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Low-temperature fabrication of fine structures on glass using electrical nanoimprint and chemical etching

Naoki Ikutame,[1] Keiga Kawaguchi,[1] Hiroshi Ikeda,[1] Daisuke Sakai,[1,a)] Kenji Harada,[2] Shiro Funatsu,[3] and Junji Nishii[1]
[1]*Research Institute for Electronic Science, Hokkaido University, Kita20, Nishi10, Kitaku, Sapporo, Hokkaido 001-0020, Japan*
[2]*Department of Computer Science, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan*
[3]*Production Technology Center, ASAHI GLASS CO., LTD., 1-1 Suehiro-cho, Tsurumiku, Yokohama, Kanagawa, 230-0045, Japan*

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Periodic structures were imprinted on a soda lime glass surface below its glass transition temperature (T_g) using a carbon-coated SiO_2 mold under application of DC voltage. The structure height increased with the applied DC voltage, although no significant increase with pressure was found. At a temperature around T_g, the height reached saturation. Chemical etching using 55% KOH solution at 70 °C increased the structure height to eight times the height before etching. Noticeable alternating depression patterns and rapid chemical etching are closely related with the selective decrease in sodium concentration, which occurred only in the surface areas that were pressurized by the mold. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819321]

I. INTRODUCTION

Nanoimprint technology is a useful process for the development of newly functional devices such as diffraction,[1] phase control,[2] antireflection,[3] and strong plasmon coupling.[4] Such fine structures are formed upon resin plates or films by ultraviolet-imprint or thermal-imprint processes.[5–7] However, the thermo-optical properties and chemical reliabilities of resin might sometimes be insufficient for use in high-quality optical elements. Excellent thermal and chemical properties of oxide glasses, however, are attractive from their practical aspects. Several fundamental reports have described the direct fabrication of fine structures upon oxide glasses above their deformation temperature.[8–13] Furthermore, an antireflective Moth Eye structure was imprinted on an optical glass lens.[14] Such technologies are anticipated for the exploitation of next-generation optics for several digital appliances. However, the severe imprint conditions at high temperature and pressure might decrease the imprinting area and throughput and consequently increase the production cost.

Recently, the electrical nanoimprint process was reported for the creation of new functions on the materials. Ressier *et al.*[15] fabricated resin gratings with surface electrostatic potential that agrees with the grating period, which was realized by application of a static electric voltage between two molds during the imprint process. Charged nanoparticles were assembled periodically on the grating. Takagi *et al.*[16] and Brunkov[17] formed surface-relief patterns on an oxide glass using a similar technique. The noteworthy advantage of the latter process is the formation of a fine structure far below the glass transition temperature (T_g), which is expected to be effective in terms of the life time of the mold. However, the mechanism of such a low temperature imprint has remained undefined, and the structure height attained using this method was much lower than the level required for binary gratings with high diffraction efficiency.[18–20] Therefore, additional improvements must be undertaken to obtain several practical structures. This paper reports the fine structure formation mechanism on a soda lime glass by the electrical nanoimprint process and the availability of subsequent chemical etching intended to enhance the aspect ratio of the imprinted structure.

II. EXPERIMENTAL

A SiO_2 glass plate of $25 \times 25 \times 2$ mm was used as the mold substrate. A one-dimensional grating of 6 μm period and 2 μm groove width was fabricated on the mold surface using conventional lithography and dry etching processes. The mold surface was coated with carbon of 40 nm thickness using the rf-sputtering method. Figure 1 shows the experimental setup, which is based on a glass molding machine (GMP-211(V); Toshiba Machine Co. Ltd.). The carbon-coated SiO_2 mold was fixed by the upper WC mold holder. Soda lime glass of $10 \times 10 \times 2$ mm ($T_g = 555$ °C; Asahi Glass Co. Ltd.) was used for the electrical nanoimprint, which was placed on the lower WC mold with a square pit of 10×10 mm and 1 mm depth. The upper and lower pressurizing axes were electrically insulated from each other. DC voltage was applied to the upper mold, and the lower mold was grounded. A Gold Image furnace was used for heating of the glass and mold in a N_2 atmosphere. During pressing of glass by the mold at 3 MPa for 180 s at a predetermined pressing temperature, an electrical field between the upper and lower mold was applied using a DC power supply (SERIES EH; Glassman High Voltage Inc.) that was controlled by a computer. The imprinted surface was observed using a scanning probe microscope (Nanocute; SII Nano

a)Author to whom correspondence should be addressed. Electronic mail: d-sakai@es.hokudai.ac.jp. Tel.: +81-11-706-9377. FAX: +81-11-706-9377.

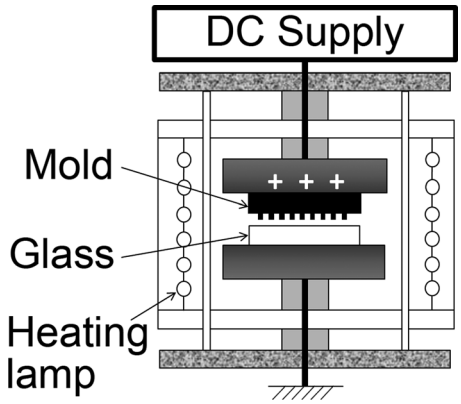

FIG. 1. Schematic of the electrical imprint machine.

