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Creation of locally selective mirror surface on $40BaO–40TiO_2–20B_2O_3$ glass by XeCl pulse laser irradiation

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Creation of mirror dots, localized areas of smooth surface with a shape of laser beam on a glass material, using a XeCl laser irradiation is reported. Laser irradiation of a $40BaO–40TiO_2–20B_2O_3$ sample heated to 300 °C induced a smooth and flat surface, where no scratches caused by a mechanical polishing were observed. The present finding indicates that the melting of the surface occurred by the combined effect of the heat-assistance and the increased absorption coefficient of TiO_2. In the present system, the absorption coefficient in the ultraviolet region, which originates from TiO_2, was found to increase with increasing temperature. The presented technique will open new possibilities in integrated optics; the surface of a small protruded or hollow area can be made smooth, which cannot be achieved by conventional mechanical polishing.

I. INTRODUCTION

The merits of oxide glass materials, such as high transparency, chemical durability, and easy modeling, make them an integral passive device in the areas of optical telecommunication and optical information processing. Additionally, the crystallization of the glass provides not only nonlinear optical properties,[1–4] but also larger electronic or ionic conductive properties than the mother glass[5–7] to the glass matrix. The various properties of glass have motivated many researchers to fabricate novel functional devices on glass.

A smooth surface of an oxide glass matrix is of crucial importance for optical devices in achieving low optical connection loss. To obtain a smooth mirror surface with low propagation loss, polishing methods with slurry are usually used. There are, however, two main limitations in mechanical polishing with slurry. One limitation is scratches by the slurry that injures the surface of nanometer scales. Another limitation is the inability of obtaining a smooth surface in such complex structures as (i) the bottom of a concaved structure, (ii) the tops of convex pillars with different heights, or (iii) a partially sloped surface. Another method for obtaining a glass matrix with a smooth surface is a float process, which is industrially in the production of sheet glass.[8] In this process, the smooth surface is obtained without mechanical polishing because a glass melt makes its free smooth surface at the air side and molten tin side. Similar to the floating process, a new method of obtaining a smooth surface should be possible by exploiting the fact that a glass melt makes its free surface at the air side. This article focuses on the creation of a locally selected smooth surface by laser irradiation. That technique realizes not only a smoothness that cannot be achieved by the conventional mechanical polishing method, but also is applicable to the complex structures mentioned above.

Recently, many studies on the local structural change of an oxide glass matrix by laser irradiation have been reported.[2,9,10] Unlike the usual heating or melting process using a furnace, laser irradiation can induce a geometrically selective structural change because only the temperature in the neighborhood of the irradiated part is heated. If the crystallization occurred, an induced structural change is permanently maintained below its glass transition temperature. Thus, laser irradiation of a glass matrix to induce a structural change is a powerful technique for functional optical materials. In this regard, a pulsed laser is expected to be more suitable than a continuous wave laser because of its much higher peak power. Indeed, our research group has reported a lined

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nanoparticle structure at the surface of the $K_2O–Nb_2O_5–TeO_2$ glass by XeCl pulse laser irradiation.[9,11] We have also reported the effect of heat assistance on the laser irradiation to the same TeO_2-based glass in which the uniformity of particle size was improved by the heat assistance.[11] However, these attempts have been limited to the TeO_2-based glass.

We selected $40BaO–40TiO_2–20B_2O_3$ (BTB40) glass as a virgin sample for the irradiation by an excimer laser because the reported glass transition temperature of BTB40 glass is relatively low,[4] at 554 °C, which is suitable for a thermally induced structural change. Because the absorption peak of Ti^{4+} exists at 350 nm,[12] the energy of a XeCl laser ($\lambda = 308$ nm) can be effectively converted into heat by 40 mol% of TiO_2. In the $BaO–TiO_2–B_2O_3$ glass system, it was reported that the crystallization of $Ba_3Ti_3O_6(BO_3)_2$ was achieved by heat treatment.[4] Because this glass system shows high optical nonlinearity in its crystalline form,[13] it has potentials for applications in optical devices. We report the surface morphological change of the BTB40 glass caused by irradiation with a XeCl excimer laser. Laser irradiation with the heat assistance was also demonstrated for comparison.

II. EXPERIMENTAL

The BTB40 glass was prepared by a conventional melt-quenching method with starting materials, $BaCO_3$ (99.95%), TiO_2 (99.9%), and B_2O_3 (99.99%). All chemicals were purchased from Kojundo Chemical Laboratory (Osaka, Japan). After the mixing and melting of batches (16 g) in a platinum crucible in an electric furnace at 1250 °C for 60 min, the glass melt was quenched on a steel plate at 160 °C. The obtained glass samples were annealed at the glass transition temperatures T_g for 30 min and were mechanically polished to obtain a mirror surface.

