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Writing Speed Dependency of Femtosecond Laser Refractive Index Modification in Poly(dimethylsiloxane)

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This report describes the filamentary refractive index change under slow-focusing conditions in polydimethylsiloxane using femtosecond pulses from a 1-kHz Ti:sapphire amplifier. The respective influences of laser writing parameters and focusing conditions were studied. The refractive index change was induced by scanning the sample up to 4 mm/s. The refractive index change with a magnitude of 2.3×10^{-4} was estimated from the diffraction efficiencies of a volume grating with 300 μm thickness.

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1. Introduction

Poly(dimethylsiloxane) (PDMS, ($[SiO(CH_3)_2]_n$)) is a silicone elastomer with useful properties such as high transparency at visible range, physical and chemical stability, and high flexibility [1,2]. Growing interest has surrounded the creation of optical structures in PDMS for many applications. Examples of devices include silicone microlenses, interference gratings, and microfluidics. PDMS also presents the potential for protection of electronic circuits and encapsulation and for lighting applications (Light Emitting Diodes: LEDs).

Femtosecond laser direct writing has been demonstrated as a powerful technique to micromachine practically any material with only slight thermal damage. When femtosecond laser pulses are focused within a transparent bulk material, nonlinear absorption can be induced in the focal volume, enabling a range of possible changes in material properties. This highly localized modification gives femtosecond laser micromachining a unique three-dimensional micro-modification capability, which has been used to create volume optical storages, waveguides, gratings, and microfluidic devices. Although different experimental conditions such as laser pulse energy and pulse duration, scanning speed, repetition rate, and focusing condition are used in different experiments, the modifications are classifiable into the main categories of refractive index change, void or cavity, and scattering damage in polymer materials [3–12] and silicone-based materials [13–22]. In one experiment, 522 nm femtosecond laser pulses with 3 nJ at 1 MHz repetition rate were focused with a 0.55-NA lens into thin PDMS film [17]. By scanning the laser beam with respect to the silicone film, a permanent refractive index modification was induced and waveguides were inscribed. Cho et al. embedded a thin (Raman–Nath type) grating in PDMS plates using a tight focusing condition (numerical aperture; NA 0.85 and NA 0.5) with a femtosecond laser (λ=800 nm, 130 fs, 1 kHz repetition rate) [18,19]. Refractive index change was induced with thin gratings (Raman–Nath type) in PDMS. Chang et al. fabricated a grating in PDMS under a focusing condition of NA =0.4 using a femtosecond laser (wavelength λ=517 nm, 350 fs, 100 kHz repetition rate) [20]. A cavity was created and air-gap type gratings were fabricated in PDMS. Kuna et al. demonstrated volume structuring of LED encapsulates by embedding one-dimensional and two-dimensional gratings [21]. Void-like structures were embedded by focusing (NA 0.65) with a femtosecond laser (λ=800 nm, 150 fs, 1 kHz repetition rate). Voids and cavities increase the scattering loss.

Under slow-focusing conditions, filaments can propagate over distances that extend up to hundreds of times the characteristic Rayleigh length. Filamentation occurs mainly as a result of the dynamic competition between Kerr self-focusing and defocusing induced by higher-order nonlinearities such as ionization and nonlinear absorption. Filament formation inside the transparent solid materials engenders filamentary modifications. Filaments have been used in the fabrication of optical components in the bulk of transparent solids because of the clamping of the peak intensity inside the filaments. However, no experimentally obtained results have examined embedded volume gratings in PDMSs with filamentary refractive index modification using femtosecond lasers.

This report describes filamentary refractive-index change under slow-focusing conditions in PDMS using femtosecond pulses from a 1-kHz Ti:sapphire amplifier. Laser parameters for induction of refractive index modifications in PDMS are investigated. The morphology and properties of structural modifications are examined for various focusing conditions, materials, and scanning speeds.

