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Refractive-index patterning of tellurite glass surfaces by laser spot heating

Satoru Inoue, Akihiko Nukui, Kazuhiro Yamamoto, Tetsuji Yano, Shuichi Shibata, Masayuki Yamane, and Tomoharu Maeseto

A dot pattern of a refractive-index change was formed by spot heating with laser-beam irradiation on sodium tellurite glasses. The 15Na₂O·85TeO₂ (mol. %) glass doped with 2 mol. % of CoO was irradiated by a green light-beam spot (532 nm) ~800 μm in diameter from the second-harmonic generator of a Q-switched pulsed YAG laser. The map of the refractive index of the glass was determined with an He–Ne laser beam by a scanning ellipsometric technique at a resolution of 100 μm, indicating that the spots possessing a refractive index lower by ~0.05 were formed at the region irradiated by the laser beam. © 1998 Optical Society of America

1. Introduction
Refractive-index patterning is a key process in the development of many kinds of optical devices, e.g., planar optical waveguides, microlens arrays, diffraction patterns. Well-known techniques for forming patterns of refractive index on glasses include chemical vapor deposition (CVD) processes, physical vapor deposition (PVD) processes, ion-exchange processes, photochemical processes, or ion-implantation processes. In the CVD and the PVD processes, the products of the reaction between the source gases (CVD) or the vapor from the sources (PVD) condense on the glass substrates, resulting in the formation of amorphous thin films on the glasses. The ion-exchange processes introduce new ions into the glasses while removing different ions from the glasses, leaving a layer of different composition near the surfaces. In the photochemical processes, the porous glass is impregnated with organometallic compounds that are then exposed to light, causing the compounds to decompose on the pore walls. After sintering occurs, the composition of the host glass is modified. The ion-implantation technique embeds ions into the glass matrix with high energy. These techniques form refractive-index patterns by changing the compositions near the surface of the glasses.

In general, the glasses exhibit intrinsically volume changes with heating and cooling shown schematically in Fig. 1. Va and Tg indicate the molar volume and the glass transition temperature of the annealed glasses, respectively. The temperature at which the glass transition takes place during cooling strongly depends on the cooling rate. The faster the cooling rate, the higher the glass transition temperature. The different molar volumes give the different densities and different refractive indices to the glasses. In other words, a different refractive index could be derived from the glass of a unicomposition by altering the cooling rates. According to Tool’s theory, these glasses have the same composition but different fictive temperatures. [Fictive temperature is a technical term in the field of glass science and corresponds to the temperature at which the glass structure would be in equilibrium, if cooled or heated very rapidly to that temperature (from Ref. 6).]

If the absorption of the glass at the laser wavelength and the power of the laser beam are tuned properly, the laser-beam irradiation onto the glass surfaces heats the irradiated part above the glass transition temperature Tg and the sudden cutoff of the laser power leads to quick cooling of the irradiated part. This would change the refractive index of
the irradiated part, resulting in a variation in the refractive-index patterns on the glasses.

Tellurite glasses are known for their high refractive index, rather large thermal expansion, and low glass transition temperature among the stable oxide glass systems.\(^7\) The high refractivity and the low glass transition temperature are favorable for a large change in refractive index with laser-beam heating, although the large thermal expansion is unfavorable in the generation of thermal stresses and the deformation of the glass surface. Among stable oxide-glass-forming systems, the tellurite system is considered to be one of the glass systems suitable for laser-beam patterning of the refractive index.

In this study, the feasibility of refractive-index patterning by laser-beam spot heating was investigated by measuring the refractive index around the irradiated parts of sodium tellurite glasses with a scanning ellipsometric technique.

## 2. Experimental Procedures

### A. Preparation of the Glasses

The composition of the sample glass was taken in the middle of the glass-forming region of the sodium tellurite system to be 15Na$_2$O·85TeO$_2$ (mol. %). The absorption of the glasses in the laser wavelength (532 nm) was controlled by the addition of 0.3, 1.0, or 2.0 mol. % of CoO. The glass batches for 40-g glasses were prepared from reagent grade TeO$_2$, Na$_2$CO$_3$, and Co$_3$O$_4$ (>99.95%). The batch was melted in a platinum crucible at 900 °C for 30 min. The melt was poured into a carbon block. Immediately after the melt lost the visible red heat radiation, the glass was moved to an electric furnace for annealing at 280 °C for 30 min, followed by cooling to room temperature at a rate of 1 °C/min. The sample glasses for the optical measurement were cut from slabs to a 10 mm width × 10 mm height × 1.5 mm thickness or 10 mm × 30 mm × 1.5 mm and were polished optically flat.

### B. Measurement of Thermal and Optical Properties

The glass transition temperatures and the thermal expansion coefficients of the glasses were determined from thermal expansion curves measured by a thermomechanical analyzer (Rigaku Model TMA-CN8098C1) at a heating rate of 5 °C/min at a temperature range near a room temperature of ~300 °C.