A XeCl pulse laser (Lambda Physik; OpTex, Chino, CA) with the pulse repetition rate, full width at half-maximum (FWHM) of pulse width, and laser intensity of 10 Hz, 8 ns, and 26 mJ/cm^2, respectively, was used. An objective lens with a focal length of 150 mm was used to focus the laser beam. A sample holder with a heat controller was used for heat-assisted laser irradiation. The temperatures of glass transition T_g and crystallization onset T_x were determined by differential thermal analysis (DTA) using a TG8120 (Rigaku, Tokyo, Japan) operated at a heating rate of 10 K/min. The refractive index was measured with a prism coupler (Metricon, Pennington, NJ) using a He-Ne laser ($\lambda = 633$ nm). The image of the glass surface was observed by atomic force microscopy (AFM) with a model SPI-3800N (Seiko Instruments, Tokyo, Japan) and secondary electron image (SEI) with a model EPMA1600 (Shimadzu, Columbia, MD). The ruggedness of the sample surface was measured with a surface profiler model SURFCOM 480A (Tokyo Seimitsu, Tokyo, Japan). The chemical composition of the surface was measured with an electron probe microanalyzer. The optical absorption spectra were measured with a spectrometer UV-3150 (Shimadzu). In measuring absorption spectra at different temperatures, the samples were set in a quartz cell with a heater, which was filled with silicone oil.

III. RESULTS AND DISCUSSION

The obtained BTB40 glass was slightly yellowish and transparent, and the refractive index of the glass was 1.88 at 633 nm. The T_g and T_x of the BTB40 glass were determined as 570 °C ± 1 °C and 718 °C ± 1 °C by a DTA measurement. Figure 1 shows the absorption spectra of BTB40 glass at 25, 100, 150, and 200 °C. The absorption coefficient in the ultraviolet region increased with increasing temperature. Figure 2 shows the plot of band gap energy E_g versus $1/T$, where E_g was estimated from the square root of absorption coefficient.[14] Because the E_g increases with increasing value of $1/T$, it indicates that the increased absorption of TiO_2 by heat assistance can work effectively for a conversion of the laser energy into heat. However, the surface profile is thought to be mainly dominated by the pulse energy density because no apparent change was observed without the focal lens even with the heat assistance at 300 °C. In the present study, the beam was focused with the objective lens to enhance the laser intensity to about 180 mJ/cm^2, but not higher than this because ablation and cracking at the surface were observed when the sample was irradiated at the focal point.

Figure 3 shows the photograph of the BTB40 glass after laser irradiation for 1000 shots at room temperature [Fig. 3(a)] and at 300 °C with heat assistance [Fig. 3(b)]. After the irradiation at room temperature [Fig. 3(a)], a small protuberance was observed at the center of the

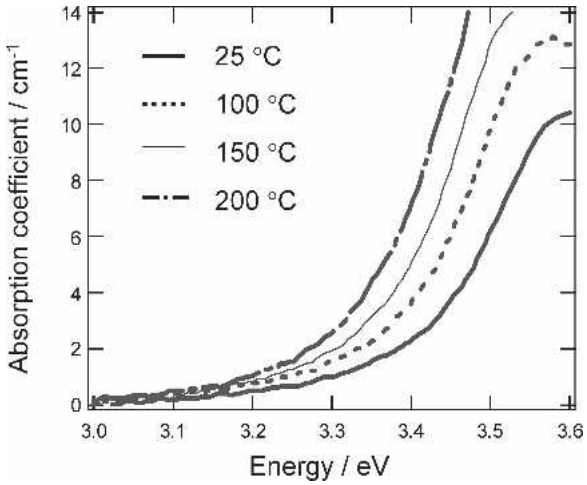

FIG. 1. The absorption spectra of BTB40 glass at different temperatures: (a) 25 °C, (b) 100 °C, (c) 150 °C, and (d) 200 °C.

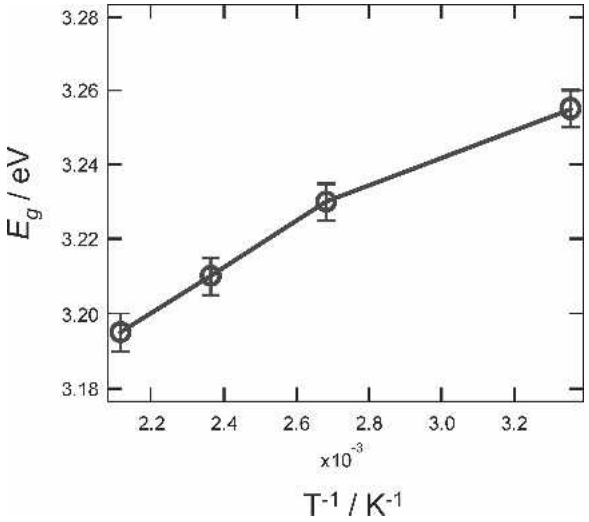

FIG. 2. An Arrhenius plot between band gap energy, E_g, and temperature.