2. Experimental procedures

Laser pulses with pulse width of 100 fs were generated using a Ti:sapphire laser system with 800 nm wavelength and a repetition rate of 1 kHz. A linearly polarized laser beam was attenuated using a rotatable half-wave plate and a Glan laser polarizer together with calibrated neutral density filters inserted before the sample. The laser pulses were polarized horizontally after passing through the polarizer. The beam was focused inside a PDMS sample using microscope objectives. The focal point was 500 µm below the sample surface. The sample was moved by a computer-controlled three-axis positioning system perpendicularly to the laser focus to produce lines of modification. A charge-coupled device (CCD) camera was used to monitor the fabrication process. The pre-polymer and a cross-linker of PDMS used in this study, were KE106 and CAT-RG respectively (Shin-Etsu Silicones of America Inc.). We first degassed KE108 with stirring under the reduced pressure with subsequent gradual pouring of CAT-RG at 10 wt% into KE108. The resulting mixture was inserted into a flat plate 5-mm-thick mold. We put this mold in the oven at 55 °C for 15 h to cure. Then we removed the cured PDMS from the mold. The optical characteristics of obtained PDMSs were equal to the values as the published estimate from Shin-Etsu Silicones of America Inc. The 5-mm-thick PDMS was put onto the glass substrate. The resulting photoinduced structural modifications (refractive index change, scattering damage) were imaged using transmission optical microscopy to determine their size and shape. The optical image of the filamentary modifications along the optical axis was observed using a CCD camera from the direction perpendicular to the optical axis through a microscope objective using a halogen lamp.

3. Experiment results

3.1 Structural modification with different pulse energies

Among the several factors influencing structural modification in PDMS, we specifically address the NA of the focusing lens, the incident pulse energy, and the scan speed used to establish the optimal irradiation conditions to induce refractive-index change.

First, to understand the difference in the morphology of refractive-index change and scattering damage, we investigated the filamentary tracks by varying the scanning speeds. The laser pulses were focused using a 10× microscope objective with a numerical aperture (NA) of 0.25. Figure 1 portrays a series of optical images of produced modifications in PDMS for various pulse energies and scanning speeds. At pulse energy of 400–1200 nJ/pulse, a refractive-index change was induced at the rate of 3 mm/s. Above 3 mm/s, dot-by-dot refractive index change was induced by a single shot. Below 3 mm/s, scattering damage was observed.

When the refractive index change was induced, the power of the transmitted incident beam was higher than 90% of that of the incident beam. In this condition, transmission optical microscopy revealed no scattering damage in the region of refractive index change. However, when scattering damage was observed, the transmitted beam power was decreased to less than 90% of that of the incident beam because of scattering. When the scattering damage was produced, the inscribed lines were found to be opaque by observation with a transmission optical microscope. Dot-by-dot refractive index change is induced because the focusing area was not overlapped at higher translation speed. Dot-by-dot refractive index change means that the region of refractive index change is discrete.

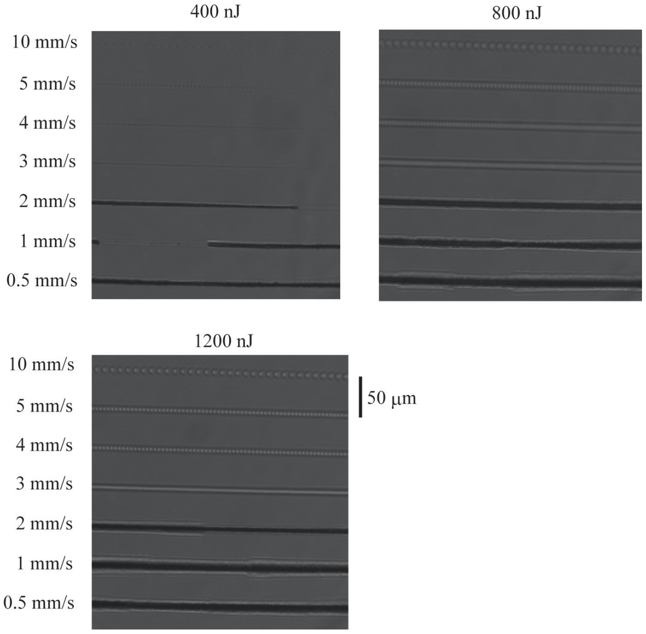
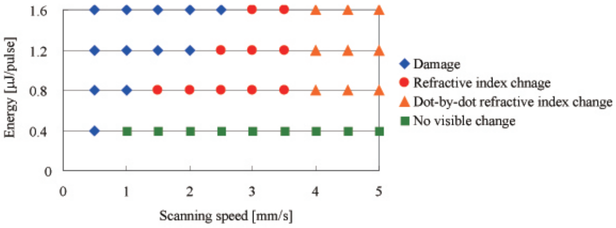


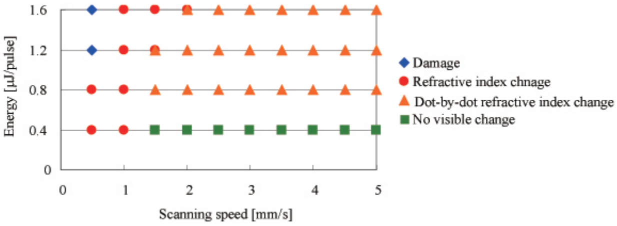
Fig. 1 Top views of structural modifications in PDMS at various scanning speeds. Laser pulses were focused using a 10× microscope objective with NA of 0.25.

