_2 - D_1 Q_1}{RT^2} \nabla T(x, y) \right]. \end{aligned} \quad (2.3)$$

Temperature dependence of the self-diffusion coefficient is expressed by the Arrhenius-type equation $D = D_0 \exp(-E_a/RT)$, where E_a is the activation energy. The time evolution of the concentration distribution of a diffusing species was calculated by Eq. (3). For the calculation, we employed experimentally estimated steady-state temperature distributions in a silicate glass during the fs laser irradiation¹¹⁻¹². The temperature distribution for one-spot laser irradiation is shown in Fig. 2(a). The pulse energy was assumed to be 0.2 μJ , which was smaller than that in the experiment. This discrepancy is related to a technical problem; a large pulse energy leads to high temperature and a sharp temperature gradient, which makes it difficult to calculate the time evolution of the concentration distribution with high accuracy. The distances between the two focal spots were set to be 1.40 and 1.12 μm . The values of other parameters for the simulation are followings: $\Omega_1 = 1.44 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $\Omega_2 = 2.72 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, $D_{0,1} = 1.18 \text{ m}^2 \text{ s}^{-1}$, $D_{0,2} = 3.53 \times 10^{-1} \text{ m}^2 \text{ s}^{-1}$, $E_{a,1} = 3.28 \times 10^5 \text{ J mol}^{-1}$, and $E_{a,2} = 3.42 \times 10^5 \text{ J mol}^{-1}$.^{13,16} The initial molar concentration ($C_{0,1} = 2.40 \times 10^4 \text{ mol m}^{-3}$ and $C_{0,2} = 2.40 \times 10^4 \text{ mol m}^{-3}$), which corresponds to the composition of 50(mol%)CaO-50SiO₂ glass, was spatially uniform. We assumed $Q_1 = 1.00 \times 10^4 \text{ J mol}^{-1}$ and $Q_2 = -1.00 \times 10^4 \text{ J mol}^{-1}$. The signs for the heat of transport values used in this calculation is based on the experimental results reported in silicate melts¹⁷. The order of magnitude of the heat of transport (10^4 J mol^{-1}) was arbitrarily determined, and we assumed that the order of magnitude of Q_1 is the same as that of Q_2 .

Figures 2(a)-(c) show the temperature distributions for the simulations. Figures 2(d)-(i) show the simulated concentration distributions of oxides CaO and SiO₂ after 10 ms. From the compositional formula, the molar concentrations of oxides CaO and SiO₂ are equivalent to those of elements Ca and Si, respectively. Our purpose is not to compare the quantitative aspects of the distributions, but rather the qualitative ones (e.g., shapes of element distributions), between experiment and simulation. All the element distributions reproduced those in the experiment of

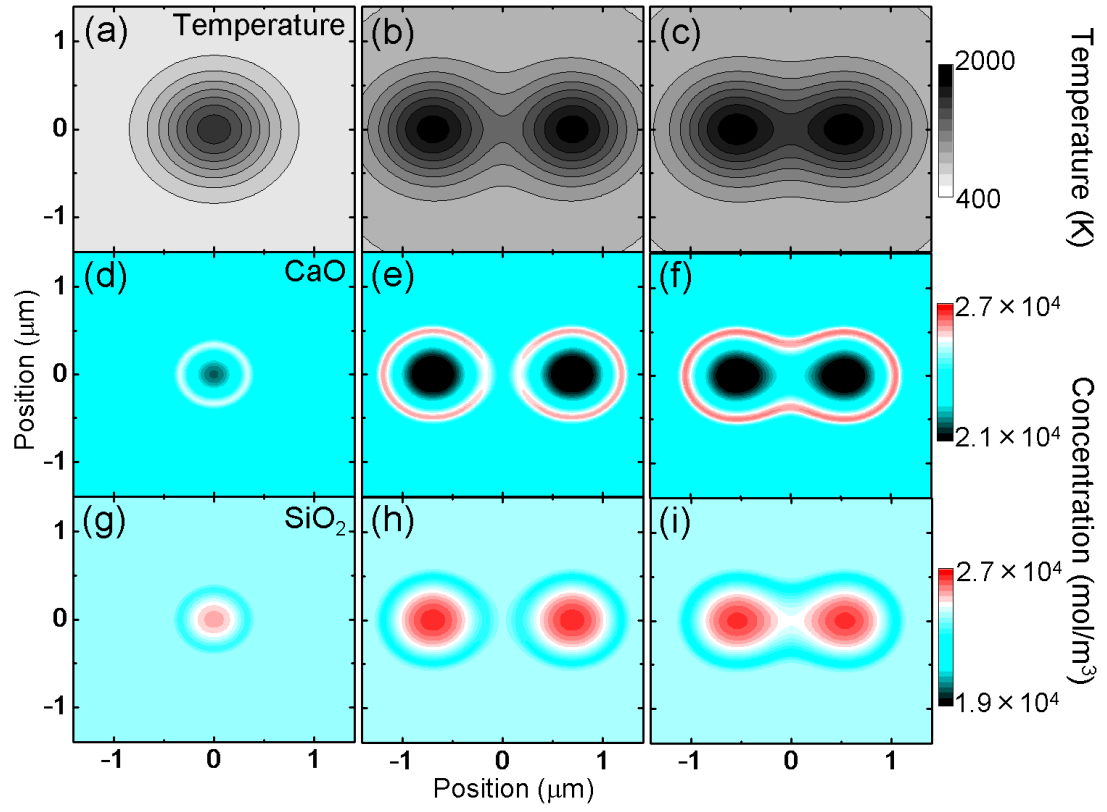


Fig. 2. (Color) (a)-(c) Temperature distributions for simulation and calculated concentration distributions of (d)-(f) CaO and (g)-(i) SiO₂ after 10 ms. (a)(d)(g) One-spot irradiation. (b)(e)(h) Two-spot irradiation with a distance of 1.40 μm between the two focal spots. (c)(f)(i) Two-spot irradiation with a distance of 1.12 μm between the two focal spots.

both single and two-spot irradiations.

2. 5 Discussion

As indicated above, the order of magnitude of the heat of transport was based on the assumption. I checked the results under various order of magnitude of the heat of transport, and concluded that change of the order of magnitude of the heat of transport does not affect the shape of the element distributions. The excellent qualitative correspondence between experiment and simulation indicates that we succeeded in qualitatively modeling the formation of element distribution. The Eq. (3) includes two factors which alter the concentration distribution; one is the concentration-gradient-driven diffusion and the other is the temperature-gradient-driven diffusion. Because the former makes the concentration homogeneous, it does not contribute the inhomogeneous element distribution formed during laser irradiation. Therefore, the temperature gradient should be responsible for element migration, i.e., this phenomenon should be interpreted as thermomigration.

I now attempt to explain which factor (temperature or temperature gradient) affects the formation of the characteristic shape of Ca distribution in Fig. 1(b) and Fig. 2(e), where the Ca does not clearly increase between the two irradiated spots. We performed numerical calculations under additional temperature conditions [Fig. 3]. The figure 3(a)-(c) and (d)-(f) shows the schematic diagrams of added temperature distributions to the default temperature of the Fig. 2(a) and the corresponding temperature distribution for the simulation, respectively. Except for the temperature, the calculation parameters for the simulation are the same as the case of the simulation in the Fig. 2. As shown in the simulation results in Fig. 3(g), compared to the case of the default temperature (black curve), the element distribution for a homogeneous elevation of the temperature by 100 K (red curve) has a higher CaO concentration. In the case of

an added temperature gradient (blue curve), although the temperature increase leads to a high CaO concentration as shown above, the CaO concentration on the right side is lower than that on the left side. Therefore, we conclude that the reason why the Ca concentration does not clearly increase between the two irradiated spots in Fig. 1(b) and Fig. 2(e) is that temperature gradient in the area decreases due to the sum of the two spatially-separated temperature elevations by the two heat sources.

The results in this study and other reports^{5,8} show that the elements strongly bonded with oxygen have tendency to migrate to the hot region [Fig. 4]. Generally, such elements have lower diffusion coefficient. In our model, the migration direction is determined by the sign of $D_2Q_2 - D_1Q_1$. Therefore, if the values of Q_1 and Q_2 were the same and positive values, we could explain above migration tendency by $D_2Q_2 - D_1Q_1$. However, the value of heat of transport Q and the relation between the property of elements and Q are not well known¹⁸. Understanding the detailed mechanism requires further investigation.

2. 6 Conclusion

In conclusion, I succeeded in qualitatively modeling the element migration as a thermomigration process. The multi-spot irradiation protocols, such as the two-spot irradiation method studied here, may effectively induce arbitrary temperature distributions and element distributions. The results in this study provide a framework to achieve the three-dimensional manipulation of glass composition and to fabricate functional optical device such as optical circuits.

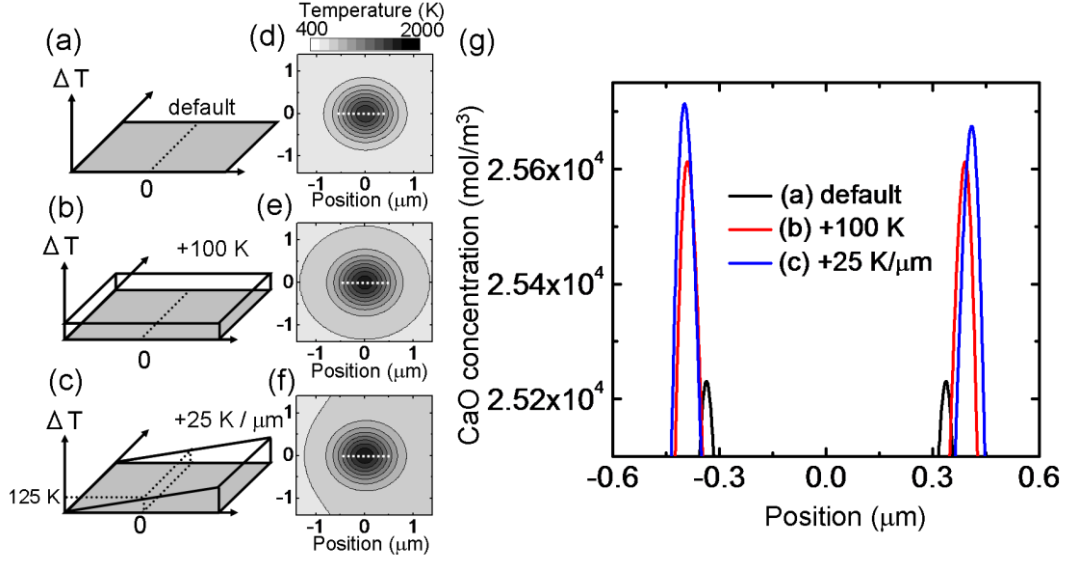


Fig. 3. (Color). Simulation results under additional temperature conditions. We used the temperature distribution shown in Fig. 2(a) as default temperature distribution, which is shown in (d). (a)-(c) Schematic diagrams of the temperature profiles added to the default temperature. (d)-(f) Two-dimensional image of temperature distribution. (g) Concentration profile of CaO along the position on the white dotted line in (d)-(f).

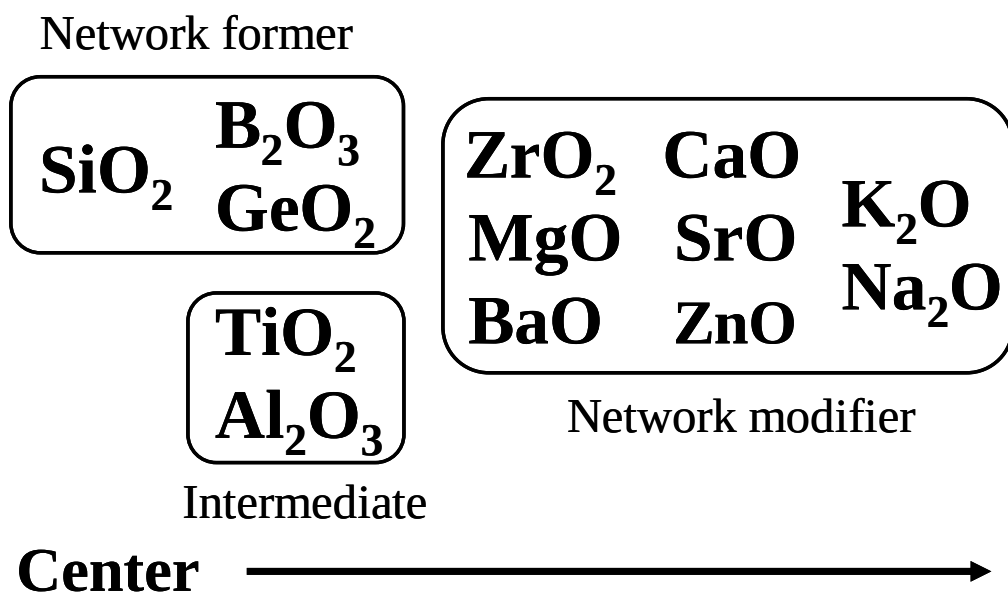


Fig. 4. Summary of tendency of element migration in silicate glass

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Chapter 3

Control of the material properties in multicomponent glasses with element redistribution using ultrafast laser irradiation at high repetition rates

3.1 Space-selective phase separation

3.1.1 Introduction

Phase separation in glasses has been used to develop nanometer- or micrometer-sized structures. In general, phase-separated glass can be obtained by heat-treating a glass, the composition of which is in a region of immiscibility¹. However, it is difficult to induce space-selective, microscopic phase separation inside a glass. The femtosecond (fs) laser has been recognized as an effective tool for the space-selective, microscopic modification of transparent materials such as glasses²⁻⁴. In recent years, the heat accumulated during fs laser irradiation at a high repetition rate (more than several hundred kilohertz) has attracted considerable attention because it is effective for the writing of low-loss optical waveguides⁵⁻⁶ and for the space-selective precipitation of functional crystals inside glass⁷⁻⁹. Several research groups as well as our group reported that the compositional distribution in a glass could be modified around the photoexcited region by focusing a number of laser pulses at a high repetition rate¹⁰⁻¹². In this study, we used an fs laser to change the glass composition in a space-selective, microscopic manner from a miscible composition to an immiscible one. Since the composition of the glass before laser irradiation is in the miscible region, phase separation does not occur in the original glass and can be locally controlled by laser irradiation and subsequent heat treatment. A schematic view of this method is shown in Fig. 1. To the best of our knowledge, this is the first report on space-selective phase separation inside a glass.

