JOURNAL OF MATERIALS SCIENCE **37** (2002) 3459– 3465

Refractive index patterning of tellurite glass surfaces by ultra short pulse laser spot heating

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Dot patterns of refractive indices were formed by the laser pulse irradiation on the tellurite glasses. The ternary tellurite glasses of TeO_2-Na_2O-Al_2O_3, TeO_2-Na_2O-GeO_2 and TeO_2-Na_2O-TiO_2 doped with 2 mol% of CoO were irradiated by a femtosecond pulse laser beam (800 nm) or by a green light beam (532 nm) from a second harmonic generator of a Q switch pulse YAG laser. The refractive index map of the glass was composed with an He-Ne laser beam by an scanning ellipsometric technique at a resolution of 100 μm $\times$ 50μm, indicating that the spots possessing refractive index lower by about 0.05–0.38 than the surroundings were formed at the region irradiated by the laser beam. The irradiation of the femtosecond laser beam generated the dot patterns roughly equivalent to the beam size. The change of refractive index could be tunable by adjusting laser power, suggesting that the process could be applied to optical recording.

1. Introduction

In general, the glasses exhibit intrinsically the volume changes with heating and cooling shown schematically in Fig. 1. The V_a and the T_g indicate the molar volume and the glass transition temperature of the annealed glasses, respectively. The cooling rate strongly affects the temperature at which the glass transition takes place. The quick cooling gives the glass transition temperature higher than T_g [1]. The glasses intrinsically could have different molar volumes as the results of how quick the melt was cooled down into the supercooled liquid. The different molar volumes give the different densities and the different refractive indices to the glasses. In other words, the glasses different in the refractive index could be derived from the glass of the same composition by tuning the cooling rates at various levels. According to the A. Q. Tool's theory, these glasses have the same composition but are different in the fictive temperatures [2].

The authors showed that the spot laser beam irradiation could generate refractive index dot patterns on the surface of a sodium tellurite glass of $85TeO_2 \cdot 15Na_2O$ (mol%) with the aid of the refractive index matching oil [3]. The map of the refractive index obtained by ellipsometry showed that the refractive index of irradiated parts was lower by about 0.05 than the surrounding matrix. The laser beam irradiation was performed on the glass samples immersed in ethanol to suppress the ablation originated from the imperfection of the surfaces of the tellurite glasses.

Femtosecond lasers produce high energy pulsed light beams with pulse width of about 100 fs which are suitable to introduce heating energy into glass surfaces effectively. Moreover the short irradiation time (100 fs) is favorable to suppress the ablation on the surfaces of the glasses, leading to the direct heating of the glass without damages. If the direct heating of the surface of glasses with the laser beam spot could generate refractive index dots, the new optical recording process is possible on the ordinary glass surfaces. The process does not need formation of any active thin films necessary for magnetic recording, magneto-optical recording etc. The new optical recording would be a very simple process and might be categorized to the recording of fictive temperatures [2].

In this study, the feasibility of the new style optical recording by the femtosecond laser beam spot heating was investigated through composing the map of the refractive index around the irradiated parts of ternary tellurite glasses by a scanning ellipsometric technique.

2. Experimental procedures

2.1. Preparation of the glasses

The batch compositions of the sample glasses were given in Table I. The ternary tellurite glasses of TeO_2-Na_2O-Al_2O_3, TeO_2-Na_2O-GeO_2 and TeO_2-Na_2O-TiO_2

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TABLE I Batch compositions of the glass samples

Glass	TeO_2	Na_2O	Al_2O_3	GeO_2	TiO_2	CoO
TN	85	15				2
TNA1	80.8	14.2	5			2
TNA2	76.5	13.5	10			2
TNG1	80.8	14.2		5		2
TNG2	76.5	13.5		10		2
TNG3	72.3	12.7		15		2
TNT1	80.8	14.2			5	2
TNT2	76.5	13.5			10	2

Fraction number was given in mol%.