beam spot. On the other hand, when the irradiation with the heat assistance [Fig. 3(b)] was carried out, a trace of the laser beam was clearly observed, of which the edge part was also protuberant. Figure 3(c) shows the SEI of the protuberant part of the BTB40 glass with laser irradiation, where the protuberant part of Fig. 3(a) and the protuberant circle of Fig. 3(b) show the same morphology in the SEI. This result indicates that the small protuberant part in the present study originates from local heating above T_g. It is speculated that rapid cooling at the air/glass interface takes place after the expansion from the inside because of a temperature difference between the air/glass interface and the irradiated part. We speculate that this rapid cooling at the surface makes the small protuberance at the surface of the matrix after the laser irradiation.

The profile of the protuberant region after the laser irradiation after more than 5000 shots was similar to that after 1000 shots, suggesting that the heat profile was practically constant during the interval of pulse irradiation. It follows that the temperature of the surface exceeds T_g for several nanoseconds and then decreases to the initial temperature within the interval of pulse irradiation. Figure 3(d) shows a cross-section profile of the irradiated area measured with a SURFCOM. The height of the protuberant areas of the heat-assisted sample was estimated as 200–400 nm from Fig. 3(d), which was comparable with that of the sample without heating. Note that a flat surface is observed in the center part of the irradiated area without apparent expansion, showing unambiguously that melting has taken place. These results show that the heat assistance at 300 °C is effective in increasing the temperature at the irradiated spot above T_g, especially in the center of the beam spot. However, no sign of crystallization was observed by x-ray diffraction in the present sample, indicating that the time duration above T_g was not enough for crystallization. It is not clear at this moment whether crystallization is favorable or unfavorable in obtaining a smooth surface.

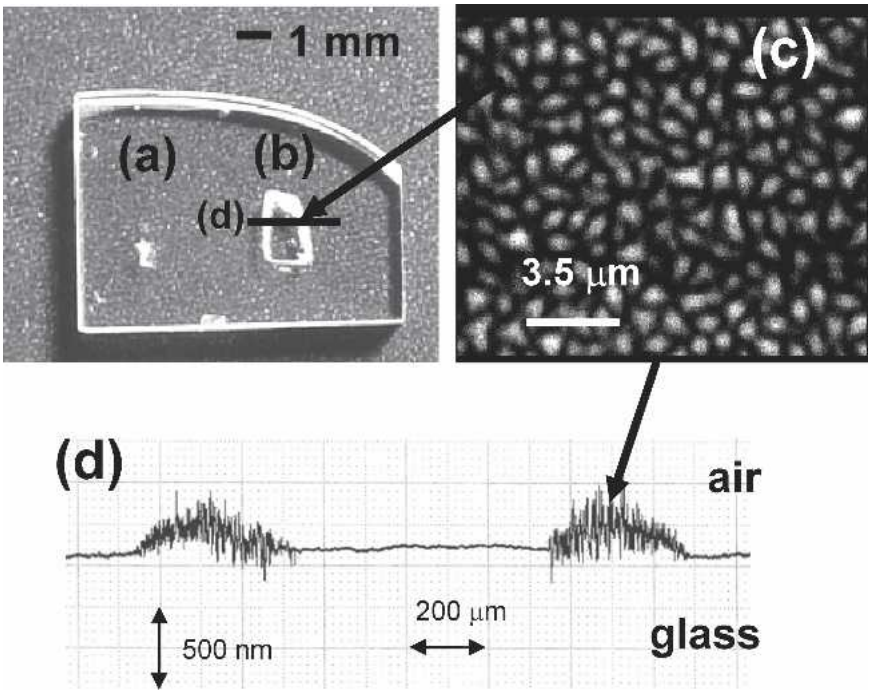

FIG. 3. (a) Photograph of $40BaO–40TiO_2–20B_2O_3$ glass after XeCl laser irradiation at room temperature and (b) with the heat-assistance at 300 °C. (c) SEI of the protuberant part of $40BaO–40TiO_2–20B_2O_3$ glass after XeCl laser irradiation and (d) the cross-section profile of irradiated area measured with a SURFCOM.