Narazaki et al. reported a method to induce local phase separation on the surface of a glass by excimer laser irradiation ($\lambda = 248 \text{ nm}$)¹³. However, when employing their method, it is necessary to select an appropriate wavelength of the laser such that the incident light is absorbed by the target glass and phase separation is restricted to the surface. In contrast, when employing our method, an absorption reagent is not required and phase separation can be induced inside a glass; this is because our method comprises the processes of non-linear absorption and heat accumulation by fs laser irradiation.

3.1.2 Experiment

I used regeneratively amplified fs laser pulses to induce phase separation in glasses. The laser pulses were generated by a Ti:sapphire laser oscillator and amplified at 250 kHz (Mira-RegA9000, Coherent Inc.). The pulse duration was 80 fs and the pulse energy was 3.0 μJ . The irradiation time of 5.0 s was controlled using a mechanical shutter. The fs-laser pulses were focused inside a glass sample using a 20 $\times$ objective lens (NA = 0.45; Nikon LU Plan). Two $\text{Na}_2\text{O-SiO}_2$ glasses with Na_2O concentrations of 21 mol% and 30 mol% were used as the glass samples. The phase separation of the $\text{Na}_2\text{O-SiO}_2$ glass system has been investigated in previous studies^{1,14}. After laser irradiation, the glasses were polished to expose the modified region on the surface. The compositional changes of the two samples around the laser-irradiated area were analyzed using a confocal Raman spectrometer (Nanofinder30, Tokyo Instruments Co.) in which a 532-nm excitation laser beam was focused using a 40 $\times$ objective lens (NA = 0.60; Nikon Plan Fluor). The method for determining the compositional change from the Raman spectrum will be explained in the subsequent section. Although the glass composition in a microscopic area is generally measured using an electron probe microanalyzer (EPMA)¹², we used a confocal Raman microspectroscope because it can detect the compositional change even

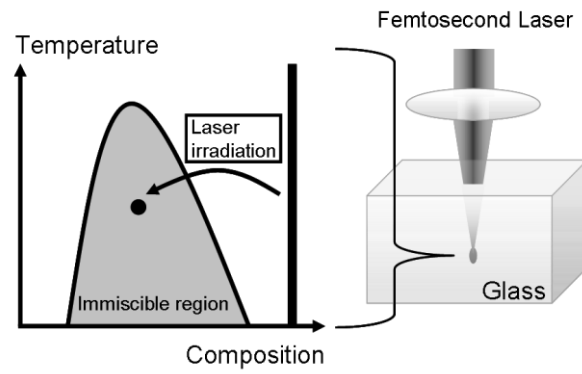


Fig. 1. Schematic view of the method used in this study. Composition of the glass is changed from miscible to immiscible only around the focal point of the femtosecond laser.

when phase separation occurs on scales smaller than the EPMA resolution. In order to promote phase separation, the 21 mol% Na₂O sample was heat-treated at 575 °C. At this temperature (i.e., above 500 °C), as per the phase diagram of this glass system, the starting composition (21 mol %) lies outside the immiscible region¹. We soaked the 21 mol% Na₂O sample in 0.46 % HF aqueous solution for 10 min and observed the etched surface using a field emission scanning electron microscope (FE-SEM; JSM-6700F, JEOL).

3.1.3 Results and Discussion

Figure 2(a) shows an optical microscope image of the laser-irradiated area in the 30 mol% Na₂O sample after polishing until the modified area was exposed. The three arrows in the image indicate circular boundaries in the modified area. The diameters of these boundaries are considerably larger than that of the photoexcited region whose diameter is approximately 2 μm. Therefore, these modifications are attributed to temperature elevation induced by the diffusion and accumulation of the heat generated during fs laser irradiation¹⁵. The outermost boundary corresponds to cracks. Because these cracks were not observed before this region was exposed by polishing, it was deduced that they were formed as the result of the relaxation of the stress generated by laser irradiation. The formations of the innermost and middle boundaries are attributed to the modification of the compositional distribution, which will be discussed later. The presence of the outermost, middle, and innermost boundaries was also confirmed in the case of the 21 mol% Na₂O sample, as indicated by the three white arrows in fig. 2(c). As in the 30 mol% Na₂O sample, the outermost boundary, which has an irregular shape in comparison with the shape of the boundary in fig. 2(a), corresponds to cracks. In both the 21 mol% and 30 mol% Na₂O samples, the shape of the outermost boundary varied from one modified area to another even under the same laser irradiation condition and for the same sample; this implies

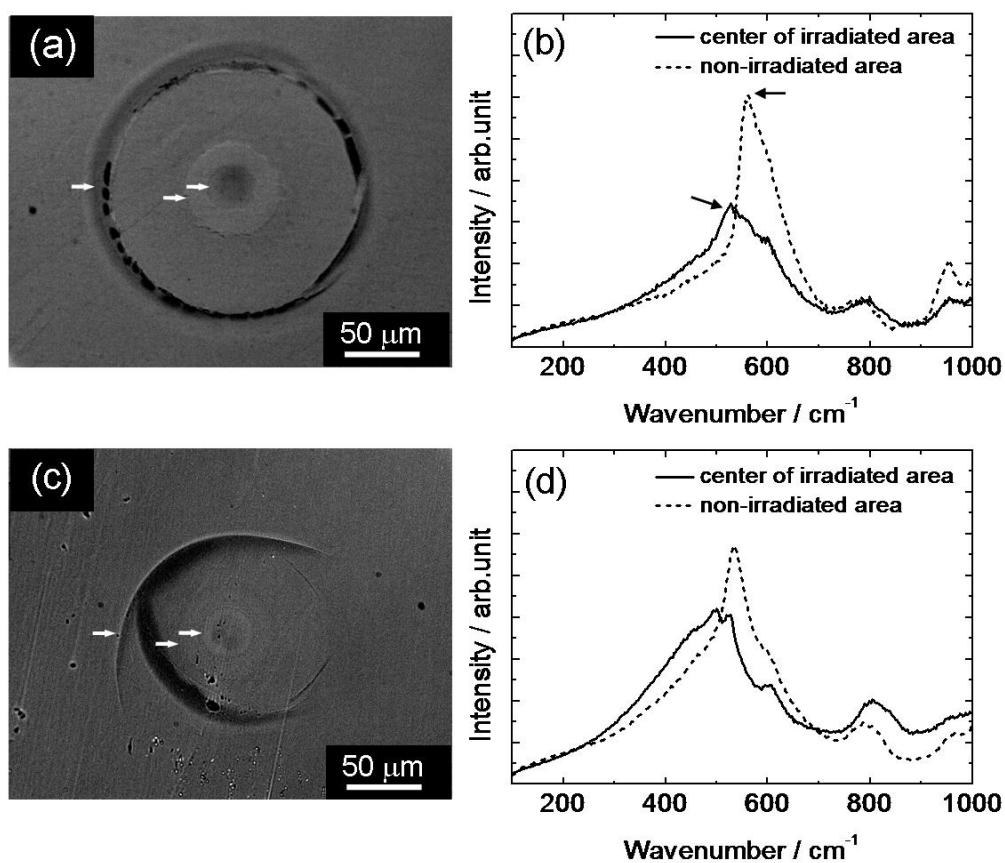


Fig. 2. Optical microscope images of the irradiated area and comparison between the Raman spectrum measured at the center of the irradiated area (solid curve) and that measured at the non-irradiated area (dotted curve). (a) and (b) 30 mol% Na₂O sample. (c) and (d) 21 mol% Na₂O sample.

that the position of crack generation and the direction of crack growth might be random. Figure 2(b) shows the Raman spectra measured at the center of the circle of the innermost boundary and in the region outside the circle of the outermost boundary. The main difference between the two spectra is with regard to the main Raman band at around 500 cm^{-1} ; while the band peak is located at 560 cm^{-1} in the non-irradiated region, it is located at 527 cm^{-1} in the irradiated region. It was reported that the wavenumber of this band changes in a systematic and sensitive manner with the Na_2O concentration in $\text{Na}_2\text{O-SiO}_2$ glasses¹⁶. The decreasing shift of the band has been attributed to an increase in the average Si-O-Si angle that occurs as a result of silicate polymerization¹⁷. Therefore, we can determine the glass composition from the wavenumber of this Raman band. The Na_2O concentration at the center of the innermost boundary is determined to be 19 mol%. Figure 2(d) shows the Raman spectra of the 21 mol% Na_2O sample. It is worth noting that the main Raman band in the spectrum measured at the center of the inner boundary has two peaks at 495 cm^{-1} and 519 cm^{-1} , which correspond to compositions of 2 mol% and 15 mol%, respectively. This means that two phases were formed in the central region of the laser-irradiated area. The immiscibility diagram of this glass system¹ shows that these compositions are similar to those obtained after phase separation at around $800\text{ }^\circ\text{C}$.

Figure 3 shows the distribution of the Na_2O concentration around the laser focal spot as estimated from the shift of the Raman band. In comparison with the Na_2O concentration in the unmodified region, the Na_2O concentration at the center is approximately 10 mol% lower and that at a distance of approximately $30\text{ }\mu\text{m}$ from the center is slightly higher. In the microscope images shown in figs. 2(a) and (c), the region between the innermost boundary and the middle boundary corresponds to the Na_2O -rich region. Therefore, the existence of the two boundaries is due to the change in the refractive index induced by the change in the composition. Moreover, this compositional change means that Na_2O migrated toward the outside and SiO_2 migrated

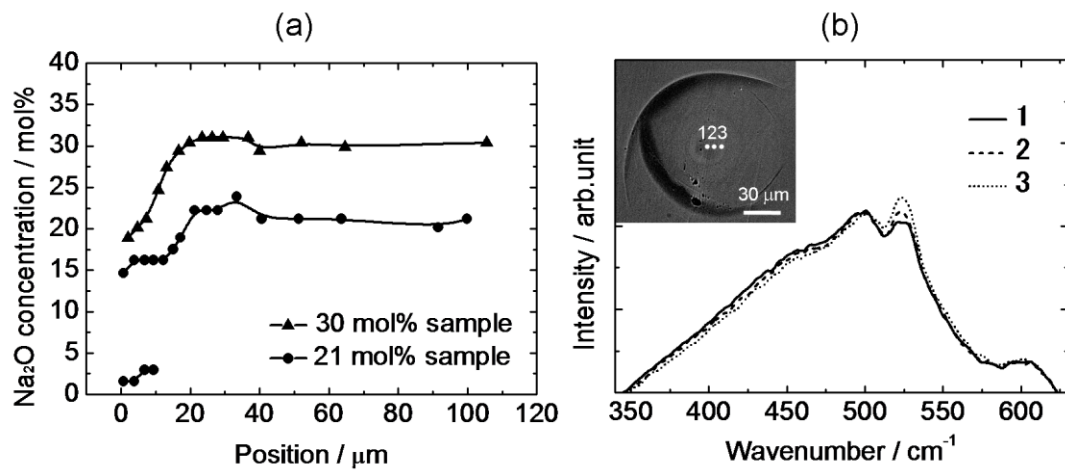


Fig. 3. (a) Na₂O concentration of the irradiated area as measured by a confocal Raman spectrometer. It should be noted that in the case of the 21 mol% Na₂O sample, there are two compositions near the center. (b) Raman spectrum of the 21 mol% Na₂O sample corresponding to the positions indicated in the inset. It should be noted that the intensities of the 520 cm⁻¹ peak are different

toward the center during laser irradiation. In a recent study, we elucidated that during the laser irradiation of soda-lime silicate glass, the temperature around the laser focal spot exceeds 1000 °C and the temperature gradient is above several tens of degrees Celsius per micrometer¹⁵. Thus, elemental migration is related to thermomigration (the Soret effect)¹⁸, which is the migration of atoms or ions under the influence of a temperature gradient. Consequently, it is understood that laser-induced elemental migration led to local phase separation in the 21 Na₂O mol% glass on account of the compositional change from the miscible region to the immiscible one.

