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<td>URL</td>
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Kyoto University
Studies on fabrication of microstructures in dielectric materials by femtosecond laser pulses

Takayuki Nakaya

2010
General introduction

In 1994, Dr. Hirao proposed a basic research idea of “induced structure” [1]. He paid attention to the fact that all materials like glasses are metastable from the viewpoint of thermodynamics. Even diamond can be changed to diamond-like carbon or glassy carbon by laser irradiation. A metastable state of glass is changed to other states in an intensive external electromagnetic field. If the external electromagnetic field induced structure and the concentration, variety, and valence state of active ions in glass can be controlled; in particular, if the induced structure or three-dimensionally and periodically distributed electronic structure in glass can be space-selectively controlled, it is expected that novel optical functions of the glass will be achieved. From the viewpoint of practical applications, it is expected to obtain glasses with properties superior to the corresponding single crystal. Based on this idea, various electromagnetic fields such as ultra-violet light, electron beam and laser were applied to make microscopic modifications to transparent materials, and many interesting phenomena were observed and the promising applications of the observed phenomena were discussed [2-8].

Herein, a femtosecond laser was selected as a powerful tool to make microscopic modifications in transparent materials. Femtosecond laser has two apparent features compared with CW and long pulsed lasers: (1) elimination of the thermal effect due to extremely short energy deposition time, and (2) participation of various nonlinear processes enabled by highly localization of laser photons in both time and spatial domains. Due to the ultra-short light-matter interaction time and the high peak power, material processing with the femtosecond laser is generally characterized by the absence of heat diffusion and, consequently molten layers [9]. The nature of ultra-short light-matter interaction permits femtosecond laser to overcome the diffraction limit [10]. Dr. Hirao started the systematic investigations on the femtosecond laser induced microstructures in transparent materials and applications in
micro-optics at the end of 1994. The reason why this laser is used is that the strength of its electric field in the focal point of the laser beam can reach up to 10 TW/cm². It is sufficient for inducing various nonlinear physicochemical reactions in materials by using a focusing lens, when the pulse width and the pulse energy are 100 fs and 1 μJ, respectively. The photoinduced reactions are expected to occur only near the focused part of the laser beam due to multiphoton processes. In the past several couple of years, a lot of research efforts have been devoted to the field of three-dimensional microscopic modifications to transparent materials by using femtosecond laser. Promising applications have been demonstrated for the formation of three-dimensional optical memory [11-14] and multicolor image [15], and fabrication of optical waveguide [16-17], coupler [18-19] and photonic crystal [20].

In this thesis, microstructure modification by femtosecond laser pulses in various transparent materials, e.g. in glasses and single crystal sapphires are studied. The purpose and conclusion of this study are given as follows.

In chapter 1, various diffractive optical elements in silica glasses and sapphire crystals were achieved by using the focused femtosecond laser irradiation. There are various practical devices incorporated with the diffractive optical elements, for instance, fiber Bragg gratings for the information technology, diffractive lenses for correction of the chromatic aberration etc. The general manufacturing of the diffractive optics relies on the photolithography technique, which requires a long processing time and expensive facilities such as a mask fabrication machine, a dry etching apparatus etc. However, by using the femtosecond laser direct-writing technique, the diffractive optical devices could be created inside the dielectric materials just by single procedure. Thus, this present technique will become useful in the rapid prototyping of various designed diffractive optics.

In chapter 2, based on the fabrication technique in chapter 1, the integration of the diffractive optical elements inside the silica glasses is demonstrated. The integration of the micro-optics has been currently developed with increasing demands for the multi functions and miniaturization of the optical platform. Usually, the integration process is carried out by the alignment and successive bonding of each
discrete optics. However, there is an excessive cost issue and the integration design is restricted by the assembling accuracy. On the other hand, by making use of the three-dimensional space selectivity of the femtosecond laser, the true three-dimensional integration of micro-optical components can be realized. This fabrication method will offer new opportunities to construct the integrated optics with novel functions.

In recent years, the developments on the miniaturization and the integration of the fluidic devices have been widely conducted as well as that of the optical devices. A promising application of the micro-fluidic devices is a micro-total analysis system (μ-TAS), which can realize chemical and biological analysis with high efficiency, high accuracy and high performance. One of the key components for the μ-TAS is a micro-channel structure in glasses. Usually, the micro-channels are produced by planar microfabrication techniques based on the photolithography and a successive bonding process. In chapter 3, three-dimensional channel structures in bulk silica glass was achieved by using the femtosecond laser and further wet etching. By incorporating this technique, the true three-dimensional micro-channels can be generated without bonding procedure. For realizing smooth flow of the liquid through the micro-channel, a relation between the repetition rate of the ultrashort pulses and the surface morphology inside the micro-channel was explored. It was found that the optimum repetition rate exited and the uniformity of the photo-induced refractive index change is important for fabricating the smooth surface. Moreover, a relation between the uniformity of the photo-induced structures and the amount of the defects in the silica glasses was analyzed.

In chapter 4, space-selective valence state manipulation and precipitation of various metal ions and coloring in glasses were realized by using focused ultrashort pulses. Persistent photooxidation of Mn$^{2+}$ to Mn$^{3+}$ in a silicate glass has been observed. Space-selective precipitation and control of silver nanoparticles in silicate glass by a laser irradiation at room temperature and further annealing at high temperature have been also confirmed. The size of photooxidation and nanoparticles and their spatial distribution can be controlled by the fabrication conditions. This
technique will be useful in the fabrication of three-dimensional multicolored industrial art objects, optical memory with ultrahigh storage density and all-optical switches with ultrafast nonlinear response.

In chapter 5, a three-dimensional nano-architecture in glasses by using the combination of femtosecond laser pulses and the new LCOS modulator is introduced. The fabrication of three-dimensional optical waveguide by femtosecond laser pulses inside various transparent materials are essential for making 3D integrated optical devices. However, the fs-laser processing consumes a lot of time for fabrication of many long waveguides. The parallel fabrication of bended optical waveguides with a spatial light modulator (SLM) by the LCOS was achieved. An efficient method for preparing computer generated holograms for the SLM is also proposed.

References

Chapter 1

Fabrication of diffractive optical elements inside dielectric materials by femtosecond laser pulses

Ultrashort pulsed laser has been used as a powerful tool to clarify elementary physicochemical processes, such as excitation-energy relaxation and both electron and proton transfer on nanosecond and picosecond time scales, that occur in a micrometer-sized area [1,2]. Ultrashort laser can also be used to make microscopic modifications in transparent materials. The reason why this laser is used is its high electric field intensity up to 10 TW/cm², which is sufficient for inducing nonlinear optical effects in materials by use of a focusing lens, when the pulse width is 100 fs and the pulse energy is 1 µJ. The photoinduced reaction is expected to occur only near the focused part of the laser beam due to nonlinear optical processes.

Up to now, there have been a lot of studies on the microscopic modifications in transparent materials by using femtosecond lasers [3-12]. Various induced structures can be produced by using pulsed laser operating at the nonresonant wavelength with pulse widths of the order of femtosecond; colored spot or line due to the formation of color center, refractive index spot due to densification and defect formation, microvoid due to remelting and shock wave, microcrack due to destructive breakdown, etc. [9]. Composite structures were also observed after the focused femtosecond laser irradiation [9]. Promising applications using these phenomena have also been demonstrated for three-dimensional optical memory, photonic crystal, integrated optical circuit, and optical display [3-12].

1.1 Fabrication of Dammann grating inside silica glasses

Dammann grating is one of the diffractive optical elements, which can generate
regular one- or two-dimensional beam patterns of equal intensity spots. Practically it is used as optical splitter in information technology [13]. Other use is for parallel digital optics, laser fabrication, etc [14]. The structure of Dammann gratings is designed under the condition that the intensity of each high order diffractive light is equal to the intensity of the zero order light [15]. Usually Dammann grating is fabricated through complicated processes, i.e. formation of a photoresist film on a glass substrate via spin coating, ultraviolet light exposure, etching etc. Usually it takes over a few days to complete all these processes. Using the writing technique by the femtosecond laser, however, can shorten the processing time for fabrication of the Dammann grating. In this section, the fabrication of Dammann gratings in bulk silica glasses by a femtosecond laser is demonstrated. Moreover, it is shown that Dammann gratings with high diffraction efficiency can be obtained through a multilayer process.

As shown in Fig. 1.1, the experimental set-up consists of a regeneratively amplified Ti:Sapphire laser delivering pulses of 150 fs duration with a maximum energy per pulse of 4µJ at a repetition rate of 200 kHz. A glass sample was mounted on a three-dimensional translation stage, which was controlled by a computer. The glass sample was a 10mm×10mm×2mm synthesized silica glass. The laser beam was focused inside the sample by a microscope objective. The average laser power was adjusted by an ND filter. The glass sample was translated perpendicular to the laser beam. The intensity distribution of the Dammann grating was measured by a powermeter (Newport, 2832-C) and detected by a CCD camera. Fig. 1.2(a) shows a photograph of the microstructure of a 6×6 Dammann grating. The average power of the laser beam was 300mW and a 20× objective lens with numerical aperture of 0.4 was used to focus the laser beam. The Dammann grating consists of many rectangle refractive index change patterns. In order to form single rectangle pattern, several lines were written in specific pitch as shown in Fig. 1.2(a). The period was 250µm both in the x and y axes. The number of period was 16. Thus, the 2D size of the grating was 1mm×1mm. Fig. 1.2(b) shows a diffraction pattern of the 6×6 Dammann grating. The light source was a He-Ne laser (633 nm). It is shown that the
Fig. 1.1 Schematic diagram of the femtosecond laser processing system.
Fig. 1.2 Photograph of the microstructure (a) and diffraction pattern (b) of a 6×6 Dammann grating.
Fig. 1.3 Intensity distribution of split light along the line A-A’ (a), and the line B-B’ (b).
laser beam was split to $6 \times 6$ beams. Fig. 1.3 (a) and (b) show the intensity distribution of the split light along the line A-A’ and the line B-B’, respectively. The intensity distribution is quite uniform. The efficiency of the $6 \times 6$ Dammann grating is estimated to be 7.7%, which is smaller than the theoretical value of 71% [16]. This may be due to the small refractive index change and short length of the structure-modified region. It is shown that the diffraction efficiency can be improved by the way of a multilayer process.

The phase shift $\phi$ of the input light passing the grating is

$$\phi = \frac{2\pi \Delta n L}{\lambda},$$

(1.1)

where $\Delta n$ is the refractive index change, $L$ is the length of the refractive index change-region in the $z$ direction, and $\lambda$ is the wavelength of the input light. Generally, the diffraction efficiency $\eta$ is proportional to $\sin^2(\phi/2)$. Thus, $\eta$ is improved with the increase of $\phi$ when $\phi$ is smaller than $\pi$. There are two ways to increase $\phi$. One is to make $\Delta n$ as large as possible by adjusting the fabrication condition and the composition of the glass. The other is to make $L$ much larger by piling another grating on the previous one, what is called a “multilayer process”. The latter method was adopted and the diffraction efficiencies for basic $1 \times 2$ Dammann gratings were examined.

In this experiment, the average power of the laser beam was 240 mW. A $10 \times 10$ objective lens with numerical aperture of 0.3 was used to focus the laser beam. The translation speed of the stage was 25 $\mu$m/s. $1 \times 2$ Dammann gratings that consisted of single layer to four layers were fabricated, and the diffraction efficiencies of each grating were measured. The phase shift was calculated from the ratio of the high order diffraction efficiencies. The least squares method was used for the calculation. Fig. 1.4 and Fig. 1.5 show the relation between the phase shift and the number of layers, and the relation between the phase shift and the diffraction efficiency, respectively. Apparently the phase shift is proportional to the number of layers and the diffraction efficiency increased with an increase of the phase shift when the phase shift is smaller than $\pi$. However, the diffraction efficiency of the grating with four layers decreases
Fig. 1.4 Relation between the phase shift and the number of layers.
Fig. 1.5 Relation between the phase shift and the diffraction efficiency. The curve is 
\[ \eta = 8\left[\sin\left(\frac{\phi}{2}/\pi\right)\right]^2, \] 
where \( \eta \) is the diffraction efficiency and \( \phi \) is the phase shift.
because the phase shift becomes larger than $\pi$. The maximum diffraction efficiency of the multilayer grating reached 70%, which is comparable to the theoretical value of 81%.

In summary, the Dammann gratings have been fabricated by the 800 nm femtosecond laser. It has been also demonstrated that the diffraction efficiency of the Dammann grating could be controlled through the multilayer process. It is easy to create three-dimensional structures in a glass by the femtosecond laser. Using this technique, it is expected that the novel optical components with composite functions can be developed.

1.2 Fabrication of diffractive lenses inside dielectric materials

Diffractive lens is one of the diffractive optical elements with a function of focusing an input light. A structure of the diffractive lens consists of several steps which can generate refractive index patterns for phase modulation and focusing of the input light. In other words, the diffractive lens is like an approximated Fresnel lens with the step structures. One of the most attractive characteristics of the diffractive lens is the compactness by means of removing spherical structures. Recently by exploiting this feature, a monolithic optical platform for optical switches has been developed [17]. Another significant characteristic is a large negative wavelength dispersion which is an opposite feature compared to usual spherical lenses. Practical applications by using this characteristic are, for instance, a CD/DVD compatible pick up lens, a hybrid lens to correct chromatic aberration, etc. In general, the diffractive lens is fabricated through photolithography process on a surface of the dielectric material. First, a photo-resist is formed onto the glass substrate via spin coating. Then ultraviolet light exposure is carried out by using a photo mask and transferred a mask pattern onto the photo resist. Next, the photo resist is developed and unnecessary resist is removed. Finally, a dry etching is applied and the resist is removed. However this process is complicated and processing time is over a few days. By employing the femtosecond laser direct-writing technique, the diffractive lens can be created inside
dielectric materials through single step without the photo mask [18,19]. The maskless process is always demanded from industrial applications, because the photo mask process has a problem of contamination due to the contact between the photo mask and the photo resist. From this point of view, the fabrication of the diffractive lens by the femtosecond laser direct writing can be an epoch-making maskless process. In this section, characteristics of the diffractive lenses inside silica glasses and sapphire crystals fabricated by the femtosecond laser direct-writing technique are demonstrated. Moreover, a numerical study on diffraction efficiency of the diffractive lenses generated by the femtosecond laser is discussed.