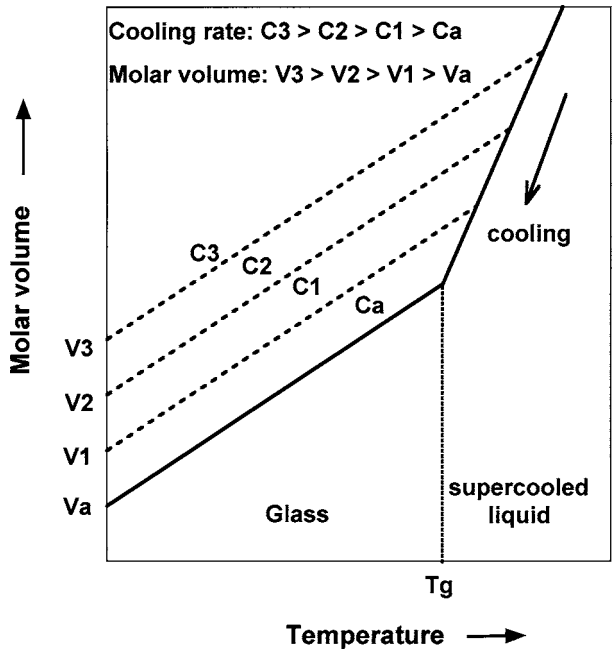

Figure 1 Schematic molar volume-temperature relations of glasses.

were prepared. The components of Al_2O_3, GeO_2 and TiO_2 were employed to decrease thermal expansion coefficients of the glasses from that of the TN glass ($85TeO_2 \cdot 15Na_2O$ (mol%)). The 2 mol% of CoO was added to the systems to increase the light absorption of the glasses. The glass batches for 40 g glasses were prepared from the reagent grade TeO_2 (>99.9%), Na_2CO_3, Al_2O_3, GeO_2, TiO_2 and Co_3O_4 (>99.95%). The batch was melted in an platinum crucible at 900°C for 30 min. The melt was poured onto the carbon block. Immediately after the melt lost the visible red heat radiation, the sample glass was moved to an electric furnace for the annealing at 280°C for 30 min followed by cooling to room temperature (RT) at a rate of 1°C/min. The sample glasses for the optical measurement were cut out of the slabs to 10 mm in width × 10 mm in height × 1.5 mm in thickness or 10 mm × 30 mm × 1.5 mm and polished to optical flat. The finished glass samples were annealed well by heating at 15°C above T_g for 30 min followed by cooling to RT at a rate of 1°C/min.

2.2. Measurement of thermal and optical properties

The glass transition temperatures and the thermal expansion coefficients of the glasses were determined from the thermal expansion curves measured by a Thermo-Mechanical-Analyzer(Rigaku, Model TMA-CN8098C1) at a heating rate of 5°C/min in the temperature range of RT ∼300°C.

The thermal diffusivities of glasses were measured with laser flash technique on the glass disks of 10 mm in diameter × 1 mm in thickness. The source of laser was CO_2 laser beam of 1 W. The mechanical shutter for cameras was used to chop the laser beam into a pulse. The thermal diffusivity was calculated on the temperature-time profile recorded at the backside of the sample after the irradiation of laser pulse of 1/8 s.

The refractive indices of the sample glasses were measured by an computerized PEM (Photo Elastic Modulator) modulation 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 sec. The light source was an He-Ne laser beam focused onto the sample at about 15 μm in diameter.

2.3. Laser beam irradiation

2.3.1. YAG laser beam irradiation

The setup for the irradiation was given in Fig. 2. The laser beam was the green light of 523 nm (SHG beam) from the second harmonic generator of the Q-switch pulse YAG laser (Spectra Physics, Model GCR-16S) operated at 10 Hz. The pulse width was 5 ns. The SHG beam was focused onto the sample in an optical glass cell as a spot of about 800 μm in diameter. Ethanol was used as an index matching oil to suppress the ablation damages at the surface. The irradiation time and power were tuned in the ranges of 125 ms–900 s and 0.06 W–1.0 W (average power). The YAG laser beam irradiation was performed to screen the glasses giving large change of refractive index among sample glasses.