In the case of the 21 Na₂O mol% glass, two compositions exist near the central area. Figure 3(b) shows the Raman spectrum measured at the position indicated in the inset. The intensities of the 520 cm⁻¹ peak increase with the distance from the center, although other parts of the spectrum remain almost constant. This suggests that the relative volume fraction of the Na₂O-rich phase increased with the distance. When the surface of this sample was observed by means of a FE-SEM after etching, the phase separation structure was found to be absent. This might be because the phase separation structure induced only by fs laser irradiation was too small to be visible. To promote phase separation, the sample was heated.

Figure 4 shows the SEM image of the laser-irradiated area after heat treatment at 575 °C for 3 hours and subsequent etching. The presence of a phase separation structure induced by fs laser irradiation was confirmed in the outer part of the immiscible composition region. The structures thus formed correspond to the SiO₂-rich phase because the HF etching rate is slower in the SiO₂-rich phase than in the Na₂O-rich phase. The apparent lack of a phase separation structure in the inner part might be due to the small relative volume fraction of the Na₂O-rich phase, which undergoes etching more easily than SiO₂-rich phase. The formation of a co-continuous structure can be confirmed in fig. 4(f), which shows a magnified image of (e). From these images, the diameter of the framework of this structure is evaluated to be

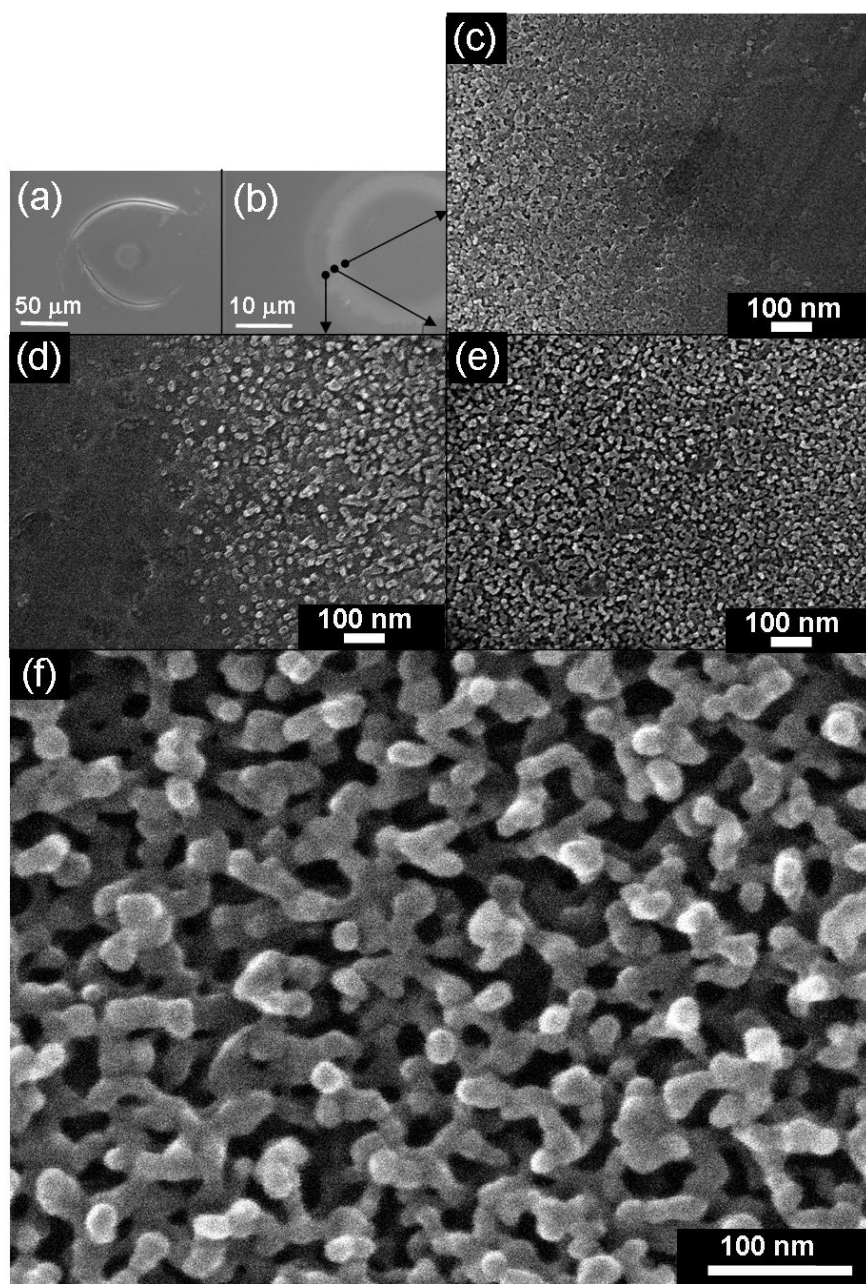


Fig. 4. SEM image of the irradiated area of the 21 mol% Na_2O sample after heat treatment at 575 °C for 3 hours and subsequent etching. (a) Overall image of the modified area. (b) Magnified image of (a). (c), (d), and (e) Magnified images of (b). (f) Magnified image of (e).

approximately 20 nm. We considered that the shape of the region in which the phase separation structure exists could be changed by increasing the relative volume fraction of the Na₂O-rich phase near the center of the modified area and that the configuration of the structure could be controlled by changing the heat treatment time.

A 26 mol% Na₂O sample was prepared and laser pulses were focused inside this glass sample using an objective lens. The irradiation condition was the same as that used for the 21 mol% and 30 mol% Na₂O samples (see the Experimental Procedures section). Figure 5(a) shows the SEM image of the irradiated area of the 26 mol% Na₂O sample after laser irradiation, heat treatment for 3 hours at 575 °C, polishing to expose the modified region on the surface, and etching. In this case, no crack was formed because the sample was polished after the heat treatment. Stress relaxation occurs during the heat treatment. Figure 5(b) shows the magnified image of fig. 5(a). Figures 5(c), (d), and (e) show the nanoscale structures formed in the laser-irradiated area shown in fig. 4(b) under various heat treatment times. After heat treatment for 3 hours, particles were observed (fig. 5(c)). This suggests that the relative volume fraction of the Na₂O-rich phase was sufficient for the formation of the phase separation structure. After heat treatment for 12 hours and 48 hours, the formation of a co-continuous structure was confirmed (figs. 5(d) and (e)). After heat treatment for 48 hours, the interspaces of the phase separation structure were found to be larger than those in the case of heat treatment for 12 hours. It is known that the pore size and specific surface area are proportional to the heat treatment time at a constant temperature ¹⁹. The above results suggest that we can control the pore size and specific surface area by changing the heat treatment time.

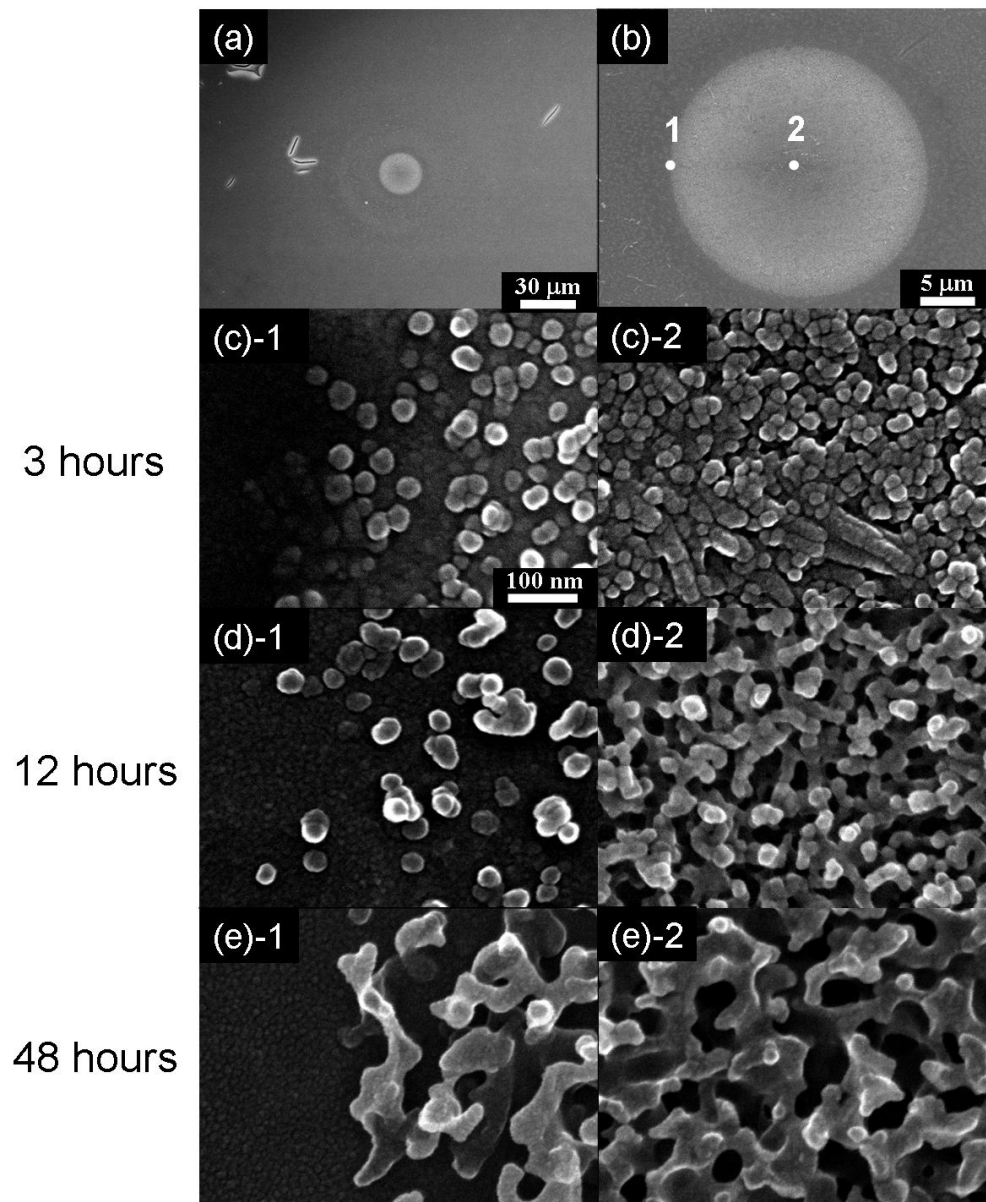


Fig. 5. (a) SEM image of the irradiated area of the 26 mol% Na_2O sample. (b) Magnified image of (a). (c), (d), and (e) Magnified SEM images for heat treatment times of 3 hours, 12 hours, and 48 hours, respectively. The numbers 1 and 2 denote the positions shown in the SEM image in (a). The magnifications of the image shown in (c), (d), and (e) are the same.

3.1.4 Conclusion

I confirmed that fs laser irradiation at a high repetition rate can induce space-selective phase separation inside $\text{SiO}_2\text{-Na}_2\text{O}$ glasses. This method can be used to develop nanoscale structures in a microscopic area of the glass surface. I believe that the method can be used for other kinds of glasses that show a region of immiscibility in their phase diagrams and is useful for the fabrication of local catalyst supports, modification of micro flow devices, and so on.

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3.2 Writing of optical waveguide

3.2.1 Introduction

The fs laser has been recognized as an effective tool for microscopically and three-dimensionally modifying transparent materials such as glass¹⁻³. In fs laser processing, the heat generated by laser irradiation has often been thought of as a disadvantage that contributes to low accuracy in processing. However, a processing method that aggressively uses the heat accumulation during laser irradiation at a high repetition rate has attracted considerable attention because it is effective for the writing of low-loss optical waveguides⁴⁻⁵ and for space-selective precipitation of functional crystals inside the glass⁶⁻⁸.

It is important for optical application to control the distribution of the refractive index. About ten years ago, our group discovered that refractive index changes on the order of 10^{-2} to 10^{-3} could be induced within various types of glasses¹⁻². However, because the increase of refractive index is related to local densification in the glass, the maximum laser-induced refractive index difference was limited to $\sim 10^{-2}$.