1.2.1 Writing characteristics for silica glasses

As described above, the diffractive lens is well known as approximated structures of the Fresnel lens. The diffractive lens consists of refractive index pattern of concentric rings. The \( m \)-th radius of \( r_m \) for the diffractive lens with \( N \)-th level approximation is given by an equation (1.2),

\[
 r_m = \sqrt{\frac{2mf\lambda}{N} + \left(\frac{m\lambda}{N}\right)^2},
\]

where \( f \) is a focal length operating at a wavelength of \( \lambda \). The maximum first-order diffraction efficiency \( \eta_1^N \) is expressed as following equation:

\[
 \eta_1^N = \left[ \frac{\sin(\pi/N)}{\pi/N} \right]^2.
\]

For example, theoretical values of diffraction efficiency for the 2 level and 4 level approximation are 40.5% and 81.1%, respectively.

Various fabrication conditions were performed to investigate the characteristics of diffractive lenses. Design values of the diffractive lens were as follows: a diameter of 1.06 mm, a focal length of 15 mm operating at a wavelength of 633 nm, the approximation level of 2 and a numerical aperture of 0.036. A sample used was a synthesized silica glass plate. The following fabrication conditions were employed to
create the diffractive lenses. The microscope objective of $5 \times$ with the numerical aperture of 0.14 was used to focus the femtosecond laser pulses. The laser scanning speed was 25 $\mu$m/s, and the average laser power was varied from 300 mW to 850 mW. The femtosecond laser was scanned in a specific scanning pitch to generate refractive index pattern of concentric rings. Fig. 1.6 illustrates the scanning pitch, a line width and the refractive index pattern of the diffractive lens. The scanning pitch adopted was 2.5 $\mu$m, which was equal to the line width so that uniform refractive index pattern without a gap of the laser non-irradiated area could be produced. Polarization states of the femtosecond laser pulses were selected either a linear or a circular polarization. Since the linearly polarized light was emitted from the femtosecond laser oscillator, a quarter-wave plate was inserted after the ND filter to obtain the circular polarized femtosecond laser pulses. Fig. 1.7 shows a microscope image of a diffractive lens inside the silica glass fabricated by the femtosecond direct-writing technique. It is clear that the refractive index modification pattern of the diffractive lens can be formed as designed. The diffraction efficiency of the diffractive lens for each fabrication condition was evaluated as the following method. An input light of a He-Ne laser with a wavelength of 633 nm was transmitted through the diffractive lens and a laser power of a focusing light was measured by a photo-detector (Q82214, Advantest Co.). A metal pinhole was utilized to separate the focusing beam and the other diffraction beams. The diffraction efficiencies were measured in two directions for the identical sample. In the case of the diffractive lenses fabricated by the linearly polarized femtosecond laser pulses, one measurement direction was to arrange the polarization of the He-Ne laser parallel to that of the femtosecond laser and another direction was to place the polarization of the He-Ne laser perpendicular to that of the femtosecond laser. In the case of the diffractive lenses generated by the circularly polarized femtosecond laser, x direction of xyz translation stage, which was parallel axis to the polarization of the linearly polarized femtosecond laser, was used as a criterion direction and the polarization of the He-Ne laser was set parallel and perpendicular to this criterion direction. The measurement results of the diffraction efficiencies by various laser powers are shown in Fig. 1.8. P and S shown in Fig. 1.8
Fig. 1.6 Schematic diagram of the diffractive lens. The left figure shows the refractive index pattern of the diffractive lens. Hatches are modified areas by the femtosecond laser irradiation. The right image, which magnifies a part of refractive index pattern, indicates the line width and the scanning pitch.
Fig. 1.7 Optical microscope image of the diffractive lens generated inside the silica glass. The diameter of 1.06 mm, the focal length of 15 mm at 633 nm, and the approximation level of 2. (a): top view, (b): cross sectional view. The fabrication condition was the laser power of 500 mW with linear polarization.
Fig.1.8 Relation between the laser powers and the diffraction efficiencies of the fabricated diffraction lenses. In (a), the lenses were formed by the linearly polarized femtosecond laser. In (b), they were produced by the circularly polarized laser. P and S indicate that the polarization of the fs laser was parallel and perpendicular to that of the He-Ne, respectively.
indicate that the polarization of the He-Ne laser was set parallel and perpendicular to that of the femtosecond laser or the criterion direction, respectively. In the case of linearly polarized femtosecond laser at parallel configuration (Fig. 1.8 (a), P), the diffraction efficiencies increased with the increase in the laser power. When the laser power reached around 140 mW, the diffraction efficiency was saturated at approximately 40 %, which was a close value of the maximum diffraction efficiency of 2 level approximation. As the laser power got larger than 140 mW, the diffraction efficiency decreased with the increase in the laser power. In the case of linearly polarized femtosecond laser at perpendicular distribution (Fig. 1.8 (a), S), the diffraction efficiencies slightly increased with the increase in the laser power but all the diffraction efficiencies were less than 3 %. This means that the diffractive lens fabricated by the linearly polarized femtosecond laser pulses has a strong polarization dependence. Several researchers have reported the polarization dependence of the micro-optics created by the linearly polarized femtosecond laser pulses [18,20]. This unique phenomenon may be attributed to nano-gratings that were embedded within the lines created by the femtosecond laser pulses [21-23]. According to the reference [21], an internal modification area produced by the femtosecond laser has periodic oxygen defects with a period of around 200 to 300 nm. These sub-wavelength refractive index modifications are expected to be sufficient to cause polarization dependent features. This phenomenon is known as a form birefringence and by employing this effect, a grating beam splitting polarizer has already been developed for an optical isolator [24]. In the case of the circular polarization as shown in Fig. 1.8 (b), it is suggested that the diffraction efficiencies for the parallel configuration increased with the increase in the laser powers and that the diffraction efficiencies for the perpendicular distribution might be saturated under the laser power condition around 200 mW. Apparently, the diffractive lenses formed by the circularly polarized femtosecond laser do not have strong polarization dependence compared to those fabricated by the linearly polarized femtosecond laser. Therefore, it is useful to create diffractive lenses without polarization dependence by the circularly polarized femtosecond laser pulses. To examine the controllability of the diffraction efficiency,
phase shift for each fabricated sample was calculated from the measurement value of the diffraction efficiency. In general, the diffraction efficiency of the diffractive lens with 2 level approximation is expressed as follows:

\[ \eta_1(\phi) = \left[ \frac{\sin(\phi/2)}{\pi/2} \right]^2, \]  

(1.4)

where \( \phi \) is the phase shift as described in section 1.1. Fig. 1.9 demonstrates the relation between the laser powers and obtained phase shifts from the calculation. In the case of the diffractive lenses produced by the linearly polarized femosecond laser at parallel configuration (Fig. 1.9 (a), P), the phase shift increased with the increase in the laser power and this tendency continued until the maximum laser power. Actually it is confirmed from the microscope observation that a length \( L \) of the laser modified region in the z direction kept increasing until the laser power reached the maximum value. From these facts, one can obtain the maximum diffraction efficiency only by controlling the laser power condition for the optimum phase shift. In this case the maximum phase shift was approximately 5 which was a close value to \( 2\pi \). Thus, diffractive lenses with almost any approximation level can be formed theoretically. Since the optimum phase shift is \( \pi \) for diffractive lenses with 2 level approximation, the best laser power is considered to be about 140 mW in this experiment. In other cases of the diffractive lenses produced by the linearly polarized femosecond laser at perpendicular configuration and by the circularly polarized femtosecond laser at both distributions (Fig. 1.9 (a), S and Fig. 1.9 (b)), the phase shift gradually increased with the increase in the laser power, however the phase shift of more than \( \pi \) could not be obtained by the laser power range used in this experiment. It is necessary to apply multilayer process to obtain a larger phase shift. The output beam intensity distributions transmitted through the diffractive lenses were also evaluated by a near field pattern measurement system (LEPAS-11, Hamamatsu Photonics K.K.), as shown in Fig. 1.10. It is obvious that the focused beam has no side peaks and that it fits well to the Gaussian fitting curves as shown in red curves. The focused spot diameter at \( 1/e^2 \) was 18 \( \mu \)m which was comparable to the diffraction limit value of 15 \( \mu \)m.
Fig. 1.9 Relation between the laser powers and the phase shifts of the fabricated diffraction lenses. The diffractive lenses were formed by the linearly polarized femtosecond laser pulses (a) and by the circularly polarized femtosecond laser pulses (b).
Fig. 1.10  Output beam intensity distribution which was focused by the diffractive lens inside the silica glass with the focal length of 15 mm. The three-dimensional distribution (a) and one-dimensional distribution at the center of the beam in the x and y direction (corresponding to the upper and lower graph, respectively) (b). In (b), black and red curves indicate measured curves and Gaussian fitting curves, respectively. The definitions of the curves are the same as ones in the graphs below. The fabrication condition was the laser power of 500 mW with linear polarization.
1.2.2 Writing characteristics for sapphire crystals

Focused femtosecond laser pulses can create induced structures inside various materials like mono crystals as well as glasses. The sapphire crystals have unique physical and optical properties, for instance, a high melting point of 2030 °C, and a large thermal conductivity of 23 W/m·K, a large refractive index of 1.77. By using these characteristics, the sapphire crystals are widely used for furnace windows, heat sinks and optical sensor windows for ultraviolet and infrared lights. Although it has many attractive features above, the sapphire is a difficult material to create a micro lens because of its hard property. The diffractive lens on the sapphire surface can be formed by the photolithography technique but the mask contact process has the same contamination problem as in the case of silica glass. In this section, the femtosecond laser direct-writing of the diffractive lens inside the sapphire crystal is performed and its characteristic is discussed.

Design values of the diffractive lens were the same as those of the silica glass lens in the section 1.2.1, i.e. a diameter of 1.06 mm, a focal length of 15 mm operating at a wavelength of 633 nm, the approximation level of 2 and a numerical aperture of 0.036. A sample used was a mono crystal sapphire plate. The following fabrication conditions were employed to create the diffractive lenses. The microscope objective of 5× with the numerical aperture of 0.14 was used to focus the femtosecond laser pulses. The laser scanning speed was 25 µm/s, and the average laser powers were selected either 400 mW or 600 mW. The scanning pitch adopted was 2.5 µm, which was equal to the line width. Polarization state of the femtosecond laser pulses was adjusted to the circular polarization by using the quarter-wave plate. Fig. 1.11 shows a microscope image of a diffractive lens inside the sapphire crystal fabricated by the femtosecond direct-writing technique. Table 1.1 shows fabrication conditions of the diffractive lenses inside the sapphire crystal and the measurement results of the diffraction efficiencies. Comparing the sample No.1 and 2, the diffraction efficiency increased with the increase in the laser power. The P diffraction efficiency of 36.1 ± 0.1 % was obtained by the laser power of 600 mW, which was the close value of the
Fig. 1.11 Optical microscope image of the diffractive lens generated inside the sapphire crystal. The diameter of 1.06 mm, the focal length of 15 mm at 633 nm, and the approximation level of 2. (a): top view, (b): cross sectional view. The fabrication condition was the laser power of 600 mW with circular polarization.
Table 1.1 Fabrication conditions of the diffractive lenses inside the sapphire crystal and the measurement results of the diffraction efficiencies.

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<th>Sample No.</th>
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<th>Diffraction efficiency [%]</th>
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<td></td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>circular</td>
<td>29.0±0.1</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>circular</td>
<td>36.1±0.1</td>
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theoretical diffraction efficiency of 40.5%. Process window of the laser power for the sapphire crystal was narrower than that for the silica glass. By using the laser power over 600 mW, there appeared a crack inside the sapphire crystal. Therefore the laser power was limited to 600 mW to avoid cracking the sapphire. This phenomenon was the main difference between the silica glass and the sapphire crystal. The output beam intensity distributions transmitted through the diffractive lenses were also evaluated by a near field pattern measurement system as shown in Fig. 1.12. It is clear that the focused beam has no side peaks and that it fits well to the Gaussian fitting curves as shown in red curves. The focused spot diameter at $1/e^2$ was 18 µm which was comparable to the diffraction limit value of 15 µm.