The thermal diffusivities of the glasses were measured by laser flash method to be located in 5.8×10^{-3} cm^2/sec–7.2×10^{-3} cm^2/sec. Therefore the possible heat loss due to the heat conduction into glass could be about 0.07% of the absorbed energy within the interval time between pulses operated at 10 Hz. The thermal conductivity of liquid ethanol and air

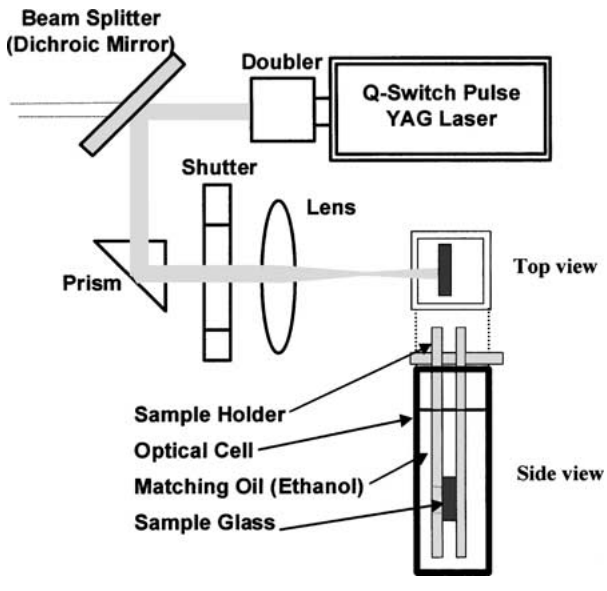

Figure 2 Configuration for the irradiation of the YAG laser beam.

at room temperature were estimated to be about 4×10^{-4}, 6×10^{-5}, respectively [4]. These values are smaller by the magnitude of 1–2 order than those of glasses, indicating that the loss of the heat from the irradiation point through the matching liquid ethanol and the air was very small. The repetition rate of the YAG laser beam, 10 Hz, is believed to be fast enough to attain cumulative heating on the glass surfaces.

2.3.2. Femtosecond laser beam irradiation

The laser beam employed was 800 nm light from the femtosecond laser facility (COHERENT, Model MIRA 900) operated at 1 kHz. The pulse width was 100 fs. The irradiation time and power were tuned at 2, 4, 8, 125, 500 ms and 0.66 w (660 μj/pulse). The configuration of the irradiation was given in Fig. 3. The original beam (6 mm in diameter) from the laser facility was focused just before the sample and the defocused beam was projected on the sample surface. The size of the irradiation beam was calculated to be about 600 μm in diameter from the principle of the geometric optics.

3. Results and discussion

3.1. Thermal and optical properties of the glass samples

The glass transition temperatures, the thermal expansion coefficients and the refractive indices of the sample glasses are summarized in Table II. The addition of Al_2O_3, GeO_2 or TiO_2 was effective to decrease the thermal expansion coefficient. The refractive index of the glass deceased with the addition of Al_2O_3 or GeO_2 but increased in the case of TiO_2.

TABLE II Thermal and optical properties of the sample glasses

Glass	T_g (°C)	Thermal expansion coefficient ($\times 10^{-7}$ °C^{-1})	Refractive index (at 632.8 nm)
TN	268	235	2.165
TNA1	292	215	2.130
TNA2	320	190	2.087
TNG1	276	234	2.127
TNG2	289	217	2.090
TNG3	302	201	2.052
TNT1	281	227	2.181
TNT2	300	211	2.192