In this research, I report on the formation of element distribution by focusing a lot of laser pulses at a high repetition rate (more than several hundred kHz) in a glass⁹. Element distribution has a potential to induce a larger refractive index change than that induced by the densification mentioned above. I will discuss about the distribution behavior of each element for various types of multicomponent glasses. In addition, I will show the application of this phenomenon to fabrication of an optical waveguide.

3.2.2 Experiment

Regeneratively amplified fs laser pulses were used to induce the element migration in glasses. The 800 nm laser pulses were generated by a Ti-sapphire laser oscillator and amplified

at 250 kHz (Coherent Inc., Mira-RegA9000). In the typical condition, the pulse duration was 70 fs and the pulse energy was 3.0 μ J. The fs-laser pulses were focused inside a glass sample with a 20X objective lens (NA=0.45; Nikon LU Plan). We irradiated inside 37.6(mol%)SiO₂-42.4Al₂O₃-20CaO, 51P₂O₅-10.2Al₂O₃-38.8CaO, and 50B₂O₃-20Al₂O₃-30CaO samples. Based on the experimental results of these glasses, the 70P₂O₅-10Ga₂O₃-10GeO₂-10K₂O and 65B₂O₃-20GeO₂-15K₂O glasses were selected to fabricate optical waveguide. Glass samples were placed on an XYZ stage and the laser focal spot was scanned at speed of 20 μ m/s along the laser propagation direction from the bottom to the top surface. After laser irradiation, the glasses were polished to expose the modified region on the surface and the elemental distribution around the modified area were analyzed with electron probe microanalyzer(EPMA). The waveguiding of a He-Ne laser beam(633nm) was conformed by imaging the intensity distribution of output light from the optical waveguide with a beam profiler(OPHIR JAPAN LTD., Beamstar-Fx-50). The distribution of refractive index change was measured with the confocal laser scan microscope(Carl Zeiss Inc., LSM410).

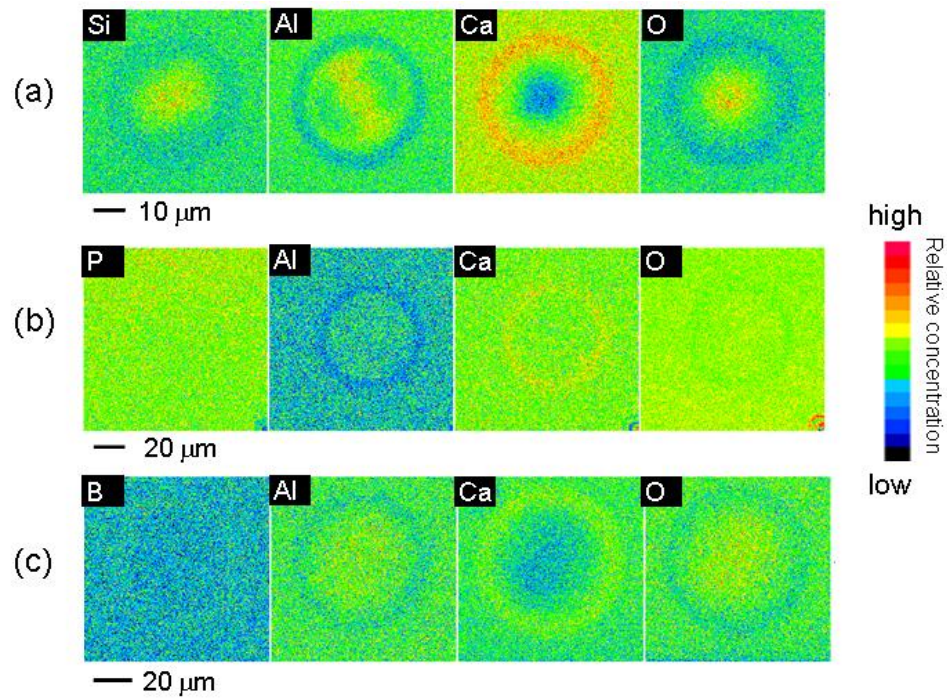


Fig. 1. Elemental distribution formed after laser irradiation measured with EPMA. (a) $37.6\text{SiO}_2\text{-}42.4\text{Al}_2\text{O}_3\text{-}20\text{CaO}$, (b) $51\text{P}_2\text{O}_5\text{-}10.2\text{Al}_2\text{O}_3\text{-}38.8\text{CaO}$, and (c) $50\text{B}_2\text{O}_3\text{-}20\text{Al}_2\text{O}_3\text{-}30\text{CaO}$ glasses.

3.2.3 Result and Discussion

The elemental distributions after fs laser irradiation inside the $37.6\text{SiO}_2\text{-}42.4\text{Al}_2\text{O}_3\text{-}20\text{CaO}$, $51\text{P}_2\text{O}_5\text{-}10.2\text{Al}_2\text{O}_3\text{-}38.8\text{CaO}$, and $50\text{B}_2\text{O}_3\text{-}20\text{Al}_2\text{O}_3\text{-}30\text{CaO}$ samples are shown in fig. 1. Figure 1(a) shows that Si and Al migrate to the center of irradiated spot and Ca migrates to the outside. Based on the experimental results(not shown in this report) of various kinds of glasses, Si always migrates to the center in a glass which contain SiO_2 . The alkaline or alkaline-earth elements always migrate to the outside. In silicate glasses which contain oxides of Al, B, Ge, or Ti, these elements sometimes concentrate in the intermediate region. These results indicate that the tendency of the elemental distribution depends on the strength of the bond between cations and oxygen ions: the strongly bonded ions like Si or Al migrate to the center of the irradiated spot, whereas weakly bonded ions such as Ca migrate to the outside. The elemental migration in $51\text{P}_2\text{O}_5\text{-}10.2\text{Al}_2\text{O}_3\text{-}38.8\text{CaO}$ and $50\text{B}_2\text{O}_3\text{-}20\text{Al}_2\text{O}_3\text{-}30\text{CaO}$ glasses are shown in figure 1(b)(c). The Al migrates to the center in the both glasses, the distribution of P almost doesn't change and the B migrates to outside a little. If the Si migrates to the center, the refractive index will decrease in the region¹⁰. Since Si always migrates to the center in silicate glass, we used phosphate and borate glasses to achieve the high refractive index in the center of the irradiated area. The elemental distributions after fs laser irradiation inside the $70\text{P}_2\text{O}_5\text{-}10\text{Ga}_2\text{O}_3\text{-}10\text{GeO}_2\text{-}10\text{K}_2\text{O}$ and $65\text{B}_2\text{O}_3\text{-}20\text{GeO}_2\text{-}15\text{K}_2\text{O}$ glasses are shown in fig. 2. In the case of $70\text{P}_2\text{O}_5\text{-}10\text{Ga}_2\text{O}_3\text{-}10\text{GeO}_2\text{-}10\text{K}_2\text{O}$, Ga and Ge, which contribute to the high refractive index, migrate to the center and the P and K, which contribute to the low refractive index, migrate to the outside. In the case of $65\text{B}_2\text{O}_3\text{-}20\text{GeO}_2\text{-}15\text{K}_2\text{O}$ glasses, Ge, which contributes to the high refractive index, migrates to the center and B and K, which contribute to the low refractive index, migrate to the outside. The intensity of reflected light measured with the confocal laser scan microscope is shown in fig.3. In the figure 3(a), the intensity in the center

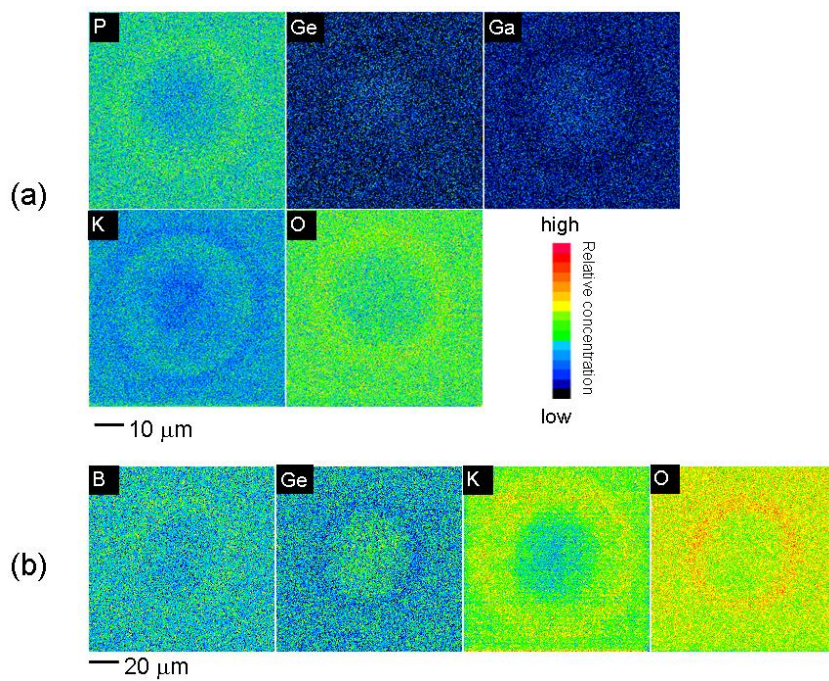


Fig. 2. Elemental distribution formed after laser irradiation measured with EPMA.
(a) 70P₂O₅-10Ga₂O₃-10GeO₂-10K₂O and (b) 65B₂O₃-20GeO₂-15K₂O.

region was higher than that in the outside. This means the refractive index in the center region increase by the elemental migration. The refractive index change estimated from the intensity of the reflected light is about 0.05. In the figure 3(b), increase of the refractive index change in the center region can not be confirmed. However, there are two dips at 60 μm and 120 μm . These dips are corresponding to the B rich region.

Figure 4 shows the intensity distribution of output light from optical waveguide. The sharp peak in the both glasses indicates the successful waveguiding. In the case of $70\text{P}_2\text{O}_5\text{-}10\text{Ga}_2\text{O}_3\text{-}10\text{GeO}_2\text{-}10\text{K}_2\text{O}$, there are many noise peaks. This might be due to the decreasing of the output light intensity originated from the scattering at cracks in the waveguide. The cracks were confirmed in the side view of the waveguide observed with an optical microscope.

Element migration inside a glass was induced space-selectively and microscopically by high-repetition femtosecond(fs) laser irradiation. The tendency of the elemental migration depended on the strength of the bond between cations and oxygen ions: strongly bonded ions like Si or Al migrated to the center of the irradiated spot, whereas weakly bonded ions such as Ca migrated to the outside. As discussed in Chapter 2, this phenomenon may be due to the thermomigration(Soret effect). The refractive index distribution was modified locally by controlling element distribution and optical waveguide was formed in phosphate and borate glasses.

3.2.4 Conclusion

I successfully fabricate the optical wave guide by the formation of element distribution under fs laser irradiation at high repetition rates.

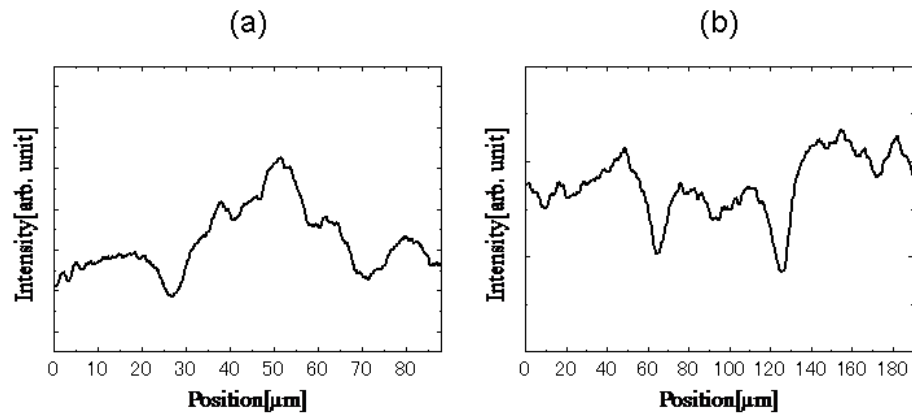


Fig. 3. Intensity distribution of reflected light around the elemental migration region measured with the confocal scan laser microscope. (a) 70(mol%)P₂O₅-10Ga₂O₃-10GeO₂-10K₂O and (b) 65B₂O₃-20GeO₂-15K₂O.