Heat-resisting property of the diffractive lens fabricated inside the sapphire crystal was also investigated. The diffractive lens inside the silica glass was produced for the reference material. Design values of the diffractive lens were the same as those employed in this section, i.e. a diameter of 1.06 mm, a focal length of 15 mm for a wavelength of 633 nm. Fabrication conditions used were the microscope objective of 5 × with the numerical aperture of 0.14, the scanning speed of 25 µm/s, the scanning pitch of 2.5 µm, linearly polarized femtosecond laser pulses, and the laser powers of 600 mW for sapphire crystal and 550 mW for silica glass. A heating furnace was utilized for the heat treatment of the fabricated samples. The diffraction efficiencies of the samples were measured each time after the heat treatment at specific temperature. The heating temperatures were 200 °C, 400 °C, 600 °C, 800 °C, 1000 °C and 1200 °C and the heating time was 6 hours for each temperature. Fig. 1.13 shows variations in the diffraction efficiencies of the diffractive lenses fabricated inside sapphire crystal and silica glass. Apparently, the diffraction efficiencies of the sapphire maintain over 20 % at 1200 °C while these of the silica glass decrease with increase in the temperature. As for the silica glass, the diffractive lens vanished after the heat treatment at 1200 °C and it could not be seen by the optical microscope. It was proved that the diffractive lens formed inside the sapphire crystal had strong heat-resisting property compared to the diffractive lens in the silica glass. The diffraction efficiencies of the sapphire went down after the heat treatment at
Fig.1.12 Output beam intensity distribution which was focused by the diffractive lens inside the sapphire crystal with the focal length of 15 mm. The three-dimensional distribution (a) and one-dimensional distribution in the x and y direction (corresponding to the upper and lower graph) at the center of the beam (b). The fabrication condition was the laser power of 600 mW with circular polarization.
Fig. 1.13 Variation in the diffraction efficiencies of the diffractive lenses with the heat treatment.
800 °C, rose up at 1000 °C and reduced again at 1200 °C. This curious phenomenon may be attributed to transfer of aluminum and oxygen atoms by the heat energy. By applying the heat treatment at the temperature of approximately 900 to 1000 °C to the sapphire plate whose surface is optically polished with small off angle from c-plain, the step and terrace structures can be generated on the sapphire surface[25]. The aluminum and oxygen atoms are reconfigured for reduction of the surface free energy. If similar reconfiguration of atoms in the modified region of sapphire crystal occurs by the heat treatment at the temperature of 1000 °C, there is a possibility that the refractive index change may increase and consequently the diffraction efficiency may improve. There might be an optimum heat treatment conditions to enlarge the refractive index change. Further investigation on the mechanism of the variation of the refractive index modification by the heat treatment is expected.

1.2.3 Numerical study on the diffraction efficiency

The diffractive lens with the 4 level approximation was created to obtain higher diffraction efficiency than 2 level approximation. The designed diffractive lens had a diameter of 1068 µm, a focal length of 15 mm at the wavelength of 633 nm, approximation level of 4. The sample used was a synthesized silica glass plate. Instead of using multilayer process, the laser powers were adjusted to derive three kinds of phase shifts according to the previous experiments shown in the Fig. 1.8 (a) and 1.9 (a). To obtain the phase shifts of \( \pi/2 \), \( 2\pi/2 \) and \( 3\pi/2 \), the deposited laser powers were 800 mW, 474 mW and 346 mW, respectively. From other experiments, it is found that the refractive index changes were negative and that the laser power of 800 mW induced the phase shift of \(-3\pi/2\) that was equivalent to \(+\pi/2\). Therefore, the phase shifts of \( \pi/2 \), \( 2\pi/2 \) and \( 3\pi/2 \) corresponded to the laser powers of 800 mW, 474 mW and 346 mW, respectively as shown in Fig. 1.16 (a) (b) and (c). Other fabrication conditions were the microscope objective of 5× with the numerical aperture of 0.14, the scanning speed of 25 µm/s and the scanning pitch of 2.5 µm. Fig. 1.14 shows optical microscope images of the diffractive lens. It can be confirmed that three
refractive index modified layers for the 4 level diffractive lens are created from the cross sectional view. The measurement value of the spot size \(1/e^2\) focused by the diffractive lens was 19 \(\mu m\) which was comparable to the theoretical value of 15 \(\mu m\) as shown in Fig. 1.15. However, the measurement value of the diffraction efficiency was 53.2 \%, which was smaller than the theoretical value of 81.1 \%.

To estimate fabrication errors which would be an origin of the discrepancy between the measurement and the theoretical values, numerical calculations on the diffraction efficiencies were carried out. Two types of fabrication errors by the process of laser irradiation were assumed. The first type is a position error and the second type is a phase error as defined in Fig. 1.16. Suppose that the position error of \(\Delta r\) and the phase error of \(\Delta \phi\) were both positive. It often occurred that the line position slightly escaped toward a radial direction if there was already a written line at the smaller radial position. It was due to the refraction of the femtosecond laser by the already written lines. That is the reason that the \(\Delta r\) was positive. The refraction of the femtosecond laser pulses also caused the short of the focusing and made \(\Delta \phi\) small. Since the phase shift by the laser irradiation was negative, the \(\Delta \phi\) was consequently positive. A focusing of the input light by the diffractive lens is expressed by the Fraunhofer diffraction. An equation of the Fraunhofer diffraction based on an approximation of the Fresnel-Kirchhoff diffraction formula is as follows [26]:

\[
U(x, y) = \int \int G(\zeta, \eta) e^{\frac{-2\pi i (s' \xi \eta)}{\lambda}} d\zeta d\eta. \tag{1.5}
\]

\(U(x, y)\) is a complex amplitude of an output beam at an observation point \((x, y)\). \(\lambda\) is a wavelength of an input beam. \(G(\zeta, \eta)\) is a pupil function at a position \((\zeta, \eta)\) in a phase object plane. In this case \(G(\zeta, \eta)\) is a transmission function of a diffractive lens. \(s'\) is a distance between an origin of xyz axes and the observation point. Fig. 1.17 illustrates the definition of each factor. An intensity of the diffraction light \(I(x, y)\) is expressed as

\[
I(x, y) = |U(x, y)|^2. \tag{1.6}
\]

Here the one-dimensional intensity distribution of the diffraction light was calculated. The pupil function for the 4 level diffractive lens is given by
Fig. 1.14 Optical microscope image of the diffractive lens generated inside the silica glass. The diameter of 1.06 mm, the focal length of 15 mm at 633 nm, and the approximation level of 4. (a): top view, (b): cross sectional view. The fabrication condition was the laser power of 346 mW, 474 mW, 800 mW with linear polarization. (c): magnified image of the step structure.
Fig. 1.15 Output beam intensity distribution which was focused by the diffractive lens inside the silica glass with the focal length of 15 mm and the approximation level of 4. The three-dimensional distribution (a) and one-dimensional distribution in the x and y direction (corresponding to the upper and lower graph) at the center of the beam (b). The fabrication condition was the laser power of 346 mW, 474 mW, 800 mW with linear polarization.
Fig. 1.16  Definition of the fabrication errors, actual structures modified by the femtosecond laser (a), position error (b), and phase error (c).

Fig. 1.17  Definition of the factors with regard to the Fraunhofer diffraction
\[
G(\xi) = C e^{\left(\frac{n\pi}{2}\Delta\phi\right)},
\]

where \(C\) is mainly dependent on the position of the light source and the observation point and usually constant in the case of the Fraunhofer diffraction regime, and \(n\) is integer from 0 to 3 that is corresponding to the 4 level approximation, for instance, 0 for laser non-irradiated part, 1 for the first step, etc. The pupil function is determined by the radius design from the Eq. (1.2), and in this case including position errors of \(\Delta r\). An example of utilized \(G(\xi)\) is depicted in the Fig. 1.18 (a). The diffraction efficiency was calculated by summing up the intensity at each observation point \(x\).

Calculation conditions were as follows: the input beam was a Gaussian beam with the beam diameter \((1/e^2)\) of 0.8 mm. The range of the position error was from 0 \(\mu m\) to 3 \(\mu m\) and that of the phase error was from 0 % to 50 %, which means

\[
\Delta\phi = P \times n \pi / 2
\]

where \(P\) is the percentage of the phase error. Fig. 1.18 (b) and (c) shows simulation results of the output beam intensity distributions focused by the diffractive lenses with the fabrication errors. Table 1.2 and 1.3 summarize calculation results of diffraction efficiencies with the position errors and the phase errors, respectively. Obviously the beam intensities become small with the increase in fabrication errors. It is speculated that the diffraction efficiencies with the phase errors are reduced more sensitively than with the position errors. If there is no position error, the phase error is estimated to be approximately 47 %. In the case of the position error of 1 \(\mu m\), 2 \(\mu m\) and 3 \(\mu m\), the phase error is expected to be 47 %, 45 % and 42 %, respectively.

From the microscope observation of the generated diffractive lens, the position errors were expected to be less than 3 \(\mu m\) because the laser irradiated and non-irradiated part could be distinguished at the largest concentric ring. However, the phase error of more than 40 % from this estimation was a considerably large value. It is suggested that adjacent modified areas may cause considerably large phase errors. The method for improving the diffraction efficiency is to deposit a larger power to compensate the phase errors. Further examinations on this issue are expected.
Fig. 1.18 The pupil function used for calculation (a), and the calculation results of beam intensity distributions with the position errors (b) and with the phase errors (c).
Table 1.2 Calculation results of diffraction efficiencies with position errors.

<table>
<thead>
<tr>
<th>Position error $\Delta r$ [µm]</th>
<th>Diffraction efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>74</td>
</tr>
</tbody>
</table>

Table 1.3 Calculation results of diffraction efficiencies with phase errors.

<table>
<thead>
<tr>
<th>Phase error $\Delta \phi$ [%]</th>
<th>Diffraction efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>79</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>30</td>
<td>69</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>50</td>
<td>51</td>
</tr>
</tbody>
</table>
In summary, the creation of the diffractive lenses inside dielectric materials such as the silica glass and the sapphire has been achieved. The polarization dependence of the diffractive lens can be controlled by the polarization state of the femtosecond laser. Moreover the diffractive lens with 4 level approximation has been produced only by the adjustment of the laser power. The fabrication errors have been also discussed by the numerical calculation and the improvement method for the diffraction efficiency has been demonstrated. The direct-writing technique by the femtosecond laser is expected as the simple fabrication process of the diffractive lenses.

References

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Chapter 2

Three-dimensional integration of micro-optics in bulk silica glass by femtosecond laser direct writing

In chapter 1, the fabrication of the diffractive optical elements inside dielectric materials by the femtosecond laser pulses has been demonstrated. Although conventional fabrication technique of the diffractive optical elements, namely photolithography technique is a well established method [1], the integration of these optics requires further procedures such as an alignment and a bonding of the several optics [2-7]. Additionally, optical designers have to consider the alignment errors and to design more severe tolerance for each diffractive optical element [8-10]. However, the femtosecond laser direct-writing technique can generate the diffractive optical elements at desired internal positions of the dielectric materials as described in the chapter 1, and expect the three-dimensional integration of the diffractive optics. As for optical waveguide fabrication, for instance, Watanabe et al. has recently reported the three-dimensional directional coupler by using this technique [11]. This is a great advantage compared to the traditional photolithography technique and single desktop femtosecond laser allows one to offer opportunities to attempt new ideas and to construct novel integrated optics in short time. In this chapter, various integrations of the diffractive optical elements inside bulk silica glass are demonstrated. First, a $1 \times 2$ Dammann grating and a diffractive lens were created and integrated inside one piece of silica glass. It was verified that the integrated optics had a new function of the combination of splitting and focusing. Next a $4 \times 4$ Dammann grating (more complicated pattern compared to $1 \times 2$ Dammann grating) and a diffractive lens were generated and integrated in the silica glass. It was also proved that performance of splitting and focusing in two-dimensional focal plane was obtained. From a practical point of view, two industrial applications are proposed. The first application is the
integrated optics with the Dammann grating and the diffractive lens for a photo-detector with high efficiency. Its concept and simple evaluation results are demonstrated. The second application is a miniature spectrometer by the integration of two diffractive lenses inside silica glass and a pin hole on its surface. Device concepts and the evaluation results are described.

2.1 Integration of a 1×2 Dammann grating and a diffractive lens

In chapter 1, the method for fabricating the Dammann grating and the diffractive lens has been developed. Based on this technique, the integration of the 1×2 Dammann grating and the diffractive lens inside one piece of glass was attempted. Design values of the 1×2 Dammann grating were a period of 45.6 µm and a size of 1 mm square. As for the diffractive lens, the design values were a focal length of 9 mm operating at a wavelength of 633 nm, an approximation level of 4 and a diameter of 1.02 mm. An optical configuration of the integration of the 1×2 Dammann grating and the diffractive lens is represented in Fig. 2.1. A dimension of bulk silica glass was 5 mm square with a length of 10 mm. The longitudinal direction was parallel to the optical axis of the integration system. A distance between the 1×2 Dammann grating and the diffractive lens was 9 mm which was equal to the focal length of the diffractive lens. As illustrated by the dashed lines in Fig. 2.1, an incident beam from the left-hand side would be split into two beams by the 1×2 Dammann grating and focused at its focal plane by the following diffractive lens. A distance between the two focused beams, namely a splitting distance, is 250 µm which was designed from the diffraction angle and the focal length. A sample was a synthesized silica glass plate (Shinetsu Suprasil P10) whose surfaces were all optically polished for observations by an optical microscope after the femtosecond laser direct writing. Fabrication conditions were as follows: an objective lens was 5× (NA 0.14), a laser scanning speed was 25 µm/s, a repetition rate was 200 kHz, and a pulse duration was 140 fs. The laser power adjusted was 550 mW and to obtain large phase modulations, the multilayer process was applied. Two layers of the refractive index modified region
Fig. 2.1 Schematic diagram of the integrated optics utilizing the $1 \times 2$ Dammann grating and the diffractive lens.
were constructed for the $1 \times 2$ Dammann grating. The integration process was very simple: first, the $1 \times 2$ Dammann grating was formed inside the glass plate at a depth of 9.5 mm from the top surface of glass. Successively, a focal point was moved up at a depth of 0.5 mm and the diffractive lens was created above the grating. No alignment or bonding was necessary. Optical microscope images of the $1 \times 2$ Dammann grating and the diffractive lens generated by the femtosecond laser direct-writing technique are shown in Fig. 2.2. Obviously, the $1 \times 2$ Dammann grating and the diffractive lens were successfully created inside a single piece of glass. In particular, as shown in Fig. 2.2 (a), one can see that there is a shade of the diffractive lens below the $1 \times 2$ Dammann grating and that transmit white light for microscope observation are focused by the diffractive lens itself.