We investigated energy thresholds for refractive index change, dot-by-dot structure, and damage in PDMS, poly(methyl methacrylate) (PMMA, Acrylite L #000; Mitsubishi Rayon Co. Ltd.), and PMMI (Pleximid 8805; Degussa Co. Ltd.). Figure 2 presents a summary of the thresholds for structural modifications. The energy was changed from 0.4 to 1.6 µJ/pulse at an interval of 0.4 µJ/pulse by rotating a HWP. Structural modifications were examined discretely at speeds of 1 mm/s, 2 mm/s, 3 mm/s, 4 mm/s, and 5 mm/s.

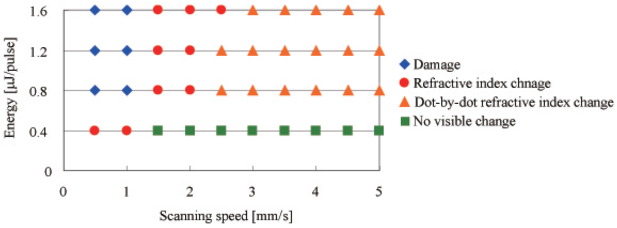
Dot-by-dot refractive index change was produced using a single shot. They were refractive index modifications. At this focusing condition (NA 0.25), refractive index change was not induced at a scanning speed of 1 mm/s. However, it was induced between 1.5 mm/s and 3.5 mm/s dependent on the incident energy. For PMMA, the refractive index change was induced below scanning speeds of 2 mm/s. For PMMI, refractive index change was induced below scanning speeds of 2.5 mm/s. These results show that the refractive index change was induced at higher scanning speeds in PDMS.



(a) PDMS



(b) PMMA



(c) PMMI

Fig. 2 Energy thresholds for filamentary tracks of refractive-index changes, dot-by-dot structure, and damage in (a) PDMS, (b) PMMA, and (c) PMMI.

To investigate the NA dependence, we monitored structural modifications in PDMS when the laser pulses were focused using a 5× microscope objective with a NA of 0.13. Figure 3 portrays a top view of structural modifications in PDMS at various scanning speeds. Below the scanning speed of 2 mm/s, damage structures were produced. At 3–4 mm/s, the refractive index change was induced. At rates higher than 5 mm/s, dot-by-dot refractive index change was produced using a single shot.

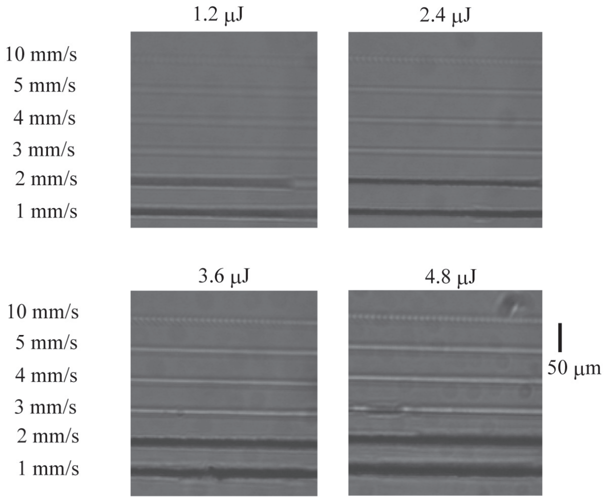


Fig. 3 Top views of structural modifications in PDMS at various scanning speeds. Laser pulses were focused using a 5× microscope objective with a NA of 0.13

3.2 Fabrication of volume grating

We fabricated internal gratings in PDMS. The laser pulses were focused using a 5× microscope objective with a NA of 0.13, and the focal point was located 500 μm below the sample surface. The energy was 4.75 μJ/pulse and the sample was translated at a speed of 3 mm/s. Figure 4 shows an optical image of the fabricated grating in PDMS with a period of 10 μm. The grating thickness was observed using a transmission optical microscope from a direction perpendicular to the optical axis. Figure 5 shows that the grating thickness was measured as 300 μm. A volume grating was embedded in PDMS under a slowly focusing condition.

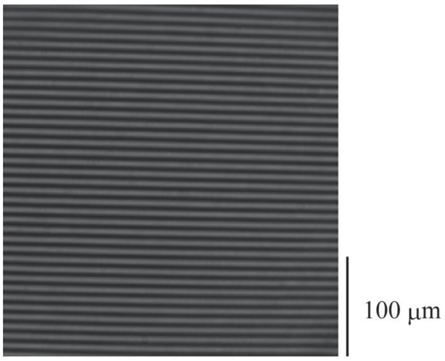


Fig. 4 Optical image of a fabricated grating in PDMS. The grating period was 10 μm.