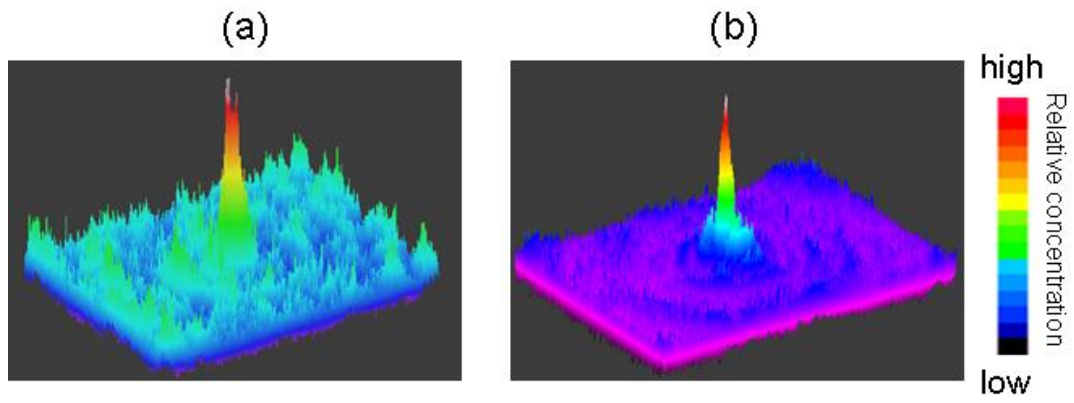


Fig. 4. Intensity distribution of output light from the optical waveguide with a beam profiler. (a) 70P₂O₅-10Ga₂O₃-10GeO₂-10K₂O and (b) 65B₂O₃-20GeO₂-15K₂O.

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3.3 Space-selective control of luminescence property

3.3.1 Introduction

Femtosecond laser microprocessing of transparent materials has been extensively used to fabricate various photonic structures¹⁻³. In recent years, high-repetition-rate femtosecond laser micromachining has attracted much interest owing to its unique advantage over the low repetition rate one in materials processing⁴⁻⁷. Generally, a pronounced heat accumulation effect would occur around the laser focal spot by using high-repetition-rate laser pulses, and a thermally driven chemical change could be locally induced inside the bulk transparent materials. Additionally, owing to the relatively low energy (approximately nanojoules) of a single laser pulse, a laser-induced breakdown producing unwanted microcracks could be avoided during microprocessing. So it is desirable to use a high-repetition-rate femtosecond laser for direct writing waveguides with low loss and precipitating optical functional crystals inside glasses⁶⁻⁷. Recently, it has been reported that after high-repetition-rate femtosecond laser irradiation, glass network modifiers such as alkaline ions and alkaline earth ions would migrate away from the laser focal region in glasses, which is of both theoretical and practical interest as a new discovery in the field of ultrafast pulsed laser–matter interactions⁸⁻⁹. Additionally, the coordination state change of some ions could also be induced by femtosecond laser irradiation in glasses^{8,10}. For many optical applications, it is useful to develop a technique for micromodification of fluorescence properties in glass via a femtosecond-laser-induced elemental distribution change combined with the environmental change of fluorescent ions doped in glass. Rare-earth-ion-doped glasses, typically used as gain media for a solid-state laser, possess eminent fluorescence properties. It is worth studying the change in fluorescence properties owing to elemental distribution and structural changes in the rare-earth-ion-doped glass induced by femtosecond laser irradiation. In this study, we successfully apply the

femtosecond-laser-induced migration of ions technique to the micromodification of fluorescence properties of a Eu^{3+} -doped silicate glass.

3.3.2 Experimental method

A glass with the composition of $20\text{Na}_2\text{O}-10\text{CaO}-70\text{SiO}_2-4\text{Eu}_2\text{O}_3$ (mol.%) was prepared for the study by a standard melting technique. Details of the glass fabrication method are available in Ref. 8. A regenerative amplified 800 nm Ti:sapphire laser (RegA 9000, Coherent, Inc.) with a 3.2 J, 80 fs, 250 kHz mode-locked pulse was employed as the laser source in the experiment. The laser beam was focused inside the glass sample placed on an XYZ stage via a 50x objective lens (NA=0.45). After the femtosecond laser irradiation, the element distribution of the ions around the focal point in the glass sample was characterized with an electron microprobe analyzer (EPMA, JEOL, model JSM-8000). The confocal fluorescence spectra were measured by a Raman spectrometer (Renishaw inVia) with a 514 nm Ar^+ laser excitation.

Laser processing lines vertical to the surface of the glass sample were written inside the glass sample with a length of 1 mm, using sample translation in the vertical (Z) direction at the speed of 5 m/s. Then the sample was polished away to expose the cross section of a laser processing line to the surface for elemental analysis.

3.3.3 Results and discussion

Figure 1 shows the backscattering electron (BE) image and the profiles of the relative concentration of the different elements in the glass around the focal point after the femtosecond laser irradiation, analyzed by the EPMA. Since the BE image is sensitive to the atomic weight of the elements of the observed surface, the ring-shaped bright contrast in the BE image reveals an element redistribution around the focal spot in the glass sample after femtosecond laser

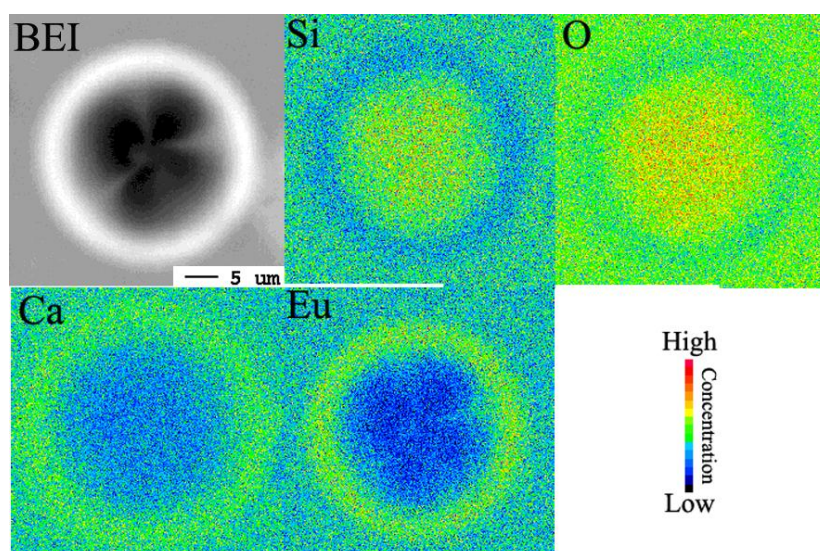


Fig. 1. (Color online) Backscattering electron image and EPMA mapping showing relative concentration change of the different ions in the glass around the focal point after the femtosecond laser irradiation

irradiation. From the EPMA mapping, the relative concentration of Eu ions and Ca^{2+} decreased at the focal point and increased in a ring-shaped region around the focal point, while the variations of element distribution of Si^{4+} and O^{2-} showed an opposite tendency. These results indicate that migration of ions was induced in the silicate glass in a very short time by the high-repetition-rate femtosecond laser irradiation. The ring-shaped Eu enriched region shows a good spatial consistency with the bright white contrast in the BE image, because the Eu element has a large atomic weight and a change in Eu content probably produces a contrast in the BE image. It has been previously reported that permanent photoreduction of Eu^{3+} to Eu^{2+} could be induced in glasses using femtosecond laser irradiation¹¹⁻¹². However, this phenomenon shows a strong dependence on the composition of the glass host, i.e., only observed in fluoride and borate glasses. Therefore, with the soda–lime–silicate glass in this experiment, it is justified to believe that the Eu dopant remained unchanged in the form of Eu^{3+} after the femtosecond laser irradiation, and the amount of Eu^{2+} generated from any laser-induced photoreduction was negligible. When the high-repetition-rate femtosecond laser is focused inside glass, the temperature at the focal spot can reach more than 3000 K, and a sharp temperature distribution will be produced with the thermal diffusion process⁵. In the femtosecond laser irradiated area, localized melting of the glass will happen at the high temperature, and all the bonds linking the network modifiers or the network formers will be broken in the glass melts. Because of high ion diffusivity stemming from the induced high temperature, various kinds of ions would diffuse away from the focal point to the cooler periphery region around the focal point, where the diffusivity of those ions is much lower. The laser-induced temperature gradient appears to be the leading driving force for the elemental redistribution in the glass. Since the diffusion coefficient of these network modifiers (Ca^{2+} , Na^+ , Eu^{3+}) is generally much larger than that of the network formers (Si^{4+}), the modifiers could enrich in a ring-shaped region around the focal point. At the

focal point the decrease of the relative content of these network modifiers led to the increase of the relative content of network formers (Si^{4+}), whose diffusivity is relatively lower. It is noteworthy that from the EPMA mapping, the Eu^{3+} enriched region has a distance of about 15 μm to the focal point, which is 4 μm shorter than that for a Ca^{2+} enriched region. This phenomenon can be also due to different diffusivities of Eu^{3+} and Ca^{2+} in the glass melt. At 1000° C, the activation energy for diffusion measured for Eu^{3+} (212 kJ/mol) is larger than that for Ca^{2+} (153 kJ/mol) in soda–lime–silicate glass melts, indicating that Eu^{3+} has a lower diffusivity than Ca^{2+} does¹³.

Figure 2 shows the confocal fluorescence spectra from different positions of a laser modified zone in a microscopic image under excitation at 514 nm. The emissions at 578, 592, 611, and 653 nm in the glass can be attributed to $^5\text{D}_0-^7\text{F}_0$, $^5\text{D}_0-^7\text{F}_1$, $^5\text{D}_0-^7\text{F}_2$, and $^5\text{D}_0-^7\text{F}_3$ transitions of Eu^{3+} , respectively. Figure 3 presents the intensities of the emissions associated with $^5\text{D}_0-^7\text{F}_1$ (592 nm) and $^5\text{D}_0-^7\text{F}_2$ (611 nm) transitions as a function of the distance from the central laser focal volume. When the position moves toward the inside of the laser-modified zone, the corresponding intensity of these emissions changes. With the scale bar in the microscopic image and the EPMA mapping, it is easy to relate the change in fluorescence intensities to the element redistribution induced by the laser irradiation. The fluorescence intensity of Eu^{3+} decreased at the focal point where Eu^{3+} concentration is low and then increased in the region where Eu^{3+} was enriched. Following the increase in the distance, the fluorescence intensity decreased to the level of the original glass host, beyond the radius of the laser-induced zone of element redistribution. In the case of the $^5\text{D}_0-^7\text{F}_2$ transition of Eu^{3+} , the intensity decreased by 50 % at the focal point and increased by 20 % in the Eu^{3+} enriched region compared with the non-irradiated glass. To figure out the mechanism for the laser-induced change in fluorescence properties in the Eu^{3+} -doped glass, the influence on environment of the

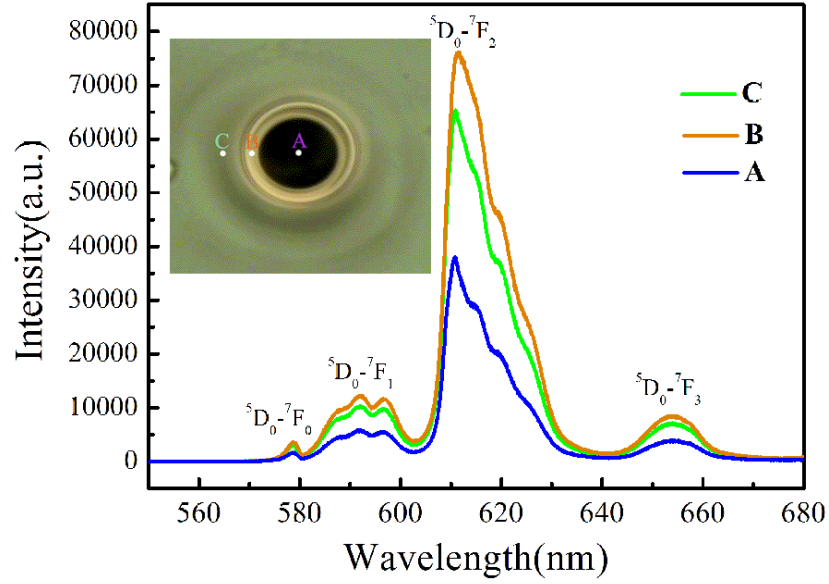


Fig. 2. (Color online) Confocal fluorescence spectra from different positions (A–C) of a laser-modified zone (the spectra were obtained with a 514 nm Ar⁺ laser as the excitation source). The inset shows the optical microscope image of the laser-modified zone.