To evaluate optical characteristics of the fabricated optics, an input beam was transmitted through the integrated optics to measure an output beam intensity distribution at the focal plane. The incident light source was a He-Ne laser with a wavelength of 632.8 nm. The output beam intensity distribution was measured by a near field pattern measurement system (LEPAS-11, Hamamatsu Photonics K.K.). Fig. 2.3 indicates measurement results of a three-dimensional beam intensity distribution and one-dimensional beam profiles of the split beams. Apparently, two split beams of equal intensity were obtained as it had been designed. Each split beam had no side peaks and the beam intensity distributions (black curves) were well fitted to the Gaussian beams (red curves). Focused spot sizes ($1/e^2$) were measured and an average value of two split beams was 13.1 µm. A measurement value of the splitting distance between the two beams was 252 µm, which was comparable to the design value of 250 µm. A diffraction efficiency was an important property in terms of an optical loss. In this experiment, the diffraction efficiency $\eta$ of the integrated optics is defined as follows:

$$\eta = \frac{\sum I_{\text{split}}}{I_{\text{in}}} ,$$  (2.1)

where $I_{\text{split}}$ is the split beam intensity at the focal plane and $I_{\text{in}}$ is the input beam intensity. By using a pin hole, each split beam at the focal plane was distinguished
Fig. 2.2 Optical microscope images of the $1 \times 2$ Dammann grating (a), (b) and the diffractive lens (c), (d). (a), (b): top views, (c), (d): side views.
Fig. 2.3 Split beam intensity distributions at the focal plane. Three-dimensional intensity distribution (a) and beam profiles of the left and right beams (b), (c), respectively. Black curves are measured values and red curves are Gaussian fitting curves.
from other diffraction lights and split beam power was measured by a photo-detector (Q82214, Advantest Co.). The measurement value of the diffraction efficiency for the fabricated optics system was 27.1 %. Additionally, we formed a 1×2 Dammann grating and a diffractive lens individually to evaluate the optical loss from the integration process. Fabrication conditions were the same as those adopted in the integrated optics. As for the individual diffraction efficiency, the measured values of the 1×2 Dammann grating and the diffractive lens were 73.5 % and 39.1 %, respectively. As summarized in Table 2.1, an estimated value from a product of the diffraction efficiencies of the individual grating and lens is 28.7 %. Comparing to the measurement value of 27.1 % for the actual integrated optics, the loss from the integration process is considered to be negligible small. Thus, the attempt of the integration by the femtosecond laser direct writing was quite successful.

2.2 Integration of a 4×4 Dammann grating and a diffractive lens

A further challenging experiment on the integration of a 4×4 Dammann grating and a diffractive lens in a silica glass was carried out. A refractive index pattern of the 4×4 Dammann grating is more complicated and precise compared to that of the 1×2 Dammann grating. The 4×4 Dammann grating has five phase transition points of 0.221Δ, 0.446Δ, 0.500Δ, 0.721Δ and 0.946Δ within a single period of Δ [12]. The maximum diffraction efficiency of the 4×4 Dammann grating is 49.9 %. Design values of the 4×4 Dammann grating were a period of 191.5 µm and a size of 1.15 mm square. As for the diffractive lens, the specifications were a focal length of 9 mm operating at a wavelength of 532 nm, an approximation level N of 2 and a diameter of 1.21 mm. As shown in Fig. 2.4, an optical arrangement of the integrated optics was as follows: A distance between the 4×4 Dammann grating and the diffractive lens was 9 mm which was equal to the focal length of the diffractive lens. A splitting distance was 50 µm. A dimension of bulk silica glass was 5 mm square with a length of 10 mm (the same dimension as the sample in section 2.1). A sample was a synthesized silica glass plate (Shinetsu Suprasil P20) whose surfaces were optically
Table 2.1 Diffraction efficiencies of the integrated optics (a), individual optics (b) and (c), and estimated value by integration of each optics (d).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diffraction efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Integrated optics with the $1 \times 2$ Dammann grating and the diffractive lens</td>
<td>27.1</td>
</tr>
<tr>
<td>(b) $1 \times 2$ Dammann grating</td>
<td>73.5</td>
</tr>
<tr>
<td>(c) Diffractive lens</td>
<td>39.1</td>
</tr>
<tr>
<td>(d) Product of (b) and (c)</td>
<td>28.7</td>
</tr>
</tbody>
</table>
Fig. 2.4 Schematic diagram of the integrated optics employing the $4 \times 4$ Dammann grating and the diffractive lens.
polished for microscope observations. Fabrication conditions were as follows: an objective lens was 5× (NA 0.14), a repetition rate was 200 kHz, a pulse width was 140 fs, a laser scanning speed was 100 μm/s, and a laser power was 400 mW. A scanning pitch for the 4×4 Dammann grating and the diffractive lens were 0.625 μm and 1.25 μm, respectively. The scanning speed and the laser power were optimized to obtain the maximum diffraction efficiency as possible. The integration process was performed in the same manner as used in section 2.1. Primary, the 4×4 Dammann grating was formed inside the glass plate at a depth of 9.5 mm from the top surface of the 5 mm square plane. Succeedingly, a focal point was moved up at a depth of 0.5 mm and the diffractive lens was created above the grating. Optical microscope images of the 4×4 Dammann grating and the diffractive lens generated by the femtosecond laser direct-writing technique are shown in Fig. 2.5. Apparently, two diffractive optical elements were embedded inside a bulk silica glass.

An input beam was transmitted through the integrated optics to evaluate an output beam intensity distribution at the focal plane. The incident light source was a green laser with a wavelength of 532 nm. The output beam intensity distribution was measured by a laser beam profiler (BeamStar FX 50, SPIRON). Fig. 2.6 indicates a two-dimensional and a three-dimensional output beam intensity distributions. Although the zero order transmit light at the center was relatively strong, 16 split beams were successfully obtained as it had been designed. An average of the splitting distances between the beams was 48 μm, which was close to the design value of 50 μm. Additionally, the diffraction efficiency as defined by Eq. (2.1) was also measured by the same way in the section 2.1. The measured diffraction efficiency of the integrated optics was 4.6 %, while those of an individual 4×4 Dammann grating and a diffractive lens were 27.8 % and 20.5 %, respectively. As summarized in Table 2.2, an estimated value from a product of the diffraction efficiencies of the individual grating and lens is 5.7 %. Thus a loss from the integration process is approximately 1 % and this means the integration process was quite successful.
Fig. 2.5 Optical microscope images of the $4 \times 4$ Dammann grating (a), (b) and the diffractive lens (c), (d). (a), (b): top views and (c), (d): side views
Fig. 2.6 Split beam intensity distributions at the focal plane. (a): two-dimensional intensity distribution, (b): three-dimensional intensity distribution.
Table 2.2 Diffraction efficiencies of the integrated optics (a), individual optics (b) and (c), and estimated value by integration of each optics (d).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diffraction efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Integrated optics with the $4 \times 4$ Dammann grating and the diffractive lens</td>
<td>4.6</td>
</tr>
<tr>
<td>(b) $4 \times 4$ Dammann grating</td>
<td>27.8</td>
</tr>
<tr>
<td>(c) Diffractive lens</td>
<td>20.5</td>
</tr>
<tr>
<td>(d) Product of (b) and (c)</td>
<td>5.7</td>
</tr>
</tbody>
</table>
2.3 Potential for industrial application: a high efficiency photo-detector

It is proposed that the integrated optics employing the Dammann grating and the diffractive lens can be applied for a high efficiency photo-detector. In general, the photo-detector consists of a photodiode array, electrodes, a can and a glass window. Since each photodiode is separated by the electrodes, the photo-detector cannot collect 100% of incident light as shown in Fig. 2.7. If an integrated optics with a Dammann grating and a diffractive lens is generated inside the glass window and it can split the input beam and focus the split beams onto each photodiode, not onto electrodes, the collection efficiency of the incident light will be improved dramatically. The splitting distance and spot sizes of the focused split beams can be controlled by designs of the Dammann grating and the diffractive lens. Fig. 2.8 demonstrates the example of controlled spot sizes by various observation planes. The spot sizes of the focused split beams became larger as the observation planes got close to the glass surface.

2.4 Potential for industrial application: a miniature spectrometer

A further experiment on the integration of the micro optics was performed. In the research filed of spectroscopy, robust spectrometers are usually used. There are several kinds of structures for the spectrometers, for example, a prism type, a grating type, etc. As for the grating type, the spectrometer consists of discrete optics such as a collimating unit for leading an incident light to the grating, the grating for separating the wavelengths and a camera lens for focusing a diffracted light onto the camera. In recent years, a micro Fresnel lens whose focal length strongly depends on wavelength has been employed for the micro spectrometer [13]. This spectrometer uses the micro Fresnel for separating the wavelength and for focusing the diffracted lights. Therefore, the Fresnel lens simplifies the conventional structure with the grating and the focusing lens. However, it consists of discrete optics such as a pin hole, a collimating lens and a Fresnel lens. It is our challenge to create an integrated structure that consists of the
Fig. 2.7 Conceptual illustration of the high efficiency photo-detector. (a): top view, (b): side view. The input beam is split and focused by the integrated optics and irradiated to each photodiode.
Fig. 2.8 Split beam intensity distributions at various observation planes. (a): at focal plane (=f), (b): at f-0.05mm, (c): at f-0.10mm.
pin hole and the diffractive lenses for a miniature spectrometer. Fig. 2.9 indicates a schematic diagram of the integrated optics. A pin hole is created on a metal film that is coated on a glass surface of an incident side. A combination of the pin hole and a diffractive lens 1 collimates an incident light when the wavelength of the input beam is equal to the design wavelength of the diffractive lens 1. A diffractive lens 2 focuses the incident light at its focal plane. Since the diffractive lens 1 and 2 have large dispersion, the focal plane is varied according to the wavelength of the incident light. If a photo-detector with a pin hole which is set after the diffractive lens 2 moves along the optical axis, the wavelengths of the input beam are transformed into the positions of the photo-detector.

Design values of diffractive lenses in this experiment were as follows: a focal length was 9 mm operating at a wavelength of 532 nm, an approximation level N was 2 and a diameter was 1.21 mm. A design diameter of a pin hole was 6 microns. As shown in Fig. 2.9, a distance between the pin hole and the diffractive lens 1 was 9 mm, and a distance between the diffractive lens 1 and 2 was also 9 mm. A sample was a synthesized silica glass plate (Shinetsu P20), $5 \text{ mm} \times 5 \text{ mm} \times 18.5 \text{ mm}$. All surfaces of the glass plate were optically polished for microscope observations. Fabrication conditions on the diffractive lenses were as follows: an objective lens was $5 \times$ (NA 0.14), a repetition rate was 200 kHz, a pulse width was 140 fs, a laser scanning speed was 100 $\mu$m/s, and a laser power was 400 mW. Fabrication conditions on the pin hole were as follows: an objective lens was $10 \times$ (NA 0.26), a repetition rate was 200 kHz, a pulse width was 140 fs, a laser scanning speed was 5 $\mu$m/s, a scanning diameter was 2 microns and a laser power was 5 mW. Primarily, a platinum film was coated on the glass surface of a 5 mm 5 mm plane. Succeedingly, the diffractive lens 1 was formed inside the glass plate at a depth of 9.5 mm from the non coated glass surface of a 5 mm 5 mm plane, then a focal point was moved up at a depth of 0.5 mm from the glass surface and the diffractive lens 2 was created above the diffractive lens 1. Finally the glass sample was upset and the pin hole was created on the surface of the Platinum film by laser ablation. Input beams with various wavelengths were transmitted through the integrated optics to evaluate distances between the glass
Fig. 2.9 Schematic diagram of the integrated optics employing the pin hole and the diffractive lenses. $f$ is a focal length operating at the design wavelength of the diffractive lens 1 & 2. $f_r$, $f_g$ and $f_b$ are the focal lengths for red, green and blue light, respectively.
surface of the 5 mm × 5 mm plane and focal planes of output beams. The incident lights used were a He-Ne laser, a green laser and a blue laser with wavelengths of 633 nm, 532 nm and 405 nm, respectively. The focal planes of the output beams were observed by the laser beam profiler (BeamStar FX 50, SPIRICON). The laser beam profiler was set on an XYZ stage, and the distances were measured by travels of the XYZ stage. Table 2.3 indicates measurement and theoretical values of the distances at various wavelengths. The theoretical values were calculated by a following method. In case of the diffractive lens, a focal length $f$ operating at an arbitrary wavelength $\lambda$ is given by following equation:

$$ f = f_1 \lambda_1 / \lambda, $$

where $f_1$ and $\lambda_1$ are design values of the focal length and the wavelength, respectively. The focal lengths at various wavelengths were calculated and the distances between the glass surface and the focal planes were simulated from the geometric optics. It was verified that the distance between the glass surface and the focal plane became smaller as the wavelength of the input beam increased. It was due to the typical dispersion characteristics of the diffractive lens. Therefore, it was confirmed that the integrated optics with the pin hole and the diffractive lenses could function as a spectrometer. However, there were discrepancies between the measurement and the theoretical values of the distances between the glass surface and the focal plane. It has been found that the focal length of the diffractive lens was varied by the written depth from the glass surface. This phenomenon may be related to the cause of the discrepancies. This issue is under study.

In summary, the integration of various micro-optics inside bulk silica glass by using the femtosecond laser direct-writing technique has been demonstrated. It has been proposed that the integrated optics with the Dammann grating and the diffractive lens has potential for the application of the high efficiency photo-detector. It was also verified that the integrated optics with the pin hole and the diffractive lenses had the function as the spectrometer. The femtosecond laser direct-writing technique is a promising method to broaden the possibility of the integrated optics.
Table 2.3 Distances between the glass surfaces and the focal planes at various wavelengths of the input beams.