3.2. Laser beam irradiation test

3.2.1. YAG laser beam irradiation

Table III shows the change of refractive index of the irradiated part of the glass sample under various conditions of the total input energy of 54 J (0.06 w for 900 s), 42 J (0.07 w for 600 s), 0.1 J (0.4 w for 1/4 s) and 0.05 J (0.4 w for 1/8 s). The total input energy was calculated with multiplying the beam intensity by the number of pulses. The refractive index change was determined as the difference between the maximum refractive index on the dot generated (generally at the center of the dot) and the initial refractive index of the glass (listed in Table II). The value in the square bracket corresponds to the change of refractive index divided by the energy input, indicating the apparent efficiency of changing refractive index. The glasses TNA1 and TNA2 gave rather large change of refractive index. The TNG2 glass showed large change of refractive index comparable

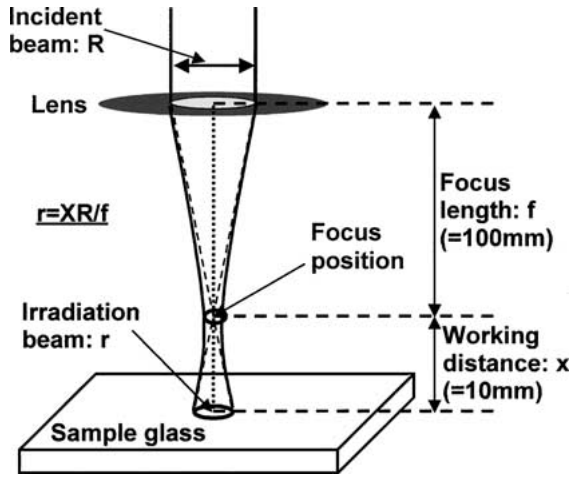

Figure 3 Configuration for the irradiation of the femtosecond laser pulse.

TABLE III Change of refractive index after irradiation of YAG laser beam

Glass	Initial refractive index	Input energy (54 J)	Input energy (42 J)	Input energy (0.1 J)	Input energy (0.05 J)
TN	2.165	−0.033 [−0.0006]	−0.030 [−0.0007]	−0.013 [−0.1]	−0.010 [−0.2]
TNA1	2.130	−0.216 [−0.004]	−0.166 [−0.004]	−0.071 [−0.7]	−0.047 [−0.9]
TNA2	2.087	−0.217 [−0.004]	−0.174 [0.004]	−0.074 [−0.7]	−0.052 [−1.0]
TNG1	2.127	−0.053 [−0.001]	−0.042 [−0.001]	−0.038 [−0.38]	−0.014 [−0.3]
TNG2	2.090	−0.123 [−0.002]	−0.038 [−0.001]	−0.057 [−0.57]	−0.041 [−0.8]
TNG3	2.052	−0.057 [−0.001]	−0.057 [0.001]	−0.032 [−0.3]	−0.013 [−0.3]
TNT1	2.182	−0.086 [−0.002]	−0.064 [−0.002]	X	X
TNT2	2.192	−0.061 [−0.001]	−0.053 [−0.001]	−0.031 [−0.31]	−0.028 [0.6]

X: ablation; [ ]: refractive index change/input energy (=apparent efficiency (J^{-1})).

with those of TNA glasses. The TNT1 glass got ablation under the input energy of 0.1 J and 0.05 J. The apparent efficiency increased with the decrease of the energy input. The decrease of the input energy brought the decrease of the volume of the glass heated by the laser beam, resulting in the increase of the apparent efficiency.

Fig. 4 shows the refractive index map of the TNA2 glass irradiated by YAG laser beam at the input energy of 0.062 J. The dots of about 1 mm in diameter were generated. The refractive index of the irradiated parts decreased from 2.087 to 2.025 at 632.8 nm. The estimated diameter of the laser beam was 800 μm but the dots generated were lager by about 25% than the irradiation beam size.