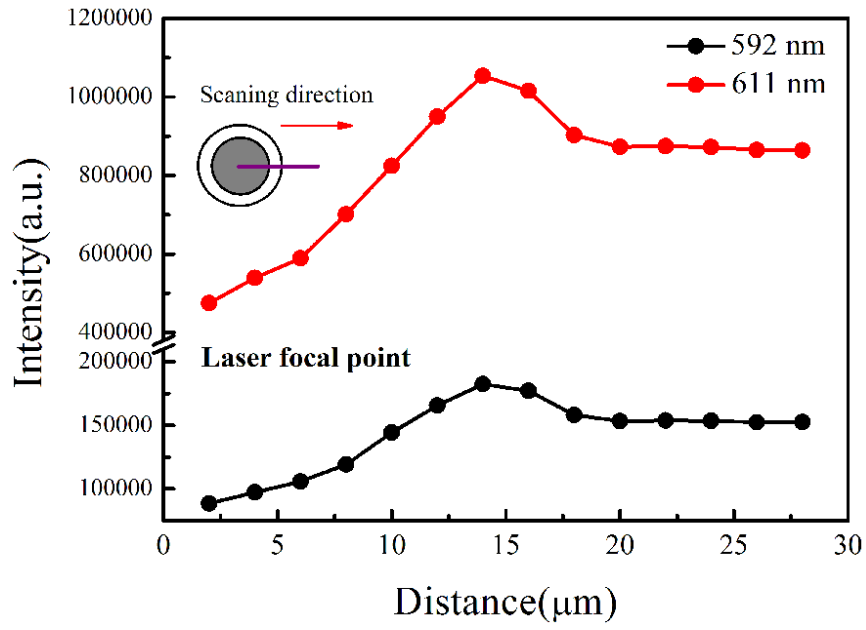


Fig. 3. (Color online) Different peak intensities as a function of distance from the central laser focal point

fluorescent ions by the femtosecond laser irradiation should also be considered. The previous study by Chan et al.¹⁰ shows that a Si coordination change could be induced in fused silica with an 1 kHz femtosecond laser irradiation. Recently, It has also been reported that B coordination changes in a borate glass under a 250 kHz femtosecond laser irradiation, hinted at with the profile change in micro-Raman spectra⁸. The single pulse energy (3.2 μ J) of the femtosecond laser employed in the experiment is comparable to that (2 – 4 μ J) done by Chan et al.¹⁰. However, it is confirmed that the profile of micro-Raman spectra for the laser-modified region and original glass shows little difference, indicating little change of coordination or intermediate range order (IRO) structure. With a 1 kHz femtosecond laser irradiation, the Si coordination change can be explained with the formation of localized plasma and a subsequent microexplosion just at the focal point inside the glass. While in our previous study, the high-repetition-rate femtosecond-laser-induced heat accumulation effect and thermal diffusion should be responsible for the formation of the laser modified zone inside the glass. The coordination change induced by the highrepetition-rate femtosecond laser irradiation involves the migration of ions [non-bridging oxygen (NBO) and network modifiers included] and rearrangement of chemical bonds linking the network formers. The BO_3 units could be transformed to the BO_4 units in a femtosecond-laser-modified zone some dozens of micrometers away from the focal point. In contrast, the SiO_4 units are so tightly bonded in the glass that it would be very hard to induce Si coordination change with the same method. Moreover, the relative intensity of the $^5\text{D}_0\text{--}^7\text{F}_2$ and $^5\text{D}_0\text{--}^7\text{F}_1$ transition of Eu^{3+} , defined as fluorescence intensity ratio R, was investigated. It has been proposed that the intensity ratio R demonstrates the strength of covalent–ionic bonding between the ion and the surrounding ligand¹⁴. When the position changed in the laser-modified zone, the intensity ratio R changes slightly from 5.36 to 5.88, within 5% compared with that (5.65) of the original glass. This result indicates a tiny

change of the ligand environment of Eu^{3+} . It could be concluded that the fluorescence intensity change in the glass was mainly ascribed to the relative concentration change of Eu^{3+} .

3.3.4 Conclusion

We have succeeded in micromodification of element distributions of Eu^{3+} in a silicate glass using high-repetition-rate femtosecond laser irradiation. It was observed that the fluorescence intensity increased by 20 % in the Eu^{3+} enriched region in the glass compared with that for the original glass. We attribute the increase in fluorescence intensity to the relative concentration change of Eu^{3+} induced by the laser irradiation. The femtosecond-laser-induced migration of ions technique is opening up new prospects for fabricating integrated optical devices such as waveguide lasers and amplifiers inside glasses.

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Chapter 4

Phase transformation in diamond under ultrafast laser irradiation at low repetition rates: Application for terahertz range

4.1 Introduction

Coherent photon pulses with duration in femtosecond regime have opened new frontiers in material research of light-matter interactions¹. The ultrafast feature of femtosecond laser pulses has been widely used for direct imaging of chemical reactions in gases² and terahertz spectroscopy based on photoconductive emitters³ excited by femtosecond lasers. As a source of localized energy deposition, intense ultrashort light pulses have become key technologies for direct modification in transparent materials due to new applications and phenomena ranging from 3D optical waveguides⁴, micro-explosions⁵ and laser nanosurgery⁶ to photonic crystals⁷ and 3D self-organized subwavelength structures⁸. The process, initiating by a multiphoton ionization, exhibits a highly nonlinear dependence on the intensity of the light beam. The light is absorbed by photoelectrons and the optical excitation ends before the surrounding lattice is perturbed, which results in highly localized breakdown without collateral damage of material⁹. In recent years the existence of non-thermal ultrafast phase transitions has been observed on the surface of several materials such as silicon¹⁰⁻¹¹, gallium arsenide¹²⁻¹³, indium antimonide¹⁴, germanium antimonide¹⁵, and carbon¹⁶⁻¹⁹. In many cases, these transient phases are metal-like disordered or glassy phases resulting from laser-induced electron-hole plasma. Recent discoveries based on such phase transitions span from source and detector of terahertz radiation²⁰ and ultrafast X-ray generation²¹⁻²² to femtosecond optical switch and high-dense rewritable optical memory¹. More recently, a variety of permanent and metastable phase transformation, which are based on the structural rearrangement due to thermal accumulation

and the shock wave generation²³⁻²⁵, has been observed^{23,26-28}. Although nonequilibrium dynamics of electrons and lattice during graphitization on diamond surface in several theoretical studies²⁹⁻³¹, the three-dimensional structuring in diamond and the electrical conductivities of the spatially modified structures are still not fully understood. Here we report the observation of a localized phase transformation in diamond induced by intense ultrashort light pulses. Apparent continuous structures consisting of a phase transformed to amorphous carbon were formed inside diamond along with the laser spot moving. Such photoinduced amorphous structures have electrical conducting properties of a maximum of 64 S/m, which can be changed, based on a localized transition from sp^3 to sp^2 in diamond depending on the laser irradiation conditions. The laser parameters such as pulse energy and writing speed affected the resultant electrical conducting properties of the amorphous regions due to recrystallization and multi-filamentation phenomena. I demonstrated that the laser-processed diamond with the periodic array of cylinders composed of amorphous carbon have the characteristic transmission properties, which are in good agreement with the finite-difference time-domain (FDTD) calculations, in terahertz region and act as metallo-dielectric photonic crystal. We anticipate that such metallo-dielectric periodic structures will open new opportunities in left-handed metamaterial³².

4.2 Localized phase transformation in diamond

The laser radiation, in a Gaussian mode, produced by a regeneratively amplified mode-locked Ti:Sapphire laser (230 fs pulse duration, 1 kHz), operating at 780 nm, was focused via a $20\times$ (NA=0.45) objective into the synthetic diamond sample (Sumitomo Electric Hard metal Corp., brand of Type Ib diamond with nitrogen impurities of ~ 100 ppm) of $3\text{ mm} \times 3\text{ mm} \times 1.5\text{ mm}$ size. A typical beam waist diameter at the focus and the laser energy fluence were estimated to be $\sim 2\text{ }\mu\text{m}$ and 28.5 J/cm^2 , respectively. A series of cylindrical structures with

certain spacing were directly written by scanning along the laser irradiation direction from the bottom to the top surface. After writing, the sample surfaces were processed by using a focused ion beam (JEOL, JIB-4500), and then the cross-sectional pieces including both the laser-irradiated and non-irradiated regions were measured by using scanning electron microscope (JEOL, JSM-6700F) and micro-Raman spectroscopy (Nicolet, Almega XR). A black and unbroken cylindrical structure was formed inside synthetic diamond sample by moving a tightly focused laser spot at 20 $\mu\text{m/s}$ (Fig. 1 (a), (b)), however, no apparent continuous structures were observed when the scanning speed is higher than 100 $\mu\text{m/s}$. To estimate structural changes in the laser-irradiated regions, a small cross-sectional piece was extracted by focused ion beam techniques. Figure 1 (c) indicates a typical secondary electron image on the cross-sectional surface extracted from the laser irradiated sample. An area indicated by a double-headed arrow d with width of 18 μm represents a laser-induced area. The points marked P_1 and P_2 in Fig. 1 (c) represent the typical points of the laser-irradiated and the unirradiated region inside diamond sample, respectively.

Although the laser-irradiated sample surface was ablated to the depth of 23 μm , it should be noted that the morphology within a laser-irradiated region in the examined cross section obviously remain densified, namely, a void does not exist. In order to reveal the microscopic structural change induced by laser irradiation, we carried out micro-Raman spectroscopy on the same cross-sectional surface with 1 μm spatial resolution (Fig. 1(d)). These Raman spectra were normalized by the diamond peak intensity and the linear background has been subtracted. It is well known that the Raman spectrum from single crystalline diamond consists of a single narrow peak at 1332 cm^{-1} , whereas for disordered carbon structure there are two Raman peaks observed: the G peak around 1500 $\sim$ 1630 cm^{-1} and the D peak around 1350 cm^{-1} , which are normally assigned to optical zone center phonons of E_{2g} symmetry involving the in-plane

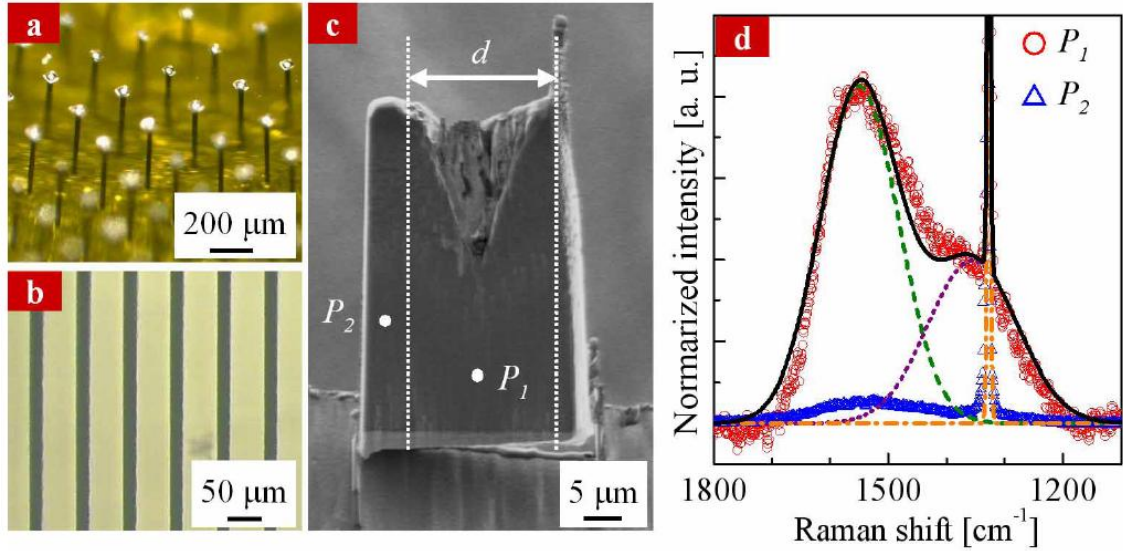


Fig. 1. Optical microphotograph being taken in an oblique direction (a) and a side view (b). Secondary electron image of the cross-sectional surface including the laser-processed region was also shown (c). The double-headed arrow d and the points marked P_1 and P_2 represent the laser-induced area, the typical points of the laser-irradiated and the unirradiated region, respectively. (d) Micro-Raman spectra at P_1 and P_2 points on the cross-sectional surface. The components of the G peak (broken line), D peak (dotted line), and diamond peak (dashed-dotted line) deduced from the peak fittings (solid line) are also shown.

bond-stretching motion of all pairs of sp^2 sites and K -point phonons of A_{1g} breathing mode of C sp^2 atoms in rings, respectively³³. The broad D peak is indicative of the existence of disordered carbon in a carbon network and the intensity ratio of I_D/I_G increases with increasing disorder³⁴. A sharp intense Raman peak at 1330 cm^{-1} and apparent broad two peaks centered at 1555 cm^{-1} and 1350 cm^{-1} , which respectively correspond to G and D peak, were observed in the laser-induced region (P_1). On the other hand, in the non-irradiated region (P_2), one can see the intense diamond peak remains, whereas no apparent D peak was observed. Based on the fact that the element constituting the initial sample is only sp^3 -coordinated carbon, we speculated that sp^2 -bonded carbon clusters were locally formed inside diamond without morphological changes. As a result, the laser-induced cylindrical structures have an electrical conductivity. To test this suggestion, we measured the electrical conductivities of the modified cylindrical structures induced by various laser energy densities.