<table>
<thead>
<tr>
<th>Wavelength of the input beam [nm]</th>
<th>Distance between the glass surface and the focal plane [mm]</th>
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</thead>
<tbody>
<tr>
<td>405</td>
<td>11.70 ± 0.10</td>
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<tr>
<td>532</td>
<td>8.68 ± 0.02</td>
</tr>
<tr>
<td>633</td>
<td>7.27 ± 0.07</td>
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References

Chapter 3

Fabrication of precision micro-holes and micro-channel structures with smooth surfaces by a high repetition rate femtosecond laser

In recent years, micro-holes and micro-channel structures have been frequently applied for the industrial fields such as micro optics and micro fluidics. The typical devices for micro-optics are micro-hole array and V-groove array for optical interconnections and optical fiber alignments. These applications have been widely utilized for the practical use into the information technology market. As for the micro-fluidics, the micro-channel structures have been currently developed by many researchers with increasing demands from various chemical and biological analyses [1-4]. In particular, the micro total analysis system (µ-TAS) is expected to be the promising method for medical diagnosis, synthesis of new materials, environmental monitoring and so on [5]. The µ-TAS is capable of measuring nano-liter or even pico-liter volume of reagents resulting in fast reaction, high speed and cost-effective analysis, minimized reagent consumption and waste product and enhanced portability. In general, µ-TAS consists of micro-channel chips for the chemical reaction, injection unit for the infusion of reagents and an optical analysis system. There are various fabrication methods for micro-channels corresponding to their applications [6]. Ordinarily, the micro-channels are created by conventional semiconductor processing based on photolithography technique. Although the photolithography technique has been well established and is suitable for surface microfabrication, complex procedures including alignment and bonding substrates is required to produce the micro-channel chip. As mentioned in the previous chapters, the femtosecond laser pulses can realize internal modification of the dielectric materials. By using this technique and combining the post chemical etching, the three-dimensional micro-holes and micro-structures in dielectric materials have been currently developed [7-13]. Compared to
the conventional photolithography technique, this direct-writing method by the ultrashort pulses has several advantages such as superior abilities to create a three-dimensional channel structure without a photomask and to manufacture the channel chip without the substrate bonding. According to [9], the micro-channels in silica glass have been fabricated by the focused femtosecond laser irradiation and following selective etching with a hydrofluoric (HF) acid solution. However, a roughness of the channel sidewalls ranged from 0.96 µm to 1.6 µm and it is not sufficiently smooth for the micro-fluidic devices that exploit laminar flow or require microscope observation of the reagents by a transmitted light. In this chapter, micro-holes and microstructures that have smooth internal surfaces with average surface roughness (Ra) of approximately 10 nm are demonstrated. These microstructures are more suitable for micro-fluidic devices.

The similar technique to the method utilized in Ref. [9] was employed. However, a femtosecond laser system with high repetition rate was incorporated to form the optically damaged structures inside a silica glass. The laser system adopted was a combination of a mode locked Ti:Sapphire laser and a regenerative amplifier with the wavelength of 800 nm, the pulse width of 150 fs, the repetition rate from 10 kHz to 300 kHz, and the maximum laser power of 800 mW at 200 kHz. To reveal the effects of the laser repetition rate on internal surface roughness of the structures, another ultrashort pulse laser system with low repetition rate of 1 kHz, the wavelength of 780 nm, the pulse duration of 150 fs and the maximum laser power of 800 mW, was utilized. As shown in Fig. 1.1, the femtosecond laser pulses focused by the microscope objective were exposed inside the glass sample that was set on the xyz translation stage. Usually, the focal point of the femtosecond laser was moved from the bottom to the top surface of the sample. The sample used was synthetic silica glass plates. After the laser irradiation, the glass was etched by an aqueous solution of HF acid to dissolve the photo induced structures. From the following section, several examples of microstructures are introduced, and the effects of laser repetition rate on internal surface roughness of the micro-holes are discussed.
3.1 Fabrication of microstructures

The first example of the microstructures created by the femtosecond laser assisted microfabrication is precision taper holes as indicated in Fig. 3.1. Fabrication conditions were as follows: The average laser power was 74 mW, the objective lens was $20 \times$ with the numerical aperture of 0.4, the repetition rate was 200 kHz, the translating speed was 36 $\mu$m/s, the translating direction was parallel to the laser beam from the bottom to the top surface of the sample, and the etching condition was HF acid solution with concentration of 47 weight % for 5 hours. The taper shape was formed due to an over etching, which dissolved a laser non-irradiated part of glass as well as the laser exposed part. Although the etch rate of the photo induced area was higher than that of the non-irradiated area, the dissolution of the non-exposed part could not be suppressed completely. As opposed to suppressing the over etching, by making use of the difference of etch rate between the modified part and the bulk, the taper shape with desired taper angel could be produced through a simple process. In this experiment, the fabricated hole had diameters of 600 $\mu$m at the top surface, 650 $\mu$m at the bottom surface, the smallest diameter of 65 $\mu$m at the waist and the taper angle of approximately 17 degrees. From the microscope observation, the internal surface of the micro-hole was smooth like a polished surface.

Another structure generated by the ultrashort pulses is a Y-shaped micro-channel as shown in Fig. 3.2. Fabrication conditions were the same as those adopted for the taper holes, as described above. Primarily, the photo induced modifications of the branches were conducted and successively, the exposure of the main stream parallel to the laser incident direction was carried out. After the HF etching, the Y-shaped micro-channel with the diameter of approximately 700 $\mu$m at the top surface and ellipse shape of a horizontal axis of 750 $\mu$m and a vertical axis of 700 $\mu$m at the bottom surface, was created. The smallest diameter at the junction of the channel was 154 $\mu$m. Apparently internal surface of these holes fabricated by the femtosecond laser with the high repetition rate were smooth and the transmitted light by the microscope observation was reflected at the internal surface of the holes like a mirror.
Fig.3.1 (a) A photograph of micro-taper hole array and (b-d) microscopic view of the taper hole. (b) top view, (c) bottom view and (d) side view. The taper angel represents an angle indicated in (d).
Fig. 3.2 (a) A photograph of micro-channel array and (b-e) microscopic view of the micro-channel. (b) top view, (c-d) bottom view and (e) side view.
The roughness of the inner surface of the hole should be quantified for the application of the micro fluidic devices. The sample with the micro-hole fabricated by this technique was polished until the internal surface appeared. After polishing, the surface roughness in an area of 4 µm square was measured by an atomic force microscope (AFM, Seiko Instruments Inc., Nanopics 1000). Since the data on the surface profile included the roundness of the micro-hole, a flattening process by the software was applied to the raw data to remove the roundness and to acquire the surface roughness of the holes. The arithmetical mean deviation of the assessed profile (Ra) and the maximum height of the profile (Rz) were evaluated and the measurement values of Ra and Rz were 4.5 nm and 63 nm, respectively. To compare these values with other surface morphology, the glass surfaces processed by grinding and polishing were also measured by the AFM. The measurement values of Ra for the grinding and polishing surfaces were 100 nm and 0.3 nm, respectively. Thus, the internal surface roughness of the hole created by the femtosecond laser assisted microfabrication was in between the grinding and the polishing surface. On the other hand, the surface roughness of Rz could be reduced less than a tenth of the sample in Ref. [9], namely formed by the femtosecond laser with the repetition rate of 1 kHz.

3.2 Effects of repetition rate on surface roughness

Moreover, the effects of the laser repetition rate on surface roughness of the hole were examined. The micro-holes were created under the identical fabrication conditions except the laser repetition rate. The common fabrication conditions were the laser intensity of $4.2 \times 10^5$ TW/m$^2$, the objective lens of 20× with the numerical aperture of 0.4, the translating speed of 145 µm/s, and the etching by HF concentration of 47 weight % for 1 hour. The material used was synthetic silica glass, Shinetsu Suprasil P-10. The repetition rate conditions were 200 kHz, 100 kHz, 50 kHz, and 10 kHz. To compare these samples with a sample similar to the Ref. [9], another sample with rather rough internal surface was created. It was fabricated by the repetition rate of 1 kHz and the laser intensity of $4.5 \times 10^6$ TW/m$^2$. Fig. 3.3 shows the
Fig. 3.3 Microscopic view of the sample (a) before and (b) after the etching of 47% HF for 1 hour.
microscope images of the samples before and after the etching. Obviously, before the etching, the samples produced by the repetition rate of 10 kHz to 200 kHz had uniform refractive index modifications while the sample exposed by the pulses with the 1 kHz had teardrop like structures. After the etching, the surface morphology of the holes inherited from the uniformity of the photo induced structure. Furthermore, the fabricated samples were processed by the grinding until the internal surfaces of the holes were revealed. Fig. 3.4 indicates the three-dimensional images of the micro-holes obtained by a scanning electron microscope (SEM, JEOL JSM-5800LV). Apparently, the samples generated by the repetition rate of 10 kHz to 200 kHz had smooth internal surfaces while the sample by the repetition rate of 1 kHz had a rather wavy surface.

The quantification of the internal surface roughness was conducted by the atomic force microscope and a laser scanning microscope (LSM, KEYENCE VK-8500). The AFM was employed for precise measurements by small evaluation areas and the precise height resolution of 0.5nm, and the LSM was used for rough measurements by the wider evaluation areas and a lower resolution of 10nm. Fig. 3.5 represents three-dimensional surface structures in the areas of 10 µm square measured by the AFM. It appears that there were not drastic differences in surface morphology. Fig. 3.6 indicates the AFM measurement result of the Ra and the Rz in the area of 4 µm square as a function of the laser repetition rate. Comparing the samples fabricated by the repetition rate of 10 kHz to 200 kHz, the measured values of the Ra were approximately 10 nm while those of the Rz ranged from 51 nm to 1.0x10^2 nm and the minimum value of 51 nm was obtained at the repetition rate of 50 kHz. Fig. 3.7 shows the LSM measurement result of the Ra and the Rz in the evaluation length of 139 µm as a function of the laser repetition rate. In the case of the samples exposed by 10 kHz to 200 kHz, the measurement values of the Ra were around 0.1 µm while the minimum value of the Rz of 0.39 µm was acquired at 100 kHz. From these results, it was found that the laser repetition rate yielded little influence on the Ra and that the optimum repetition rate condition existed for the Rz. In the case of the micro-holes fabricated by 1 kHz, the measurement value of the Ra by the AFM was about 10 nm, which was similar to those of other cases. As for the Rz measured by the AFM and the
Fig. 3.4 SEM images of the holes’ internal surfaces. From 10 kHz to 200 kHz the samples have smooth internal surfaces. The 1 kHz sample has a rather wavy surface.
Fig. 3.5 Three-dimensional surface structures measured by an atomic force microscope. A measurement area was 10 µm × 10 µm.
Fig. 3.6 Measurement results of the surface roughness by an atomic force microscope. The horizontal axis is represented as a logarithmic scale. The variation among the measured values of roughness is small.
Fig. 3.7 Measurement results of the surface roughness by a laser scanning microscope. The horizontal axis is represented as a logarithmic scale. The roughness tends to increase with the decrease in the repetition rate.
Ra and Rz by the LSM, obtained values were obviously larger than those of other conditions.

Structural variations of the glass by the laser irradiations were also analyzed. The photo-induced refractive index change inside the glass samples were produced under the same laser conditions as for the previous surface roughness experiment. Parallel modified lines with an interval of 10 µm and a length of 3 mm were formed inside a glass in an area of 3 mm square. The increase in absorbance before and after the laser irradiation for each sample was measured by a spectrophotometer (Shimazu, UV-2400PC). Fig. 3.8 illustrates the measurement result of the increase in absorbance as a function of a wavelength. Obviously, the curve obtained from the 1 kHz sample had a peak at the wavelength of 245 nm and another peak at 215 nm. These peaks at the wavelength of 245 nm and 215 nm can be attributed to oxygen deficiency centers ODC (II) and E’ centers, respectively [14]. The other curves acquired from the samples fabricated by the repetition rate of 10 kHz to 200 kHz had the same peaks although the intensities of the increase in absorbance were not so strong. Thus it is presumed that the sample formed by 1 kHz has the largest amount of defects and that the nonuniformity of the photo-induced structures might cause the increase in the amount of the defects. The origins of the nonuniform structures were related to several factors such as an overlap between the laser pulses, a variation of the pulse energies, etc. Although other defects might occur [15, 16], further investigation on this matter is expected.

In conclusion, the unique microstructures with smooth internal surfaces by utilizing the femtosecond laser with the high repetition rate have been demonstrated. The surface roughness of the holes formed by different repetition rates has been also examined and it has been demonstrated that the optimum laser repetition rate exited for reduction of the surface roughness. Moreover, it is suggested that increase in surface roughness might be related to the increase in the amount of defects by the laser irradiation.
Fig. 3.8 Measurement results of the increase in absorbance before and after the laser irradiation by a spectrophotometer. The peak intensity of absorbance tends to increase with the decrease in the laser repetition rate.
References

Chapter 4

Valence state manipulation of metal ions and coloring in glasses
induced by femtosecond laser pulses

Materials with three dimensionally modulated microstructures have potential applications in optical field [1,2]. Up to now, there have been much investigation on the three-dimensional microfabrication [3–5]. Braun and Witzius have successfully fabricated three-dimensional structures of semiconductors by template-directed electrochemical deposition [3]. Cumpston et al. have succeeded in the fabrication of microoptical elements with two-photon photopolymerization [4]. Holographic lithography has been used to fabricate three-dimensional photonic crystals, which have periodical dielectric structures and can manipulate light in much the same way that a superconductor manipulates electrons [5].