3.2.2. Femtosecond laser beam irradiation test

The refractive index map of the TNA2 glass irradiated by the femtosecond laser beam is given in Fig. 5. The dots of about 600 μm in diameter were observed on the map. The refractive index of the dots was 1.905 and lower by 0.182 than the initial index of 2.087. The phenomenon is different from the results obtained from the experiments, in which the high energy femtosecond laser beam was focused into the transparent glass, resulting in the increase of the refractive index at the irradiated region [5]. E. N. Glezer and E. Mazur [6] reported that the femtosecond laser beam focused into a transparent glass drove micro-explosions at the focused area, forming a cavity and a region of compacted

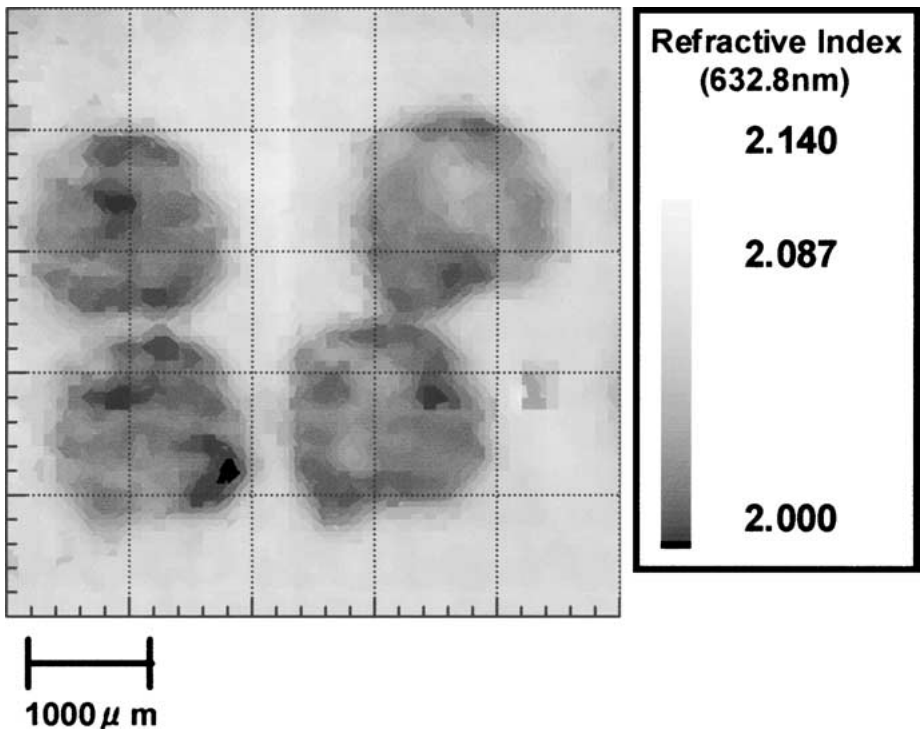

Figure 4 Refractive index map of irradiated parts on TNA2 glass. (input energy: 0.0625 J).