4.3 Characterization of the localized modified structure

The laser-processed samples with various energy fluence ($28.5 \sim 427\text{ J/cm}^2$) were coated on the bottom surface by Au evaporation (thickness of 150 nm) in order to connect electrically between each lines of modified cylindrical structures. The absolute electrical resistance of two distinct cylinders penetrating from the bottom to the top of the sample was measured by the four-terminal method (Fig. 2(a), (c)), which can eliminate the effects of any contact resistance, in a scanning electron microscope (JEOL, JFAS-7000BT Beam Tracer). The electrical resistance of two pairs of cylinders ($2R$) can be obtained from I-V measurements ($2R = (V_A - V_C)/I_{sup}$), where V_A , V_C is the electric potential of the anode and cathode, I_{sup} is the supply current (Fig. 2(b)), respectively. From the measured resistance (R) and the diameter (d) of the cylinder, and the thickness of the diamond sample (t), the specific electrical conductivities (σ) were obtained

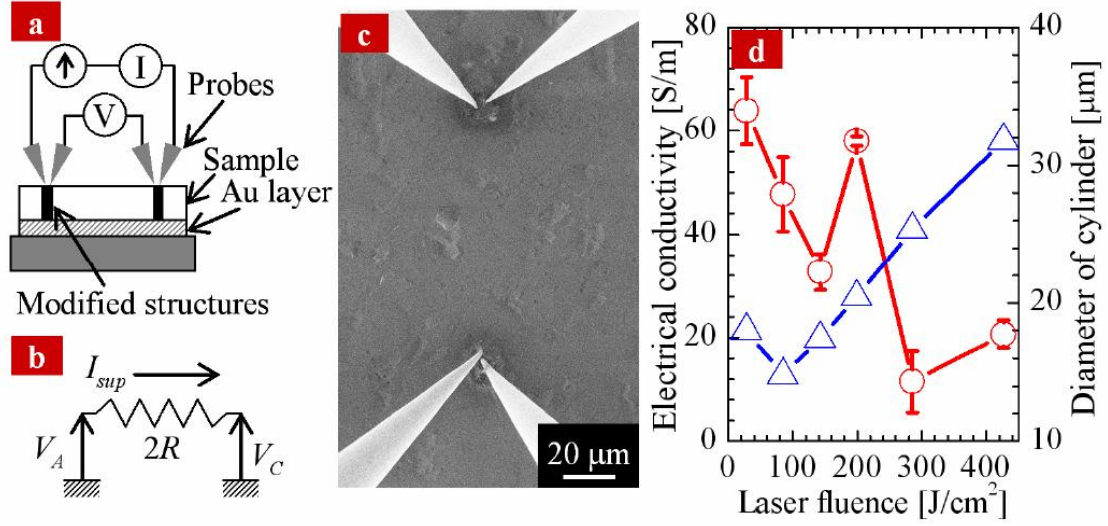


Fig. 2. Schematic illustration (a) and equivalent circuit (b) of the four-terminal method, where R is the electrical resistance of a modified cylindrical structure, V_A , V_C is the electric potential of the anode and cathode, I_{sup} is the supply current, respectively. Scanning electron micrograph during the measurements with four-point probe was also shown in (c). (d) Specific electrical conductivity (unfilled red circle) and radius (unfilled blue triangle) of the cylinder as a function of the laser energy fluence.

$$(\sigma = 4t/\pi R d^2).$$

Figure 2(d) indicates electrical conductivity and diameter of the modified cylinder as a function of the energy fluence of the femtosecond laser pulses. The diameter increased in proportion to the laser fluence, whereas the electrical conductivities decreased when the laser energy fluence is higher than 200 J/cm². The specific electrical conductivities reached a maximum of 64 S/m at laser energy fluence of 28.5 J/cm². The following explanation of why the lower electrical conductivities were obtained at higher laser energy fluence is proposed. When the femtosecond laser pulses are tightly focused inside diamond, the intensity in a focal volume becomes high enough to produce self-focusing arising from Kerr effect. Simultaneously, a high free electron density is produced by multiphoton ionization and avalanche, the material has the properties of plasma, which defocuses the light pulses. As a result, the femtosecond laser pulses are alternatively self-focused and defocused, self-guiding the light on a straight path³⁵. A large number of regularly located filaments can be formed when the peak power of the light pulses is sufficiently large³⁶. Indeed, the spatially periodic modulation of the G peak with a period of 8.1 μm due to the multiple filaments in the directions transverse to laser propagation has been observed at the higher laser energy fluence of 427 J/cm² (Fig. 3(d)), the divided structures of thinner cylinders were formed, compared with the lower laser fluence. Simultaneously, *sp*²-bonded carbon clusters were discretely formed, namely the cylindrical structures were partially torn in the laser propagation direction corresponding to the refocusing. On the other hand, the continuous structures consisting of *sp*²-bonded carbon clusters, which have electrical conducting properties, were formed at lower laser energy fluence than 200 J/cm² (Fig. 3(b)). We have also observed the modified structures inside diamond have a graphitic structure consisting of *sp*²-bonded carbon clusters and these dendritic structures are extend in the laser incident direction, regardless of the laser energy fluence (Fig. 3(a), (c)). This is may be

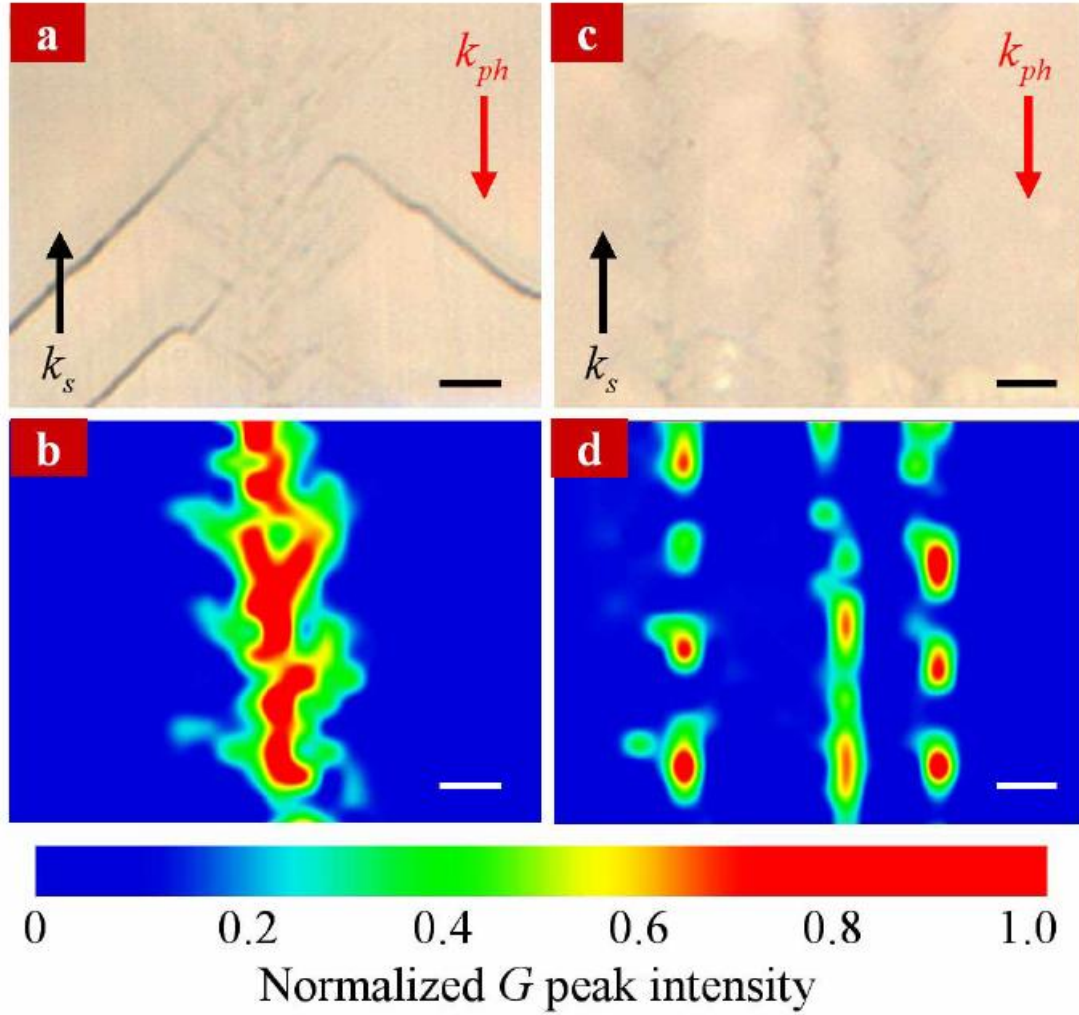


Fig. 3. Optical microphotograph and Raman spectra mapping on the cross-sectional surface after the laser writing with laser energy fluence of 200 J/cm² (a, b) and 427 J/cm² (c, d) at the same scanning speed of 20 μ m/s. Scale bars are 5 μ m. Arrows show the direction of the laser incidence (k_{ph}) and the scanning of the focus (k_s). Color bar indicates the normalized Raman G peak intensity.

due to the extent of diffraction of the laser as it propagates through the plasma³⁷.

Another interesting phenomenon was observed in the scanning speed dependence of electrical conductivity. Figure 4(a) shows the evolution of the Raman spectra of the cross sectional sample surface after the laser irradiation with different scanning speeds. Electrical conductivity and Raman peak intensity ratio of I_D/I_G in the modified structures as a function of laser scanning speed are also shown in Fig. 4(b). The laser energy fluence was set at 28.5 J/cm² in all experiments. At slower scanning speeds than 20 $\mu\text{m/s}$, the G peak position shifts downward from 1615 to 1590 cm^{-1} , while I_D/I_G peak intensity ratio increases with increasing scanning speed. These tendencies indicate a larger amount of sp^2 content with a higher degree of disorder was formed at slower scanning speeds³³. Such sp^2 structure acts as a conduction part of the amorphous carbon network. It should be noted that I_D/I_G peak intensity ratio reached its maximum at the scanning speed of 20 $\mu\text{m/s}$, corresponding to the maximum electrical conductivity. Furthermore, the increase of the D peak intensity and the narrowing of the G peak at slower scanning speeds than 20 $\mu\text{m/s}$ indicate the reduction of bond angle disorder at sp^2 aromatic rings³³, namely graphitization of the initial diamond structure occurs, which is in agreement with the theoretical studies²⁹⁻³¹. From these results, the lower electrical conductivities at the slower scanning speed than 20 $\mu\text{m/s}$ are assumed to be due to the recrystallization from amorphous structure to nanodiamond and/or the formation of tetrahedral amorphous carbon structure. On the other hand, for scanning speed above 20 $\mu\text{m/s}$, the G peak position keeps around 1590 cm^{-1} and the intensity ratio of I_D/I_G is approximately constant, however, a steep decrease in conductivity can be observed (Fig. 4). This may be due to the discontinuous structures, which were formed between the bottom and the top of the sample. Indeed, no apparent continuous structures consisting of sp^2 -bonded carbon clusters were observed when the laser scanning speed is higher than 100 $\mu\text{m/s}$. As a result, the electrical conductivity of the

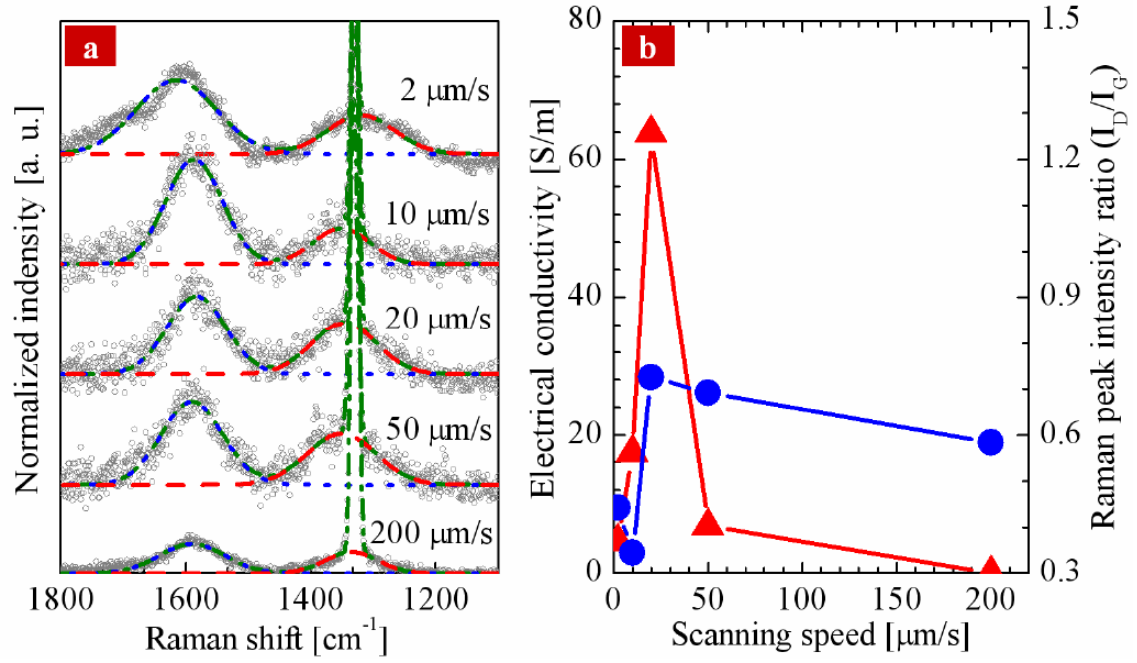


Fig. 4. (a) Sequential Raman spectra taken as a function of laser scanning speed. (b) Profiles of electrical conductivity (red filled triangle) and Raman peak intensity ratio of I_D/I_G (blue filled circle) in the modified structures as a function of laser scanning speed. The Raman spectra are vertically displayed for clarity. The laser energy fluence was set at 28.5 J/cm^2 in all experiments.

spatially modified structures in diamond reached a maximum of 64 S/m, which is between the typical value of crystalline graphite ($\sim 10^4$ S/m) and of amorphous carbon ($\sim 10^{-2}$ S/m), at the scanning speed of 20 $\mu\text{m/s}$.