It is well known that laser light can be pulsed and focused to a spot of wavelength order. Ultrashort pulsed laser has been used as a powerful tool to clarify elementary processes, such as excitation-energy relaxation and both electron and proton transfer on nanosecond and picosecond time scales, that occur in a micrometer-sized area [6,7]. Ultrashort pulsed laser can also be used to make microscopic modifications to transparent materials. The reason for using this laser is that its electric field intensity can reach 10 TW/cm², which is sufficient for inducing nonlinear optical effects in materials by use of a focusing lens, when the pulse width is 100 fs and the pulse energy is 1 µJ. The photoinduced reaction is expected to occur only near the focused part of the laser beam due to nonlinear optical processes.

Up to now, there have been a lot of studies on the microscopic modifications in transparent materials by using femtosecond lasers [8–14]. Various induced structures can be produced by using pulsed laser operating at the nonresonant wavelength with pulse widths of the order of femtosecond; colored lines due to the formation of color
center, refractive index spot due to densification and defect formation, microvoid due
to remelting and shock wave, microcrack due to destructive breakdown, etc. [14]
Composite structures were also observed after the focused femtosecond laser
irradiation [14]. Promising applications using these phenomena have also been
demonstrated for three-dimensional optical memory, integrated optical circuit, and
optical display [8–14].

4.1 Space selective valence state manipulation of transition metal ions inside
glasses

In this section, the observation of space selective valence state manipulation of
transition metal ions in transparent materials is described. Space selective persistent
photo-oxidation of Mn$^{2+}$ to Mn$^{3+}$ in a silicate glass, which was induced by focusing
120 fs laser pulses from a regeneratively amplified Ti sapphire laser through a
microscope objective lens, was observed. Absorption and electron spin resonance
spectra were measured for the glass before and after the femtosecond laser irradiation.
The mechanism of the phenomenon is also discussed.

Glass composition of the Mn and Fe ions codoped silicate glass sample used in
this study was 0.05Fe$_2$O$_3$.0.1MnO.70SiO$_2$.10CaO.20Na$_2$O(mol%). Regent grade
SiO$_2$, CaCO$_3$, Na$_2$CO$_3$, Fe$_2$O$_3$, and MnO were used as starting materials. An ～40 g
batch was mixed, and placed into a platinum crucible. Melting was carried out in an
electronic furnace at 1550 °C for 1 h under the ambient atmosphere. Glass sample was
obtained by quenching the melt to room temperature. The glass sample thus obtained
was transparent and colorless. The glass sample was cut, polished, and subjected to
experiments.

A regeneratively amplified 800-nm-Ti sapphire laser that emits 120 fs, 1 kHz,
mode-locked pulses was used for our study. The laser beam with an average power of
400 mW was focused by a 10× objective lens with a numerical aperture of 0.30 on
the interior of the glass sample with the help of an XYZ stage. The spot size (diameter)
of the laser beam was estimated to be 10 µm.
Absorption spectra of the glass samples were measured by a spectrophotometer (JASCO V-570). Electron spin resonance (ESR) measurements were carried out at X-band frequency (9.8 GHz) by an ESR spectrophotometer (JEOL-FE3X). The microwave power, time constant, modulation amplitude, and sweep time was 1 mW, 0.03 s, $1 \times 10^2$, and 4 cm/min, respectively. All of the experiments were carried out at room temperature.

Fig. 4.1 shows the image of the spots after irradiation by the focused infrared femtosecond laser on each spot for 1/63 s (i.e., 16 pulses). A 4 µm spot was formed in the focused area of the laser beam in the Mn and Fe ions codoped glass sample. In addition, a purple colored area with diameter of about 30 µm was observed around the spot. The length of the induced structure along the axis of the laser beam was about 1.5 mm via the observation of optical microscope. To measure the absorption spectrum of the glass sample after the laser irradiation, we wrote a “damaged” plane of $3.0 \times 3.0$ mm$^2$ inside the glass sample, which consisted of “damaged” lines at an interval of 10 µm by scanning the laser beam at a rate of 1 mm/s. The distance of the plane from the surface of the glass sample was about 0.5 mm.

Fig. 4.2 shows the absorption spectra of the glass sample before (a) and after (b) the femtosecond laser irradiation. No apparent absorption was observed for the unirradiated glass sample in the wavelength region from 400 to 1000 nm, while there was an apparent increase in the absorbance in the wavelength region from 300 to 1000 nm in the irradiated region. The inset of the Fig. 4.2 shows the difference absorption spectrum of the glass sample after and before the femtosecond laser irradiation. A peak ranging from 400 to 800 nm, peaking at 520 nm was observed. This peak can be ascribed to the absorption of Mn$^{3+}$ ions [15,16]. In addition, a peak was observed at 320 nm, which can be assigned to the absorption of hole-trapped centers as observed in the x-ray irradiated silicate glasses [17].

Fig. 4.3 shows the absorption spectra of the femtosecond laser-irradiated glass sample annealed at various temperatures for 1 h. No apparent decrease was observed in the laser-induced absorption at temperature below 300 °C. Any variation for the absorption of the induced Mn$^{3+}$ ions at room temperature was not observed even after
Fig. 4.1 Image of induced spots in the Mn and Fe ions codoped silicate glass after focused 800 nm femtosecond laser for 1/63 s on each spot. Distance between adjacent spots is 50 µm.
Fig. 4.2 Absorption spectra of the Mn and Fe ions codoped silicate glass before (a) and after (b) the femtosecond laser irradiation. The inset shows the difference spectrum between absorption of the glass sample after and before the femtosecond laser irradiation.
Fig. 4.3 Absorption spectra of the irradiated Mn and Fe ions codoped silicate glass annealed at various temperatures for 1 h.
one month. Therefore, the induced Mn$^{3+}$ ions are thermally stable.

Fig. 4.4 shows the electron spin resonance spectra of the glass sample before and after the femtosecond laser irradiation at room temperature. The spectrum of unirradiated glass exhibits a resolved hyperfine structures of six lines spread over a range of about 500 G in width centered at 3350 G (splitting coefficient $g \sim 2.0$). The spectrum showed a pattern similar to those observed for various glasses containing Mn$^{2+}$ ions [18]. The low resolution of the hyperfine lines is due to the dipolar broadening. In Fig. 4.1, no apparent absorption due to Mn$^{3+}$ was observed in unirradiated glass. Therefore, most of Mn ions are present as divalent state in glass. Two new signals at $g$ of 2.010 and 2.000 were observed in the glass sample after irradiation. The signals can be assigned to hole-trapped centers in the glass matrix [19].

From the above results, a part of Mn$^{2+}$ was oxidized to Mn$^{3+}$ after the femtosecond laser irradiation. Mn and Fe codoped silicate glass sample has no absorption in the wavelength region near 800 nm. Therefore, photo-oxidation of Mn$^{2+}$ to Mn$^{3+}$ should be a nonlinear optical process. It is suggested that multiphoton absorption be one of the mechanism of the observed phenomenon [20]. Free electrons are generated by the multiphoton absorption of the incident photon and consequent avalanche ionization. Mn$^{2+}$ captures a hole to form Mn$^{3+}$, while Fe$^{3+}$ as well as active sites in glass matrix may act as electron trapping centers, resulting in the formation of Mn$^{3+}$. However, the length of the induced structure (1.5 nm) is far longer than that of the Rayleigh length of the focused beam (200 µm). Therefore, other mechanisms also should be taken into consideration. Since the power density is larger than $10^{12}$ W/cm$^2$, nonlinear refractive index largely contributes to the refractive index of the glass during the laser irradiation. The refractive index increases when the intensity of the laser increases and self-focusing of the laser beam occurs. On the other hand, formation of electron plasma due to electric field, causes a decrease in the real part of the refractive index and induces self-defocusing of the beam. The balance between the self-focusing due to the increase of refractive index and self-defocusing due to the plasma formation results in a phenomenon called self-trapping or filamentation [21].
Fig. 4.4 Electron spin resonance spectra of the Mn and Fe ions codoped silicate glass before (a) and after (b) the femtosecond laser irradiation.
In the filaments, white light supercontinuum containing Stokes and anti-Stokes wave is generated due to self-phase modulation. The single or two-photon absorption of short wavelength component of the white light supercontinuum causes photoionization of transition ions as well as glass matrix, leading to the formation of \( \text{Mn}^{3+} \). It was confirmed that the length of the induced structure was directly proportional to the square root of the average power of the laser beam. If it is assumed that the length of the induced structure is directly proportional to the length of the filament, the result is in good agreement with the theory of Zverev et al. [22]. Therefore, filamentation due to the balance of self-focusing arose from an increase in refractive index and self-defocusing arose from plasma formation which takes an important role in the oxidation of \( \text{Mn}^{2+} \) to \( \text{Mn}^{3+} \). The trap levels of defect centers may be deep, thus resulting in the stable \( \text{Mn}^{3+} \) at room temperature. The structural difference among the cross section of the induced structure may result from the high temperature and high pressure at the center part due to the strong plasma formation, and ionization of transition metal ion as well as glass matrix due to the multiphoton absorption of the incident laser and single or two photon absorption of the white light supercontinuum.

In summary, persistent photooxidation of \( \text{Mn}^{2+} \) to \( \text{Mn}^{3+} \) in a silicate glass by a focused infrared femtosecond pulsed laser at room temperature has been observed. \( \text{Mn}^{2+} \) is suggested to act as hole trapping centers while \( \text{Fe}^{3+} \), active sites in glass matrix act as an electron trapping center. White light supercontinuum takes an important role in the formation of \( \text{Mn}^{3+} \). Since the focused area becomes purple after the laser irradiation, it is possible to write a three-dimensional colored image inside the transparent and colorless glass as shown in Fig. 4.5.
Fig. 4.5 Image of a butterfly in purple color written inside the glass using the femtosecond laser.
Since the length of the induced structure is directly proportional to the square root of the average power of the laser beam, it is possible to control the longitudinal spreading of the oxidation area from several hundred nanometers to several millimeters by selecting the proper irradiation condition. This method should also be useful for the space-selective valence state manipulation of other transition metal ions inside transparent materials. Therefore, the present technique will be useful in the fabrication of three-dimensional colored industrial art object, optical memory, and micro-optical devices.

4.2 Space selective precipitation of metal nanoparticles inside glasses

Noble metal nanoparticle-doped glasses exhibit large third-order nonlinear susceptibility and ultrafast nonlinear response [23, 24]. They are expected to be promising materials for an ultrafast all-optical switch in the THz region [25]. There have been extensive studies conducted on the fabrication and characterization of metal nanoparticle-doped glasses [26–33]. The fabrication methods discussed so far include traditional melting and annealing, sol gel, chemical vapor deposition, sputtering, ion exchange, and ion implantation [26–33]. Hofmeister et al. [31] and Chen et al. [32] have succeeded in the synthesis of nanosized silver particles via electron-beam irradiation, x-ray irradiation, and successive annealing. Recently, Valentin et al. [33] demonstrated complete control over the metal cluster density, average size, and size distribution of copper by room-temperature MeV ion irradiation. Of the aforementioned fabrication processes, ion exchange and ion implantation can realize space-selective precipitation of nanoparticles. However, both the composition of the glass matrix and the nanoparticle-precipitated area after further treatment are restricted in the ion-exchange method. In the case of ion implantation, the glass matrix is usually damaged severely and some impurities may be induced. In addition, both the size and space distribution of nanoparticles are broad from the surface to the inside of the glass sample.

Recently, an ultrashort pulsed laser has been used as a powerful tool to make
microscopic modifications to transparent materials [34–38]. The reason for using this laser is that its electric field intensity can reach 10 TW/cm², which is sufficient for inducing nonlinear optical effects in materials by the use of a focusing lens when the pulse width is 100 fs and the pulse energy is 1 µJ. The photoinduced reaction is expected to occur only near the focused part of the laser beam due to nonlinear optical processes.

Stookey [39] developed photosensitive glasses early in the 1950’s. These glasses contain noble metal photosensitive ions such as Ag⁺ and Au⁺ together with Ce³⁺, which act as a sensitizer. After the irradiation by UV light, Ce³⁺ releases an electron to form Ce⁴⁺, while Ag⁺ or Au⁺ captures the electron to form an Ag or Au atom. After subsequent heat treatment, crystallites, e.g., LiF and Li₂SiO₅, precipitate in the UV-irradiated area due to the nucleation by the metal cluster or colloids. It is possible to fabricate a two-dimensional designed structure when a mask is used. However, it is impossible to fabricate a three-dimensional modulated structure inside glasses since the UV light resonates with the absorption band of Ce³⁺.

In this section, the space-selective precipitation and control of noble metal nanoparticles in transparent materials are demonstrated. Space-selective photoreduction of the Ag⁺ ion to the Ag atom in a silicate glass, which was conducted by focusing 120 fs laser pulses from a regeneratively amplified Ti: Sapphire laser through a microscope objective lens, was observed. Absorption and electron spin resonance spectra were measured for the glass sample before and after femtosecond laser irradiation, as well as after further annealing at 550 °C. The mechanism of the occurrence of the phenomenon is also discussed.

The glass composition of the Ag⁺-doped silicate glass sample used in this study was 0.1 Ag₂O.70 SiO₂.10 CaO .20 Na₂O (mol%). Reagent grade SiO₂, CaCO₃, Na₂CO₃, and Ag₂O were used as starting materials. Details of the glass-preparation procedure have been described in the previous section.

A regeneratively amplified 800 nm Ti: Sapphire laser that emits 120 fs, 1 kHz, mode-locked pulses was used in our experiments. The laser beam with an average
power of 400 mW was focused by a $10 \times$ objective lens with a numerical aperture of 0.30 on the interior of the glass sample with the help of an XYZ stage. The spot size (diameter) of the laser beam was estimated to be 10 µm.