The optical absorption spectra of the sample glasses in a wavelength range of 200–2500 nm were measured at room temperature (RT) by a spectrophotometer (JASCO Model V570) as well as under heating by the arrangement shown in Fig. 2 at a wavelength range of 350–750 nm. The heated sample was irradiated with the light of a Xe lamp, and the transmitted light was analyzed with a monochromator of 25-cm focal length.

Before the measurements of the temperature dependence of the refractive index were taken, the sample glasses were reheated at 285 °C for 30 min and cooled to RT at a rate of 1 °C/min to afford the same thermal history, in other words, to have initially the same fictive temperature. The refractive index of the sample glasses was measured by computerized photoelastic modulator (PEM) ellipsometer (JASCO Model M-150), in which the optical constants (the refractive index and the extinction coefficient) were determined automatically at an incident angle of 45° within 1 s. The light source was an He–Ne laser beam focused onto the sample at an ~15-μm diameter. The beam diameter was estimated by multiplying two by the minimum spot size calculated from the equation (corresponding to the size of the Gaussian beam west of the lens), \((4/3) \times (1.22\lambda /D) \times 1000\), where \(\lambda\) is the wavelength (632.8 nm), \(f\) is the focal length of the focusing lens (22 mm), and \(D\) is the effective aperture size of the lens (3.0 mm). The measurement of the temperature dependence of the refractive index was made by using the heating stage shown in Fig. 3 with the ellipsometer. The temperature of the sample on the heating stage was sensed with a type K sheet thermocouple clamped to the front of the sample.

### C. Laser-Beam Irradiation

The experimental arrangement for laser-beam irradiation is illustrated in Fig. 4. A laser wavelength of 532 nm was produced by the second-harmonic generation (SHG) of a Q-switched pulsed YAG laser (Spectra-Physics Model GCR-16S) operated at 10 Hz. The beam profile was a Gaussian type. The SHG...
beam was introduced into the focusing lens after the YAG beam was filtered through a dichroic mirror. The SHG laser beam was projected onto the sample in an optical glass cell. Before the experiments were performed, a paper was set at the sample position to be abraded by the SHG beam. The diameter of the SHG laser beam was estimated to be \( \approx 800 \, \mu \text{m} \) from the size of the image of an abrasion spot enlarged by a copy machine. The optical glass cell was filled with ethanol to suppress the abrasion damages at the sample surface because of the reflection. The irradiation time and power were varied over ranges of 0.5–30 min and 0.01–0.1 W (average power) to survey the optimum conditions for patterning. Before irradiation, the sample glasses were heat-treated as in the measurements of the temperature dependence of the refractive index. After irradiation, the glasses were observed with a polarizing optical microscope in the reflection mode and with a stereoscopic optical reflection microscope. The map of the refractive index was composed at RT by using a mounting \( X \)-\( Y \) stage driven by a computer at a resolution of 100 \( \mu \text{m} \) (\( X \) direction) \( \times 50 \, \mu \text{m} \) (\( Y \) direction) on the ellipsometer.

3. Results and Discussion

A. Thermal Properties and Optical Absorption Spectra
The determined glass transition temperatures \( T_g \) and thermal expansion coefficients are \((264 \, ^\circ\text{C}, 235 \times 10^{-7}/\circ\text{C})\), \((265 \, ^\circ\text{C}, 235 \times 10^{-7}/\circ\text{C})\), \((265 \, ^\circ\text{C}, 226 \times 10^{-7}/\circ\text{C})\). The glass transition temperatures differed by 3 deg, and the thermal expansion coefficients differed by \(-4\%\) between the maximum and the minimum. These differences are very small, and the measured thermal properties of the glasses are considered to be essentially equivalent. The penetration depth of the irradiated light was estimated from the measured absorption spectra. The penetration depth was determined as the thickness of the glass at which the light intensity became half of the incident intensity. The penetration depth is plotted as a function of the wavelength in Fig. 5. The undoped glass is transparent to light from the visible to the near IR. The addition of CoO to the glasses increases the absorption of the glasses at 532 nm, and the 2.0-mol. % addition allows a very small penetration of light into the glasses in the wavelength range from 500 to 700 nm. The heated volume should be large enough to leave the patterns stable but should be as small as possible to heat only the beam-irradiated parts efficiently. Therefore penetration of light should be finished quite near the surface of the glass. The addition of CoO by more than 1 mol. % is large enough to convert all the energy of the penetrated light into heat near the glass surface (\( \approx 100 \, \mu \text{m} \)) for 532-nm light.

The tellurite glasses containing transition metal oxides exhibit thermochromic behavior in the visible region. Figure 6 shows the absorption spectra of the glass added with 0.3 mol. % of CoO recorded at various temperatures. The transmission spectra shifted and decreased with the increase in temperature, exhibiting thermochromism. The absorption of glass in the wavelength range between 510 and 620 nm remained appropriate with the heating. Therefore the wavelength range of 510–620 nm is considered to be favorable for laser-beam heating on the tellurite glasses with CoO added.