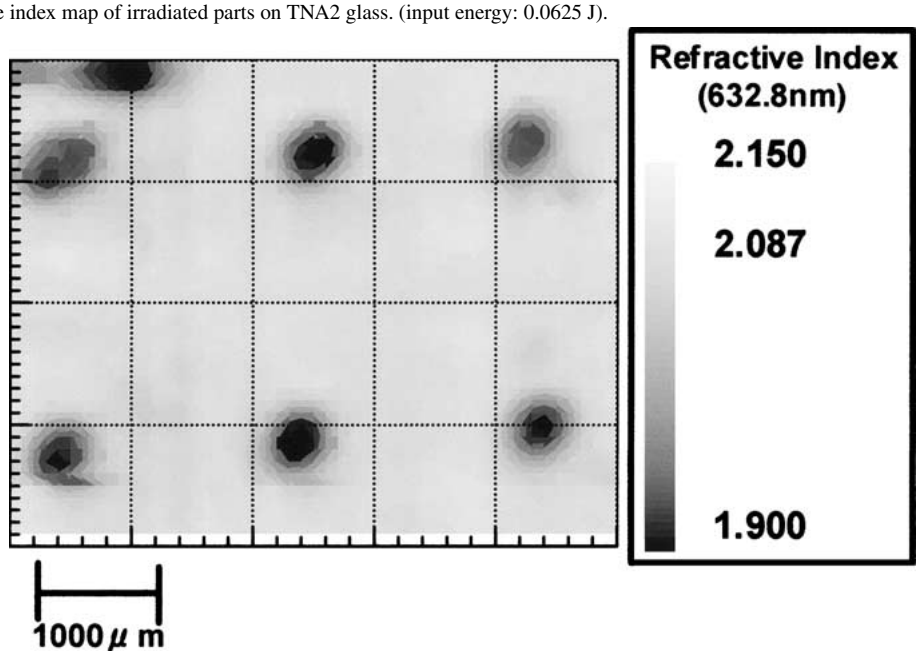

Figure 5 Refractive index map of the parts irradiated by femtosecond laser beam on TNA2 glass. (input energy: 0.00132 J (=2 pulses)).

material in the glasses. Taking the experimental conditions of the two studies by K. Miura *et al.* [5] and E. N. Glezer *et al.* [6] into account, the femtosecond laser beam focused into a transparent material is believed to cause micro-explosions in the closed system (glass capsule), leading to the generation of compacted region, that is, high refractive index region. In the case of this study, the laser beam irradiated on the surface of the glasses was converted into heat near the surface due to strong absorption. Therefore the absorbed energy might cause micro-explosions in the system opened to atmosphere, resulting in the formation of expanded region, that is, low refractive index region.

The change of the refractive index was 3 times larger than that of the YAG laser irradiation on the TNA2 glass (Fig. 4). Taking the estimated size of the beam (=600 μm) into account, the femtosecond laser beam generated the dots of the sizes equivalent to the irradiation beam size. In the case of the femtosecond laser, the power density was high enough to heat the glass above T_g with short irradiation and the area of the heated above T_g on the glass surface was considered to be equivalent to the beam size. The power density of the YAG laser beam was not so high as the femtosecond laser and the long irradiation was necessary to heat the glass above T_g. The long irradiation in the YAG laser