Absorption spectra of the glass samples were measured by a spectrophotometer (JASCO V-570). Electron spin resonance (ESR) measurements were carried out at X-band frequency (9.8 GHz) by an ESR spectrophotometer (JEOL-FE3X). The microwave power, time constant, modulation amplitude, and sweep time were 1 mW, 0.03 s, $1 \times 100$, and 4 cm/min, respectively. All of the experiments were carried out at room temperature.

After irradiation by the focused infrared femtosecond laser on each spot for $1/63$ s, a 10 µm spot was formed in the focused area of the laser beam in the Ag$^{+}$-doped glass sample. In addition, a gray-colored area with a diameter of about 40 µm was observed around the spot. The length of the induced structure along the axis of the laser beam was about 1.5 mm as observed by optical microscope. To measure the absorption spectrum of the glass sample after laser irradiation, a “damaged” plane of $3.0 \times 3.0$ mm$^2$, which consisted of damaged lines at intervals of 10 µm by scanning the laser beam at a rate of 1 mm/s, was created inside the glass sample. The glass sample was further annealed at 550 °C for 10 min. The laser-irradiated part became yellow after the heat treatment.

Fig. 4.6 shows the absorption spectra of the glass sample before [Fig. 4.6(a)] and after [Fig. 4.6(b)] femtosecond laser irradiation, and [Fig. 4.6(c)] after further annealing at 550 °C for 10 min. No apparent absorption was observed for the unirradiated glass sample in the wavelength region from 600 to 800 nm, while there was an apparent increase in the absorbance in the wavelength region from 220 to 600 nm in the irradiated region. The inset of Fig. 4.6 shows the difference in absorption spectra of the glass sample before and after the femtosecond laser irradiation. The absorption peaks at about 240 and 350 nm can be assigned to the atomic silver and hole trap centers at nonbridging oxygen near Ag$^{+}$ ions, respectively [40]. Therefore, an electron was driven out from the $2p$ orbital of a nonbridging atom near the Ag$^{+}$ ions after femtosecond laser irradiation, while Ag$^{+}$ captured the electron to form an
Fig. 4.6 Absorption spectra of the Ag$^+$-doped silicate glass before (a) and after (b) the femtosecond laser irradiation, and (c) after further annealing at 550 °C for 10 min. The inset of Fig. 4.6 shows the difference in absorption spectra of the glass sample before and after the femtosecond laser irradiation.
Ag atom. Fig. 4.6 also shows that a new peak appeared at 450 nm in the absorption of the glass sample after further annealing at 550 °C. The peak can be assigned to the absorption due to the surface plasmon of the silver nanoparticle [41]. Preliminary observation with a JEM-2010FEF transmission electron microscope also showed that spherical particles with sizes ranging from 1 to 8 nm precipitated in the sample. The photon-reduced Ag atoms aggregated to form nanoparticles after the heat treatment. An unirradiated glass sample precipitates nanoparticles only at temperatures above 600 °C. Therefore, it is suggested that the neutralized Ag promotes nucleation. Femtosecond laser irradiation can be used to separate and control the nucleation and growth processes.

Fig. 4.7 shows the ESR spectra of the glass sample before [Fig. 4.7(a)] and after [Fig. 4.7(b)] the femtosecond laser irradiation at room temperature, and [Fig. 4.7(c)] after further annealing at 550 °C for 10 min. No apparent signal was detected in the unirradiated glass sample, while the spectrum of the glass sample after femtosecond laser irradiation showed a broad signal at $g \sim 2.10$ and two signals at $g \sim 2.00$. The broad signal at 2.10 may be due to the Ag atom, [42] while two signals at $g \sim 2.00$ can be assigned to hole trap centers (HC), e.g., HC$_1$ and HC$_2$ [43]. The HC$_1$ and HC$_2$ are holes trapped at the nonbridging oxygen in the SiO$_4$ polyhedron with two and three nonbridging oxygen, respectively.

Several experiments were carried out to clarify the mechanism of the formation of induced structures after femtosecond laser irradiation. It was observed that the size of the nanoparticle-precipitated area is the same as the area in which supercontinuum white light was observed during femtosecond laser irradiation and is also the same as the dark area induced by femtosecond laser irradiation. There is now a consensus that multiphoton absorption due to the fundamental wave and supercontinuum white light, which arises from self-phase modulation of the laser beam, plays an important role in the formation of induced structures. In the present case, electrons are driven out from the 2$p$ orbital of the nonbridging oxygen in the SiO$_4$ polyhedron via the multiphoton absorption of the incident photon. Ag$^+$ captures the electron to form an Ag atom. It was also confirmed that the length of the femtosecond laser induced structure was
Fig. 4.7 ESR spectra of the glass sample before (a) and after (b) the femtosecond laser irradiation, and (c) after further annealing at 550 °C for 10 min.
directly proportional to the square root of the average power of the laser beam. This result is in good agreement with the theory of Zverev et al., [22] if it is assumed that the length of the induced structure is directly proportional to the length of the filament, which is due to the balance between self-focusing arising from an increase in the refractive index and self-defocusing arising from plasma formation. It has been also confirmed that no change is observed in the absorption spectrum of the nanoparticle-precipitated glass sample after heat treatment at room temperature even for 6 months, indicating that the precipitated nanoparticles are stable at room temperature. In addition, it has been also realized the space-selective precipitation of gold and other metal nanoparticles. These results showed that the color of the gold nanoparticle-precipitated area changed from violet to red when the power density of the laser increased from $10^{12}$ to $10^{15}$ W/cm$^2$. The different color is due to the different size of gold nanoparticle. The details will be reported elsewhere.

In summary, space-selective precipitation and control of noble metal nanoparticles in transparent materials have been observed by a focused infrared femtosecond pulsed laser irradiation at room temperature and further annealing at high temperature. Nonbridging oxygen is suggested to act as HCs while the Ag$^+$ ion acts as an electron-trapping center, thus resulting in the reduction of Ag$^+$ ions to Ag atoms. White light supercontinuum plays an important role in the formation of Ag atoms. Since the focused-on area becomes gray after laser irradiation and then becomes yellow after heat treatment, it is possible to draw a three-dimensional multicolored image inside the transparent and colorless glass sample, as shown in Fig. 4.8.
Fig. 4.8 Photograph of butterflies drawn inside the glass sample by using the femtosecond laser: Gray color (after femtosecond laser irradiation, at the right and the lower part) and yellow color (after femtosecond laser irradiation and further heat treatment at 550 °C for 10 min, at left and the upper part).
The length of the induced structure is directly proportional to the square root of the average power of the laser beam; therefore, it is possible to control the longitudinal spreading of the structurally changed area from several hundred nanometers to several millimeters by selecting the appropriate irradiation condition. These results demonstrated the possibility of space-selective precipitation of nanoparticles in a micrometer-small dimension inside a transparent material by using a focused nonresonant femtosecond pulsed laser and heat treatment. This technique will be useful in the fabrication of three-dimensional multicolored industrial art objects, optical memory, and integrative waveguidelike optical switches with ultrafast nonlinear response.

References

Chapter 5

Three-dimensional nano-architecture in glasses using the combination of femtosecond laser pulses and the new LCOS modulator

In the past several couple of years, a lot of research efforts have been devoted to the field of three-dimensional microscopic modifications to transparent materials by using femtosecond laser. Promising applications have been demonstrated for the formation of three-dimensional optical memory and multicolor image, and fabrication of optical waveguide, coupler and photonic crystal.

Among them, fabrication of three-dimensional optical waveguide by femtosecond laser pulses inside various transparent materials has attracted great interests as one of the essential techniques for making 3D integrated optical devices [1-6]. Because an integrated optical device should have a lot of elements such as optical coupler, splitter and interferometer, the development of waveguides are required to bend in order to change the light propagation direction. One critical problem of fs-laser processing is fabrication efficiency, because a lot of time is consumed for fabrication of many long waveguides. As one candidate for improvement of fabrication efficiency, a holographic laser processing method using a spatial light modulator (SLM) has been demonstrated [7]. In this method, multiple beam spots are generated from one beam whose phase distribution is modulated by a computer generated hologram (CGH) in a SLM, and photoexcitation is induced at multiple spots in a material.

5.1 Design method of CGHs for LCOS modulator

Experimentally, an efficient method for preparing CGHs which changes the
position of light spots as gradually as possible is proposed and the parallel fabrication of bended optical waveguides with a SLM is demonstrated. Using a holographic method, parallel drawing of multiple waveguides can be performed by making horizontally arrayed light spots and moving the glass sample in the vertical direction as shown Fig. 5.1(a). In this case, the fabricated optical waveguides are mutually parallel. When the bended waveguides are made by a holographic method, CGHs which change the positions of light spots have to be switched (Fig. 5.1(b)). The problem is that the step of the beam position change is finite ($\Delta X_{\text{step}}$), because a CGH is composed by discrete elements. As a result, the fabricated waveguide structure is discrete at the CGH switched position as shown in Fig. 5.1(b). This problem prevents us from making smooth bended waveguide by a holographic method.

For parallel drawing of multiple bended waveguides, CGHs which change light spots as gradually as possible have to be prepared. First, the method for calculating a CGH is explained. In holographic laser processing system, laser beam is reflected on a SLM and the reflected beam is focused by a lens. The photoexcitation is induced by the light pattern focused on the image plane, which is located inside a glass sample (Fig. 5.1(a)). According to the diffraction theory, the relation between the electric fields on a SLM [$F(x,y)$] and that on the image plane [$E(X,Y)$] is given by Fourier transform. Therefore, a hologram is calculated using the following equation:

\[
E(X_k,Y_l) \propto \sum_{m,n=-N/2}^{N/2-1} F(x_m,y_n) \ast \exp[i2\pi \frac{x_m X_k + y_n Y_l}{\lambda f}] \quad (k,l,m,n = -N/2,\ldots,N/2-1) \quad (5.1)
\]

where $(x,y)$ and $(X,Y)$ are positions on the SLM plane and the image plane, respectively, $N$ is integer, $\lambda$ is the wavelength of laser beam, and $f$ is a focal length of an objective lens. Because the phase distribution of $F(x,y)$ is modulated by a SLM, $F(x,y)$ is written by

\[
F(x,y) \propto \exp[i\Delta\Phi(x,y)] \quad (5.2)
\]

where $\Delta\Phi(x,y)$ represents the distribution of phase shift by a SLM and it was assumed that the phase distribution of laser beam before a SLM is uniform. It is convenient that the sampling interval of $x$ and $y$ is same as that of CGH ($\Delta x_{\text{CGH}}$),
Fig. 5.1 (a) Parallel drawing of several waveguides by a holographic fs laser processing with a SLM. (b) Illustration of waveguides fabricated by a holographic fs laser processing. The position of the right beam spot is changed during a glass scanning by switching CGH from CGH1 to CGH2.
because one element in a SLM gives nearly equal phase shift. The discrete Fourier transform determines the relation between $\Delta x_{CGH}$ and $\Delta X$ as follows:

$$\Delta x_{CGH} \Delta X = \frac{\lambda f}{N} \quad \text{(5.3).}$$

From this relation, the position of the beam spot is restricted: $X_k = k\lambda f / [\Delta x_{CGH} N]$. This relation means that larger $N$ is better if one wants to change the position of the beam spot as gradually as possible. However, as $N$ becomes larger, the time needed for calculating Eq. (5.1) becomes longer, because the calculation time of 2D FFT is approximately proportional to $(N\log_2 N)^2$ [8]. To reduce the calculation time, the desired intensity distribution $I(X,Y)$ was expressed by the product of independent intensity distributions of $X$ and $Y$:

$$I(X,Y) = I_X(X) * I_Y(Y) \quad \text{(5.4).}$$

In this case, the phase distribution $\Delta \Phi(x,y)$ can be expressed by

$$\Delta \Phi(x,y) = \Delta \phi(x) + \Delta \varphi(y) \quad \text{(5.5),}$$

where $\Delta \phi(x)$ and $\Delta \varphi(y)$ are the optimal phase distributions (CGHs) for $I_X(X)$ and $I_Y(Y)$, respectively.

If $\Delta \phi(x)$ and $\Delta \varphi(y)$ are calculated independently, the calculation time for FFT reduced to $2N\log_2 N$, which is much shorter than that needed for calculating $\Delta \Phi(x,y)$ directly. The intensity distribution expressed by Eq. (5.4) is restricted. For example, when $\Delta \phi(x)$ makes four light spots parallel to the $X$ axis and $\Delta \varphi(y)$ makes two light spots parallel to the $Y$ axis, $\Delta \Phi(x,y)$ makes eight light spots on $X$-$Y$ plane shown in Fig. 5.2 (a). This restriction has no problem for this study, because only horizontally arrayed light spots are sufficient for the fabrication of waveguide.

### 5.2 Parallel drawing of bended optical waveguides

The waveguide structures were fabricated by moving a silica glass plate in the vertical direction at 20 $\mu$m/s during fs laser irradiation which was modulated by a CGH. On a SLM, a CGH was switched to another to change the distance between two
Fig. 5.2 (a) Simulated typical light intensity distribution used for a parallel drawing of four waveguides. The 2D intensity distribution is a product of $I_X(X)$ and $I_Y(Y)$. (b) Structure of fabricated bended waveguides. The waveguides were fabricated from the bottom to the top.
adjacent waveguide structures. CGHs were calculated by Eq. (5.5) and Gerchberg-Saxton algorithm [9]. The laser beam for drawing waveguide structures was from a generatively amplified mode-locked Ti: sapphire at 1 kHz (Coherent Mira-Legend; 800 nm, 100 fs). The spatial phase distribution of the laser beam was modulated by a LCOS-SLM (Hamamatsu) [10], and was passed through a telescope to change the beam diameter (M=0.3), and was focused inside a silica glass plate by a 20× objective lens (f= 10 mm; Nikon LU-Plan). The LCOS-SLM contains 800(H)×600(V) elements (N_{SLMX}=800, N_{SLMY}=600) with a vertical and horizontal length of 20 μm (i.e. Δx_{SLM}=20 μm). Because this optical system contains a telescope with M=0.3, Δx is M*Δx_{SLM}=6 μm. To make a CGH, N=16,384 (2^{14}) was used. According to Eq. (5.3), we can calculate the minimum resolution of the beam spot: ΔX_{min}=0.081 μm.