B. Thermal Change in Refractive Index
The change in the refractive index of the glasses doped with 2.0 mol. % of CoO under rapid cooling is...
shown as a function of time in Fig. 7. First, the sample glasses were heated to temperatures of 250 °C, 265 °C, 268 °C ($T_g$), and 280 °C at a rate of 5 °C/min. Immediately after the temperature of the sample reached the scheduled values, we cooled the glasses by switching off the heater current while continuing the cool water flow. The refractive index of the sample glass was sampled every 1 s and recorded for 40 min on the ellipsometer. The cooling rate at the surface of the sample glass was ~35 °C/min, and the temperature of the sample glass passed the glass transition region within 1 min. The refractive indices of the glasses reached 2.142, 2.148, 2.152, and 2.157 after 40 min for the cases of heating to 280 °C, 268 °C, 265 °C, and 250 °C, respectively. The higher the fictive temperature, the lower the refractive index of the glass after rapid cooling. The results indicate that the refractive index of the supercooled liquid was frozen in after quick cooling as shown in Fig. 1.

C. Test of Laser-Beam Irradiation
The results of the irradiation at 532 nm under various pulse lengths and power are summarized for glasses doped with 2.0 mol. % of CoO in Fig. 8. At an average power of 0.05–0.07 W, a favorable refractive-index change without abrasion was observed. Under 0.06 W, an optimum irradiation time was obtained between 15 and 30 min, whereas under 0.07 W, it was restricted within 3 min between 8 and 11 min. The increase in the irradiation power caused abrasion, and the optimum power was found to be around 0.06 W.

A sample glass was irradiated at 0.06 W for 20 min and was subsequently observed by a stereoscopic optical microscope, a polarizing optical microscope, and a scanning ellipsometer. A photograph of the surface taken by the stereoscopic reflection microscope is shown in Fig. 9. The white circles indicate the general position of the irradiated area. As seen in the figure, the surface of the glass inside the circles has a different appearance. Moreover the polishing scratches seen outside the circles are observed to cross the circles without disturbance, which appears to indicate that the surface of the changed area was not deformed because of heating above the glass transition temperature. Figure 10 shows photographs from the polarizing microscope taken on the laser-irradiated parts [15Na$_2$O·85TeO$_2$ glass + 2 CoO (mol. %)].
beam irradiated area in the reflection mode in opened Nicols and crossed Nicols conditions. The circles indicate the general position of the irradiated area. The crossed Nicols photograph shows that the central part of the irradiated region presents a weak birefringence. The birefringence of the glasses is normally derived from the existence of crystals or residual stresses. The size of the area showing birefringence is much smaller than the sizes of the changed area observed on the stereoscopic reflection micrographs, and the shapes and the outline of the birefractive area are not clear, suggesting that the birefringence is derived from stresses. Therefore the different appearance of the irradiated parts is considered not to be derived from crystallization of the glasses.

Figure 11 is a map of the refractive index around the area that is laser-beam irradiated. The initial refractive index of the annealed sample glass was 2.165. The black circle indicates the general position of the irradiated region. The inside of the circle shows a refractive index lower than the surroundings. The inside of the circle was heated with the laser beam followed by quick cooling, and the refractive index is lower than the surroundings as seen in Fig. 7. Therefore the reduced refractive index is believed to be derived from a change in the fictive temperature of the glass as a result of the laser-beam spot heating followed by quick cooling. The region possessing a refractive index higher than the surroundings is observed at the outside of the irradiated region. The densification of the glass is considered to be the origin of the formation of a high-refractive-index region. The decrease in the sodium-ion content is one possible reason for such densification. The crossed Nicols observation on the polarizing microscope gave no detectable birefringence outside the spot, implying that there is no stress-induced densification. Details of the mechanisms yielding refractive dot patterns are not yet clear, but the results indicate that laser-beam irradiation of the glass can form spot patterns of refractive index without crystallization or a distinct deformation of the glasses.

As shown in Fig. 6, the change in the refractive index of the heated glass is terminated by rapid cooling at different values that depend on the temperature reached. It means that the contrast in the refractive index of the region that is laser beam irradiated with the surroundings can be changed by varying the irradiation time, in other words, changing the ultimate temperature achieved. Therefore this patterning technique can produce a stepped-index variation at various contrasts. If the irradiation is tuned properly, multiplex code digital photorecording would be a possible application.

4. Conclusion
A refractive-index dot pattern has been formed through quick heating by laser-beam spot heating on sodium tellurite glasses. The 15Na2O · 85TeO2 (mol. %) glass doped with 2 mol. % of CoO shows an appropriate absorption of the laser beam (wavelength, 532 nm) of ~800 μm in diameter from the SHG of a YAG laser. The map of the refractive index of the glass was composed by a scanning ellipsometric technique at a resolution of ~100 μm, indicating that the spots possessing refractive indices lower by ~0.05 than the surroundings were formed at the region irradiated by the laser beam. The observation with the polarizing optical microscope and the stereoscopic optical microscope suggested that crystallization did not take place.
References