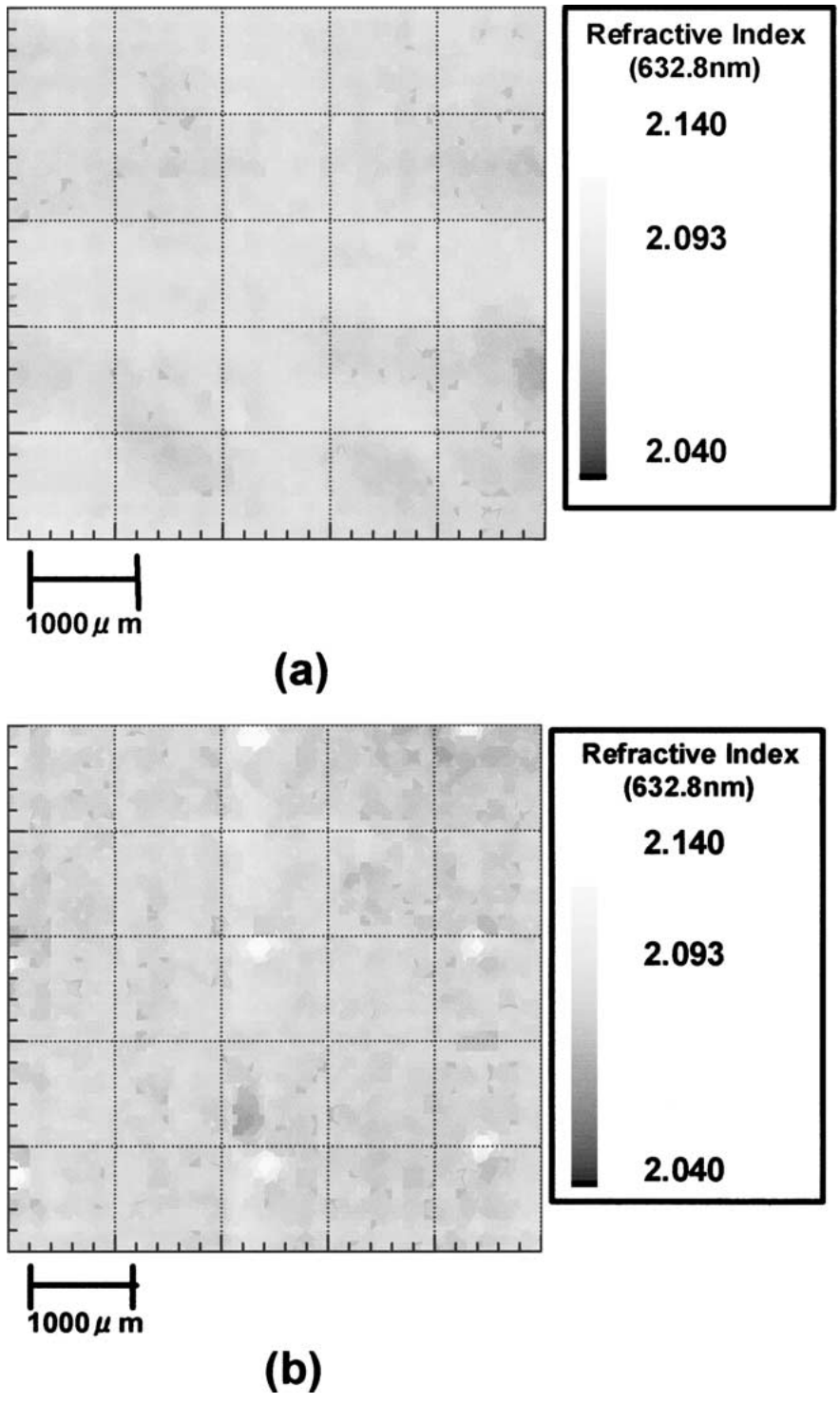

Figure 6 Refractive index map of the parts irradiated by femtosecond laser beam on $85TeO_2 \cdot 15Na_2O$ (mol%) glass. (input energy: (a): 0.00132 J (=2 pulses), (b): 0.165 J (=125 pulses)).

case increased the volume heated above T_g, leading to the increase of the size of the dot. The femtosecond laser (1 kHz) provided the pulses every 1 msec and promoted cumulative heating more efficiently than the YAG laser (10 Hz) case where the pulses were irradiated every 100 msec.

Fig. 6a shows the refractive index map of the $85TeO_2 \cdot 15Na_2O$ (mol%) glass exposed to the two shots of the femtosecond 800 nm laser pulse. No dot patterns were detected at the resolution of the ellipsometry. The glass is transparent to the 800 nm beam and the laser beam just passed through the glass. Fig. 6b indicates the refractive index map of the $85TeO_2$-$15Na_2O$ glass irradiated by the 125 femtosecond laser pulses. The refractive indices of the irradiated parts were observed to be larger than the initial value on the map, but the parts were damaged so heavily. The bright dots in Fig. 6b did not reflect the real refractive index change but the disturbed reflection area at the holes. These results indicate that the laser beam energy absorbed by the cobalt ions originated the change of refractive index.

3.2.3. Relation between the change of refractive index and the laser power

Fig. 7 shows the correlation between the change of refractive index and the peak power of the laser pulse. The peak power was calculated by dividing the pulse energy by the pulse width in second. The plots were produced on the cases of the irradiation by 1 or 2 pulses. The change of refractive index increased with the increase of the peak power of the pulse, indicating that the high peak power pulse laser was favorable to induce large change of refractive index.

G. W. Scherer [7] analyzed the refractive index change originated from the glass structural relaxation above T_g and reported the possible refractive index change of the NBS 710 glass (SiO_2-CaO-Na_2O-K_2O system) would be the order of 10^{-3} for the temperature change of 50°C. The thermal expansion coefficients of tellurite glasses are about 4 times larger than that of the NBS710 glass and the volume change of the tellurite glasses would be about 4^3 (=64) times larger than the NBS 710 glass case. Therefore the possible