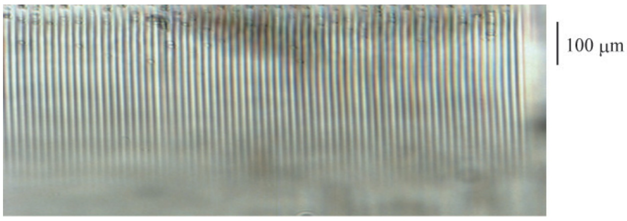


Fig. 5 Side view of a fabricated grating in PDMS.

The grating diffraction efficiency was measured using a cw He-Ne laser at a wavelength of 632.8 nm. The beam from the He-Ne laser was incident upon the grating at the Bragg angle, and the diffracted beam pattern was projected on a screen placed 500 mm from the sample. The first-order diffraction efficiency (η_1) of the grating was calculated using measuring the beam intensity in the first-order diffraction spot with a power meter.

The Q value, a parameter used to judge the type of diffraction a grating thickness parameter, is given as equation $Q = 2\pi\lambda L/n\Lambda^2$, where λ, L, Λ, and n respectively denote the beam wavelength (632.8 nm), the diffraction grating thickness (300 μm), the grid interval the grating period (10 μm), and the refractive index of PDMS. The Q value of the fabricated grating was greater than 1. Therefore, η_1 can be written as $\eta_1 = \sin^2(\pi\Delta nL/\lambda\cos\theta)$, where Δn and θ respectively signify the refractive index change and the Bragg angle [23]. We estimated the refractive-index change using the equation presented above. The value of η_1 in PDMS was 10%. The transmittance was 98.6% at 632.8 nm. We determined the magnitude of the refractive index change from the diffraction efficiencies of the fabricated internal grating. The refractive index change with a magnitude of 2.3×10^{-4} was estimated from the diffraction efficiencies of a volume grating.

4. Discussion

Refractive index change was induced by scanning the sample up to 4 mm/s in PDMS at a slowly focusing condition (NA 0.25 and NA 0.13). These results are in agreement with the fact that the refractive index change was induced in PDMS plates by a tight focusing condition (NA 0.85 and NA 0.5) with femtosecond lasers (λ=800 nm, 130 fs, 1 kHz repetition rate) at a rate of 5 mm/s [18,19].

Okoshi *et al.* demonstrated direct writing of silica optical waveguides on the surface of silicone ($[SiO(CH_3)_2]_n$) rubber by F_2 laser at a wavelength of 157 nm [24–27]. They reported that F_2 laser irradiation of silicone in the presence of oxygen can modify the surface into carbon-free silica photochemically. Nakamura *et al.* reported that femtosecond laser irradiation drives similar photochemical processes, namely silicone photo-dissociation in the same framework of the 157-nm F_2 laser irradiation [17]. They reported that photo-dissociation of $SiCH_3$ and photo-production of SiOH are induced by femtosecond laser irradiation. Furthermore, the modification of silicone apparently results from hybrid photo-dissociation and pyrolysis.

Actually, in principle, the index change can be positive or negative. The diffraction grating experiments can not elucidate the difference. Nakamura [17] and Cho [18,19] demonstrated that induced refractive index change was positive. Refractive index change remains under investigation and will be the subject of a future study.

Mochizuki *et al.* investigated refractive index change in various polymers using femtosecond laser pulses [5]. They reported that a low-density polymer with a large free volume apparently contracts more easily than a denser material does. The PDMS density of is low with a value of 0.98 g/cm^3. This tendency was not true for the mechanism in the induction of refractive index change in PDMS. The tensile strength of PDMS (8 MPa) is higher than that of PMMA (75 MPa) and PMMI (87 MPa), implying that it might be easier to modify PDMS (compared to PMMA) physically using femtosecond laser pulses. Although details of the physical mechanisms responsible for infrared photosensitivity of PDMS in the femtosecond regime are still under investigation, femtosecond lasers can induce filamentary refractive index modification in PDMS.

Conclusions

We demonstrated the difference in the morphology of structural modifications induced by varying the scanning speed and the energy under slow-focusing conditions in PDMS. We investigated laser parameters for induction of refractive index modifications in PDMS. The refractive index change was induced by scanning the sample up to 4 mm/s. This value is higher than those in PMMA and PMMI. Refractive index change with a magnitude of 2.3×10^{-4} was estimated from diffraction efficiencies of a fabricated internal grating with 300 μm thickness. The selective change of the refractive index in silicone is a promising method for use in fabrication of photonic structures in LED applications.

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