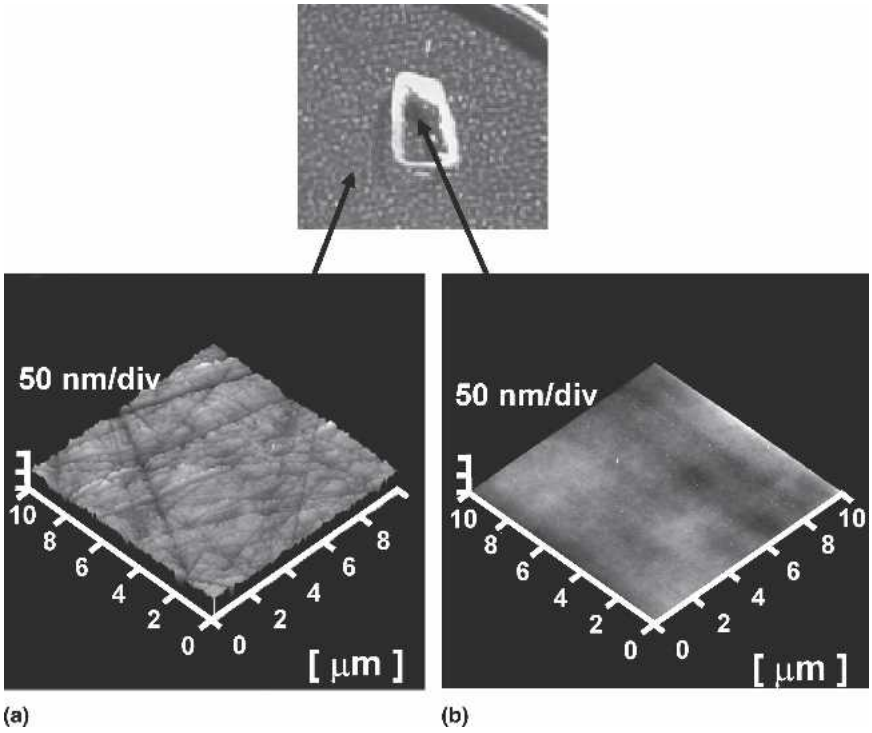

FIG. 4. AFM images of $40BaO–40TiO_2–20B_2O_3$ glass after XeCl laser irradiation with the heat-assistance at 300 °C; (a) outside and (b) inside the irradiated spot.

Figure 4 shows the AFM images of BTB40 glass after XeCl laser irradiation with heat assistance at 300 °C; the outside [Fig. 4(a)] and inside [Fig. 4(b)] of the irradiated area. In the AFM image outside the circle [Fig. 4(a)], many nanoscale scratches produced by mechanical polishing are observed. These scratches are inherently observed at the surface of the glass after polishing with slurry, and the maximum surface area without scratches was estimated as less than 0.01 μm^2. In contrast, no scratches were observed at the center of the laser irradiated spot [Fig. 4(b)], resulting in at least 1 mm^2 of a smooth surface. The root-mean-square and the roughness average of the surface after laser irradiation [Fig. 4(b)] were 0.601 nm and 0.456, which are much smaller than that before irradiation [Fig. 4(a)], at 6.032 nm and 4.64, respectively. The chemical composition ratio of Ba, Ti, and B determined by electron probe microanalyzer was the same at the center of irradiated spot, at the protuberant part, and outside the circle. This indicates that the change in surface morphology is from local melting because if it is from surface ablation by irradiation, the chemical compositional change was sometimes observed.[15] Because the surface profile of the center of irradiated spot was flat and smooth, as shown in Figs. 3(d) and 4(b), it suggests the surface melting after laser irradiation. Thus, we can conclude that the local melting gives a smooth surface area with a beam shape, that is, a mirror dot at the surface.

The creation of mirror dots at the surface of the glass matrix can be performed by optimizing the XeCl irradiation condition such as the pulse energy density, the pulse repetition rate, and sample heating. If the laser power is high enough to induce the protuberance without the focal lens, heat assistance may be unnecessary for melting. There is a possibility that after the threshold values of cracking and ablation are measured, we can do without heat assistance by a precise choice of irradiation conditions. Even if a smooth surface is obtained without ablation when heat assistance is not used, the smooth area will be much smaller than in the present study because of an energy distribution in the beam profile. Thus, the heat assistance is effective for obtaining a smooth surface with about 1 cm^2, which is comparable with the incident laser beam spot.

The same surface morphological change should be obtained by using excimer lasers with other gases, such as XeF (351 nm), because of the broadness of the absorption of Ti^{4+} with a center at 350 nm. It is also predicted that the same effect is possible in oxide glass systems containing other transition metals that show a large absorption coefficient in the ultraviolet region similar to Ti.

IV. CONCLUSION

We have successfully created mirror dots on the surface of BTB40 glass with XeCl excimer laser irradiation. No scratches on the scale of nanometer commonly found in mechanical polishing were observed at the center of

the irradiated spot, which means that surface melting has occurred by the laser irradiation with heat assistance at 300 °C. The absorption of TiO_2 in the ultraviolet region is responsible for the temperature increase. The excimer laser irradiation of the TiO_2 containing glass matrices has been proven to be useful for the creation of a localized smooth area. The present technique is expected to open new applications of glass materials in integrated optic devices by drastically reducing optical loss at the interfaces between optical elements on a single substrate.

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