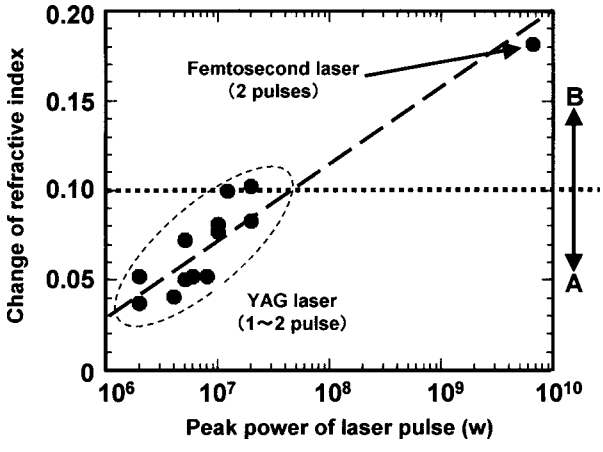

Figure 7 Relation between the change of refractive index and the peak power of the laser pulse.

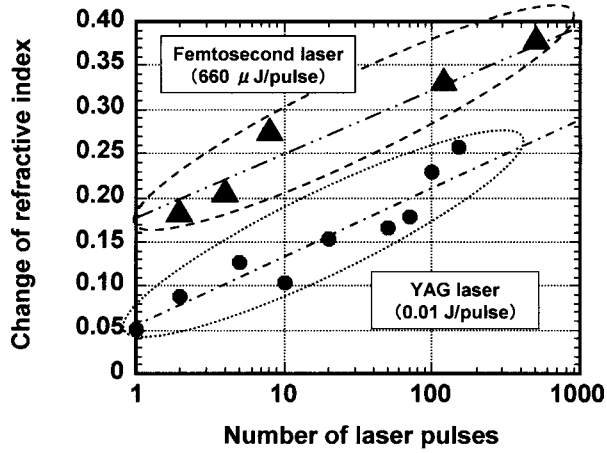

Figure 8 The change of refractive index with the number of laser pulses.

refractive index change of tellurite glasses generated by structural relaxation is estimated to be larger by one order of magnitude than that of NBS 710, and then to be the order of 10^{-2} for the temperature change of 50°C.

As seen in Fig. 7, the change of refractive index of the glasses were the order of 10^{-2} for the YAG laser 1–2 pulse irradiation in the region A, indicating that the refractive index has been changed due to the relaxation of the glass structure, in other words, the change of fictive temperature [2] of the glass. On the other hand the irradiation of femtosecond laser 2 pulses caused the change of refractive index larger than 10^{-1} in the region B, suggesting that the change mechanism was different from the YAG laser 1–2 pulse irradiation case and might be related with non-linear optic effect.

The change of refractive index was plot against the number of laser pulses irradiated in Fig. 8. The change of refractive index increased with the increase of the number of pulses, indicating that the change of refractive index could be tunable by adjusting the number of pulses.

4. Conclusion

The ternary tellurite glasses of TeO_2-Na_2O-Al_2O_3, TeO_2-Na_2O-GeO_2 and TeO_2-Na_2O-TiO_2 doped with 2 mol% of CoO were irradiated by a femto-second laser pulsed beam (800 nm) or by a green light beam (532 nm) from a second harmonic generator of a Q switch pulse YAG laser. The refractive index map of the glass indicated that the spots possessing refractive indices lower by about 0.05–0.38 than the surroundings were formed at the region irradiated by the laser beam. The phenomenon is derived from the intrinsic property of glassy state where the molar volume after glass transition could be changed by the cooling ratio in the supercooling. Therefore the process is principally applicable to any kinds of materials possessing glass transition points, that is, glasses. The change of refractive index increased with the increase of the peak power of the laser pulse. The femtosecond laser pulse was effective to change the refractive index of the glass. The refractive index change could be tunable by adjusting laser power, suggesting that the process could be applied to optical recording. The TeO_2-Na_2O-Al_2O_3 glass gave large change of refractive index and would be one

of the candidate glass systems suitable for the optical recording.

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Received 29 June 2001
and accepted 29 March 2002