4.4 Metallo-dielectric photonic crystal structure

Apart from the fundamental importance of the observed phenomenon as the first direct evidence of the localized transition from sp^3 - to sp^2 -bonded structure embedded in diamond, the observed phenomenon could be useful for the fabrication of metallo-dielectric photonic crystal in terahertz region. It is well known that diamond exhibits a low absorption and a high refractive index of 2.35 with a low dispersion in the terahertz region. To evaluate the availability of these techniques, we carried out terahertz time-domain spectroscopy (THz-TDS) characterization of the periodically modified diamond with embedded electrically conducting structures created by intense femtosecond light pulses. We measured the transmission and phase-shift spectra in THz region (Fig. 5). In this measurement, the two dimensional square lattice of cylinder array with lattice constant (Λ) of 80 μm and diameter (d) of 25 μm inside diamond, which was placed in 10 rows and 30 columns, was used. The incident THz wave passed through an aperture with a diameter of 1 mm was focused on a sample by a paraboloidal mirror. The directions of incidence and detection of THz wave were set along the $\langle 10 \rangle$ direction of the square lattice. The finite-difference time-domain (FDTD) simulations were also performed on an 32×184 two-dimensional square grid with cell size 1 μm and a time step of 5 fs using the relative permittivity and the specific electrical conductivity of the graphitized amorphous carbon ($\epsilon_g = 5.5$, $\sigma_g = 300$ S/m) and the diamond ($\epsilon_d = 5.5$, $\sigma_d = 0$ S/m). The excitation was a plane wave and line source of 160 μm placed 100 μm away from the cylindrical structure. Transmission intensity was corrected according to Fresnel's equation, matching the experimental conditions.

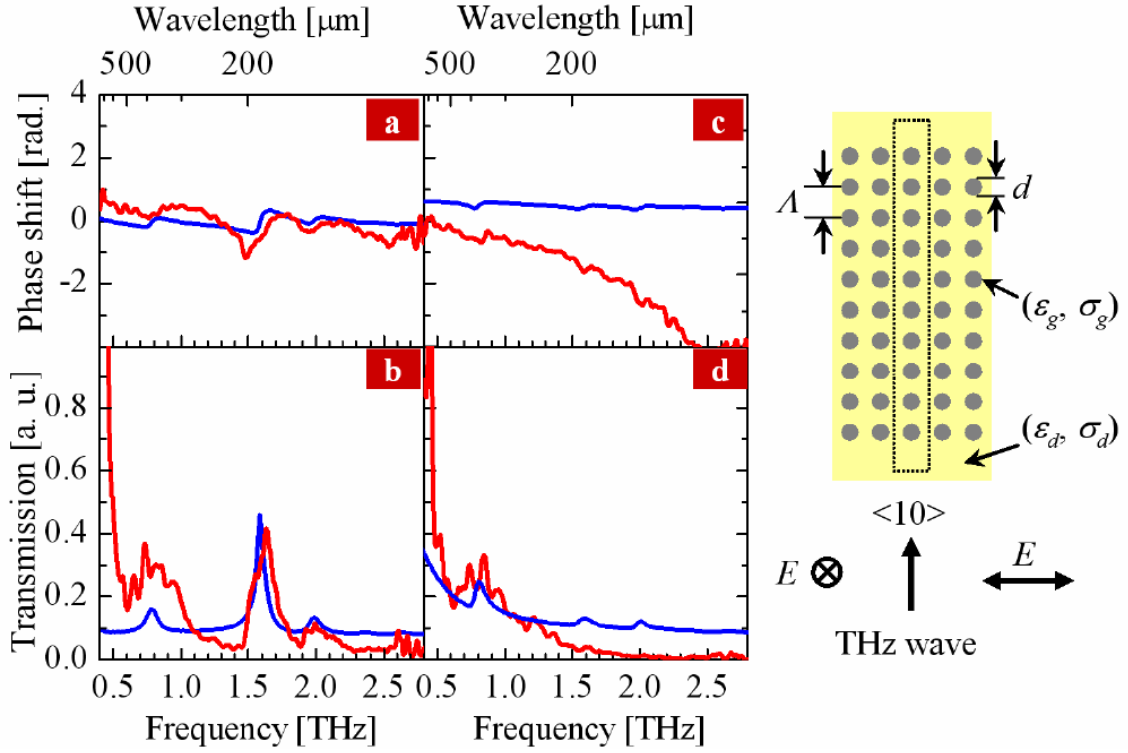


Fig. 5. Comparison between measured (red line) and calculated (blue line) transmission intensity and phase shift of the square metallo-dielectric photonic crystal with lattice constant of $\Lambda = 80 \text{ } \mu\text{m}$. The calculation model (enclosed area with dotted line) and the two polarization configurations (E) are shown on the side of the graphs, where (ϵ_g, σ_g) and (ϵ_d, σ_d) represent a set of the specific permittivity and the specific electrical conductivity of the modified cylindrical structure and the initial diamond, respectively. The direction of incidence, which was polarized parallel (a, b) or perpendicular (c, d) to the longitudinal axis of a cylinder with a diameter of $d = 25 \text{ } \mu\text{m}$, was set along the $\langle 10 \rangle$ direction of the square lattice.

The configuration of incidence, which was polarized parallel (TM) or perpendicular (TE) to the longitudinal axis of cylinder array, was also shown.

At the frequency below 0.46 THz, the transmission exceeded the geometric transmission of 69 %. This phenomenon of transmission enhancement for TM polarization was similar to the extraordinary transmission through metal hole arrays³⁸. In the case of TM-polarized THz wave, an apparent bandpass characteristic was observed at 1.6 THz corresponding to the period of the cylinder array (Fig. 5(b)). Furthermore, phase shift also showed a sharp change in the bandpass region (Fig. 5(a)). This increase in the phase shift indicates the decrease in the group velocity due to the multiple scattering between the cylinders. On the other hand, no transmission in frequency range over 1.4 THz was observed for TE polarization (Fig. 5(d)). This monotonic decreasing behavior of phase shift (Fig. 5(c)) is under investigation. From comparison of experimental and theoretical results, although disturbance in the measurement spectra may be due to the multireflection between the aperture and the front surface of diamond, the measured transmission and phase shift are in good agreement with those of FDTD calculations. The phenomenon could be interpreted in terms of the simultaneous negativity of the electric permittivity and magnetic permeability³⁹. Additionally we have confirmed that the bandpass frequency can be controlled based on the lattice constant. Indeed, when the lattice constant increased from 60 μm to 100 μm , the bandpass region shifted from 143, 188, to 231 μm corresponding to the period of the cylinder array in diamond (Peaks 2 in Fig. 6). Furthermore, the bandpass frequencies corresponding to twice the lattice constant were also observed (Peaks 1). Although the other weak transmissions (Peaks 3) at the normalized frequency of 1.27 were observed, the details are under investigation.

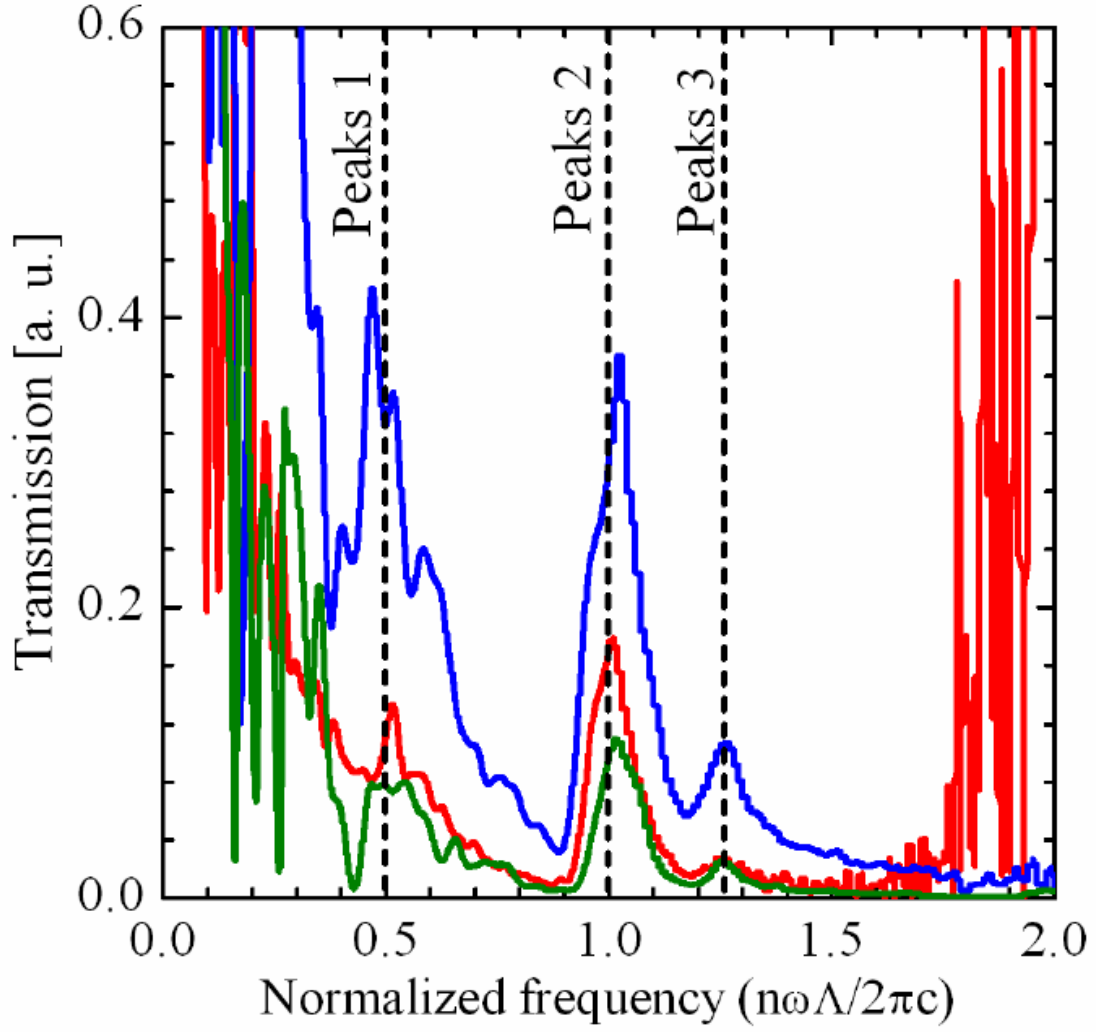


Fig. 6. Transmission spectra of the square metallo-dielectric photonic crystal with lattice constant of $\Lambda = 60 \mu\text{m}$ (red), $80 \mu\text{m}$ (blue), and $100 \mu\text{m}$ (green), respectively. The horizontal axis is a normalized frequency ($n\omega\Lambda/2\pi c$), where n is the refractive index of diamond ($= 2.35$). Dotted lines indicate the characteristic peak positions.

4.5 Conclusion

I demonstrated how a new localized structural-phase transformation, and then this technique can be useful for the manufacture of a metallo-dielectric photonic crystal. Apart from the fundamental importance of the observed phenomenon as the first direct evidence of the localized transition from sp^3 to sp^2 in diamond, the fabricated periodic structures will open new opportunities ranging from wire-grid polarizer, and plasmonic metamaterials, to integrated electrical circuit.

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Chapter 2

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