The structure of fabricated waveguides was illustrated in Fig. 5.2 (b). Four waveguides were fabricated and each waveguide was numbered for indication. Because the horizontal positions of the two middle waveguides ‘2’ and ‘3’ are shifted by about 20.75 μm, 256 CGHs (20.8 μm/ΔX_{min}~256) were prepared to change the beam position by a minimum step ΔX_{min} on switching CGHs. Figs. 5.3 (a)-(c) show the optical microscope images of the fabricated waveguides. The four waveguides were numbered as shown in Fig. 5.3(a). In Figs. 5.3 (a) and (c), four waveguides are parallel each other, which means that the same CGH was used during drawing waveguides. In the region shown in Fig. 5.3 (b), the horizontal positions of the middle two waveguides were changed by switching one CGH to the other. There is no apparent disconnected structure in the waveguides due to switching of CGHs. It was observed that He-Ne laser beam at 633 nm wavelength was guided through the four waveguides. Fig. 5.3 (d) shows the near field profiles of the guided beam. The output positions of the beam from the waveguides ‘2’ and ‘3’ were shifted by about 20 μm in the horizontal direction from those of the waveguides ‘1’ and ‘4’. The difference in the beam output position means that the waveguides ‘2’ and ‘3’ are bended, i.e. the horizontal positions of the output are shifted by 20.75 μm from those of the input. The intensity of the beam from the bended waveguides was 84 % of that from the straight waveguides, i.e. the propagation loss by the bended structure is 0.75 dB.
Fig. 5.3 (a)-(c) Optical waveguides fabricated by fs-laser irradiation observed by an optical microscope. (d) Images of the beam guided thorough the optical waveguides (left) and horizontal intensity distribution at the maximum (right).
In summary, a parallel drawing of bended waveguides by a holographic laser processing with a SLM was demonstrated, and it was shown that the fabricated bended waveguides are able to guide a He-Ne laser beam. The loss of the fabricated bended waveguides which shift the output position by 21 µm in the horizontal direction was about 0.75 dB. Because the loss of the bended waveguides fabricated by a parallel laser processing with a SLM depends on not only the step of the beam position change but also the switching time of CGHs, the optimal step has to be selected to make the low loss waveguides. The demonstration of bended waveguides presented here promises various application of efficient laser fabrication. For example, a beam splitter such as a Y coupler [6] and directional coupler [3-5] can be fabricated more efficiently by a parallel drawing using a SLM.

References


Summary

The interaction between intense laser pulses and transparent materials is an important research area, both for its intrinsic scientific value and for the technological applications that it feeds. Intense femtosecond pulses enable highly localized material modification in virtually any material, and thus femtosecond lasers are excellent tools for fabricating optical microstructures. Because of the nonlinear interaction between the femtosecond laser pulse and the medium, the interaction is confined to the focal volume, allowing precise machining in three dimensions in the bulk of the sample. In addition, this method provides the ability to process large sample areas and volumes quickly.

When a femtosecond laser pulse is tightly focused inside a transparent material, the intensity in the focal volume is high enough to cause absorption through nonlinear processes. The absorption of the laser energy creates a micrometer-sized, highly excited plasma inside the material. The energy, initially contained in the plasma, is subsequently transferred to the lattice in the form of heat and shock waves. In solids, this energy transfer permanently alters the material. Because the absorption is strongly intensity-dependent, it is possible to create permanent damage inside the materials, leaving the surface unaffected. Here, some of the essential conclusions of this thesis are reviewed.

In chapter 1, various diffractive optical elements in silica glasses and sapphire crystals have been achieved by using the focused femtosecond laser irradiation. Primarily, the fabrication of the Dammann gratings inside silica glasses by generating the periodic patterns of refractive index modifications was introduced. As expected, the designed split beam pattern was obtained by transmitting the He-Ne laser through the fabricated gratings. Furthermore, the multi layer process for higher diffraction efficiency has been developed and it was demonstrated that the phase shift was controlled in the range over $\pi$. 
The diffractive lenses inside the silica glasses and sapphire mono crystals have been also achieved by creating photo-induced refractive index changes with the focused ultrashort pulses. The fabricated diffractive lens could focus the transmitted light with the wavelength of 633 nm nearly to the spot size of the diffraction limit. The optimizations on fabrication conditions were conducted in detail, and the results demonstrate that it is possible to control the diffraction efficiency by adjusting the average laser power and to manipulate the generation and disappearance of the birefringence of the diffractive lens by altering the polarization state of the fs laser. Thus, the diffractive lens with strong polarization dependence can be also utilized as a polarization splitter. In addition, diffractive lens with the 4 level approximation achieved the diffraction efficiency of 53.2 %. The difference of the diffraction efficiencies between the theoretical and measured value was numerically examined and the estimation of the fabrication error was carried out.

In chapter 2, by using the fabrication technique based on chapter 1, the integration of the diffractive optical elements inside the single piece of silica glass has been demonstrated. By incorporating the three-dimensional space selective modification of the focused femtosecond laser, the integration of micro optical components such as the Dammann grating, the diffractive lens, the pin hole, etc. has been achieved. The integration of optics, which requires the alignment and bonding by the conventional process, could be realized simply by translating the focal point of the fs laser.

Moreover, promising industrial applications by using integrated optics have been proposed. The high efficiency photo-detector can be realized by embedding the Damman grating and the diffractive lens inside the photo-detector window by the femtosecond laser pulses. The miniature spectrometer that was composed of the diffractive lenses and the pin hole could separate the three beams with different wavelengths as the position of the diffractive lens. The simple integration method by utilizing the desktop femtosecond laser will offer new opportunities to intend and construct the excellent integrated optics with novel functions.

In chapter 3, true three-dimensional channel structures in bulk silica glass were
achieved by using the focused femtosecond laser irradiation and successive chemical etching. By incorporating this technique, the arbitrary shaped micro-channels can be generated without bonding of the separate glass pieces. Besides, the effects of the repetition rate of the ultrashort pulses on the surface morphology inside the micro-channels were investigated. It was presented that the optimum repetition rate exited and the uniformity of the photo-induced refractive index change was significant for fabricating the smooth surface. Moreover, a relation between the uniformity of the photo-induced structures and the amount of the defects in the silica glasses was analyzed. The increase in absorbance before and after the laser irradiation for various fabrication conditions revealed that the peaks at the wavelength of 245 nm and 215 nm could be attributed to oxygen deficiency centers ODC (I) and E’ centers, respectively, and that nonuniformity of the photo-induced refractive index alteration might promote the amount of these defects.

In chapter 4, space-selective valence state manipulation and precipitation of various metal ions and coloring in glasses have been realized by using focused ultrashort pluses. Persistent photooxidation of Mn$^{2+}$ to Mn$^{3+}$ in a silicate glass has been observed. Mn$^{2+}$ is suggested to act as hole trapping centers while Fe$^{3+}$, active sites in glass matrix act as an electron trapping center. Since the focused area becomes purple after the laser irradiation, it is possible to write a three-dimensional colored image inside the transparent and colorless glass.

Space-selective precipitation and control of silver nanoparticles in a silicate glass, which was formed by a laser irradiation at room temperature and further annealing at high temperature, have been also confirmed. Nonbridging oxygen is suggested to act as HCs while the Ag$^+$ ion acts as an electron-trapping center, thus resulting in the reduction of Ag$^+$ ions to Ag atoms. Since the focused-on area becomes gray after laser irradiation and then becomes yellow after heat treatment, it is possible to draw a three-dimensional multicolored image inside the transparent and colorless glass sample.

The size of photooxidation and nanoparticles and their spatial distribution can be controlled by the fabrication conditions. This technique will become useful in the
fabrication of three-dimensional multicolored industrial art objects, optical memory with ultrahigh storage density and all-optical switches with ultrafast nonlinear response.

In chapter 5, a three-dimensional nano-architecture in glasses by using the combination of femtosecond laser pulses and the new LCOS modulator have been introduced. An efficient method for preparing computer generated holograms for the spatial light modulator was proposed. The parallel fabrication of bended optical waveguides with a spatial light modulator by the LCOS was achieved, and it was shown that the fabricated bended waveguides were able to guide a He-Ne laser beam. The loss of the fabricated bended waveguides which shift the output position by 21 µm in the horizontal direction was about 0.75 dB. The demonstration of bended waveguides presented here promises various application of efficient laser fabrication. For example, a beam splitter such as a Y coupler and directional coupler can be fabricated more efficiently by a parallel drawing using a SLM.
List of publications

Chapter 1

Integration of micro-optics inside a silica glass by using a femtosecond laser direct-writing technique

Takayuki Nakaya, Daisuke Shibata, Hidetoshi Takeda, Toshiro Kotaki, Kazuhiko Sunakawa, Yoichi Yaguchi, and Kazuyuki Hirao

Fabrication of Dammann gratings inside glasses by a femtosecond laser

Takayuki Nakaya, Jianrong Qiu, Changhe Zhou, and Kazuyuki Hirao

Crack Propagation in a Ruby Single Crystal by Femtosecond Laser Irradiation
Chiwon Moon, Shingo Kanehira, Masayuki Nishi, Kiyotaka Miura, Takayuki Nakaya, Eita Tochigi, Naoya Shibata, Yuichi Ikuhara, and Kazuyuki Hirao

Periodic surface nanostructures on Ti$^{3+}$:Al$_2$O$_3$ crystals irradiated by femtosecond laser pulses
Nobuhiro Kodama, Koshun Saito, Takayuki Nakaya, Tomoko Takahashi, Daisuke Shibata, and Hidetoshi Takeda
Physical Review Letters, to be submitted.
Chapter 2

Three-dimensional integration of micro-optics in bulk silica glass by femtosecond laser direct writing: potential for industrial applications

Takayuki Nakaya, Daisuke Shibata, Yoshihito Hatazawa, Kazuhiko Sunakawa, Yoichi Yaguchi, and Kazuyuki Hirao


Integration of diffractive optics inside silica glass by femtosecond laser pulses

Takayuki Nakaya, Daisuke Shibata, Yoshihito Hatazawa, Jianrong Qiu, and Kazuyuki Hirao

*Optics Letters*, to be submitted.

Chapter 3

Fabrication of precision micro-holes and structures with smooth surfaces by a high repetition rate femtosecond laser

Takayuki Nakaya, Daisuke Shibata, Hidetoshi Takeda, Hiroaki Toshima, Toshiro Kotaki, Kazuhiko Sunakawa, and Yoichi Yaguchi


Space-selective phase separation inside glass by controlling the compositional distribution with femtosecond laser irradiation

Masahiro Shimizu, Masaaki Sakakura, Yasuhiko Shimotsuma, Kiyotaka Miura, Takayuki Nakaya, and Kazuyuki Hirao

*Applied Physics Letters*, to be submitted.

Mechanism of heat-modification inside a glass after irradiation of high-repetition rate femtosecond laser pulses

Masahiro Shimizu, Masaaki Sakakura, Masatoshi Ohnishi, Yasuhiko Shimotsuma,
Chapter 4

Space-selective valence state manipulation of transition metal ions inside glasses by a femtosecond laser
Jianrong Qiu, Congshan Zhu, Takayuki Nakaya, Jinhai Si, Kazuo Kojima, Fumito Ogura, and Kazuyuki Hirao

Space-selective precipitation of metal nanoparticles inside glasses
Jianrong Qiu, Mitsuru Shirai, Takayuki Nakaya, Jinhai Si, Xiongwei Jiang, Congshan Zhu, and Kazuyuki Hirao

Chapter 5

Three-dimensional nano-architecture in glasses using the combination of fs laser pulses and the new LCOS modulator –parallel drawing of bended optical waveguides-
Kazuyuki Hirao, Masaaki Sakakura, Tsutomu Sawano, Yasuhiko Shimotsuma, Kiyotaka Miura, Bin Hua, and Takayuki Nakaya
Acknowledgements

The present thesis has been carried out at Graduate School of Engineering, Kyoto University under the direction of Professor Kazuyuki Hirao.

The author wishes to express his sincere gratitude to Prof. Kazuyuki Hirao, who supervised the present work, for his helpful guidance, valuable suggestions and hearty encouragement throughout this thesis.

The author is grateful to Prof. Jianrong Qiu at Department of Materials Science and Engineering, Zhejiang University, for his valuable and helpful suggestion and advice, lively discussion. Grateful acknowledgements are also made to Prof. Jinhai Si of Xi’an Jiaotong University and Prof. Kodama of Akita University for their helpful supports and occasional discussions.

The profitable suggestions from Associate Professor Kiyotaka Miura, Associate Professor Yasuhiko Shimotsuma and Dr. Masaaki Sakakura are also gratefully acknowledged.

The author wishes to show his appreciation for Chairman and CEO Shoji Namiki, President Yoichi Yaguchi, President of NJC Institute of Technology Kazuhiko Sunakawa from Namiki Precision Jewel Co., who gave opportunity for writing this thesis. Many thanks are made to coworkers, Daisuke Shibata, Hidetoshi Takeda, and Yoshihito Hatazawa for their excellent assistance.

Finally, the author is deeply grateful to his wife, Mrs. Takako Nakaya for her continuous understanding and support.

Kyoto, Winter 2010

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