Technology Inc.) and was analyzed using Energy Dispersive X-ray Spectrometry (EDS; JED-2300, JEOL Ltd.). Chemical etching of the imprinted surface was conducted in a 55 wt. % KOH solution at 70 °C.

III. RESULTS AND DISCUSSION

Figure 2 shows the surface topographical image of the mold and the imprinted glass measured using SPM. The electrical imprint was conducted at 450 °C, 3 MPa, for 180 s. DC voltage of 200 V was applied for 1 min during the pressurized period. The mold pattern was imprinted clearly on the glass surface far below its T_g. Figure 3(a) shows the current profile during the imprint. The current increased steeply with the voltage. Subsequently, it decreased gradually, which is expected to be a typical DC polarization phenomenon because of the drift of sodium ions in glass.[21] The relation between the current profile and the structure height was investigated carefully, as shown in Figure 3(b). The structure height increased depending on the time. Then it saturated at the end stage of DC polarization.

Figures 4(a) and 4(b) show the variation of imprinted structure height with the applied voltage and temperature, respectively. In the case of the former, the temperature was kept at 450 °C. The height increased monotonically with the voltage. The latter was obtained at 200 V in applied voltage, in where the height increase should be closely related to the increase in alkali ion mobility with temperature. The carbon film was apt to be damaged and less conductive at voltages greater than 250 V. Therefore, the voltage was kept below 200 V in this study. However, a saturation of the structural height was observed when the imprint temperature was between 450 and 500 °C, then slightly decreased at

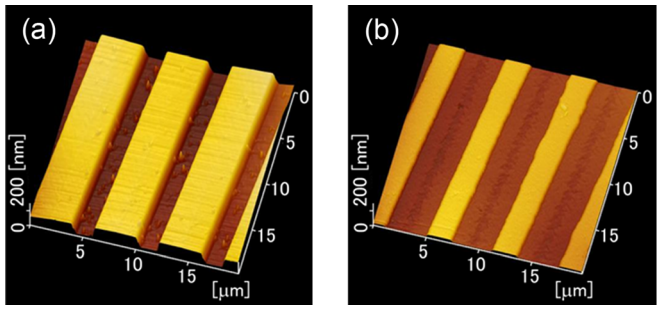

FIG. 2. SPM images of (a) the carbon-coated mold (groove depth = 150 nm) and (b) the glass surface imprinted at 450 °C, 200 V, and 3 MPa for 180 s.

temperatures higher than 500 °C. Furthermore, as shown in Figure 4(c), no dependence of structure height against the applied pressure was found down to the 3 MPa lower pressure limit of our apparatus. From these results and considering the fatal damage of the conductive carbon film on the mold, the preferred imprint condition is expected to be 450 °C, 200 V and 3 MPa.

Figure 5 depicts the changes in structure heights against the total charge monitored during the electrical imprint, as estimated by the time integration of the current. The data shown in Figures 3(b), 4(a), and 4(b), were used in Figure 5. The imprinted specimens fabricated below 450 °C exhibited a linear relation, meaning that the structure height depends closely on the amount of charge carrier in the glass. The structure heights imprinted at temperatures higher than 500 °C, however, were insensitive to the total charges, which remains unexplained. Figure 6 exemplifies the concentration profiles of cations in the surface layer of electrically imprinted glass at 450 °C, 200 V, and 3 MPa. The sodium concentration clearly changed depending on the surface relief profile. The peak top of the sodium profile was of the same level as that of the pristine glass preform. Consequently, the diffusion of Na^+ to a horizontal direction can be negligible. The imprint atmosphere was strictly filled with N_2 gas above 5 N purity. Therefore, no cation substituting Na^+ is expected to occur around the specimen. This phenomenon is similar to that observed in the thermal poling process of soda lime glass.[22] The glass structure of the sodium depletion layer changes depending on the poling atmosphere: after poling in ambient air, the replacement of Na^+ with H^+ supplied from H_2O molecules was recognized in the anodic surface layer, while irreversible structural rearrangements such as the formations of oxygen vacancies and oxygen molecules were detected in an Ar gas atmosphere. In our case, the latter structural changes must proceed in the

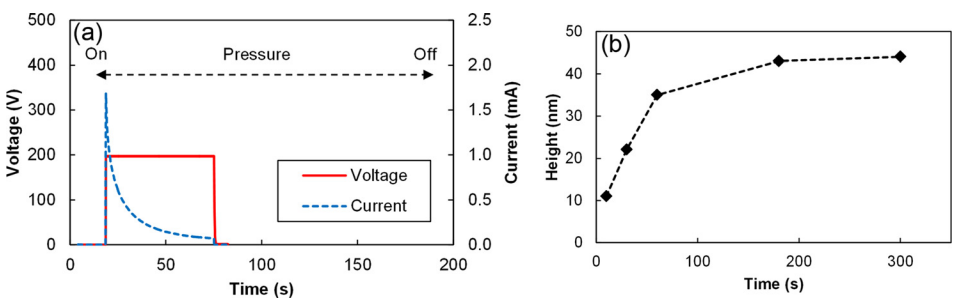

FIG. 3. (a) Current profiles during imprinting and (b) time dependence of the imprinted structure height at 450 °C with 200 V. The applied pressure was 3 MPa for 180 s.

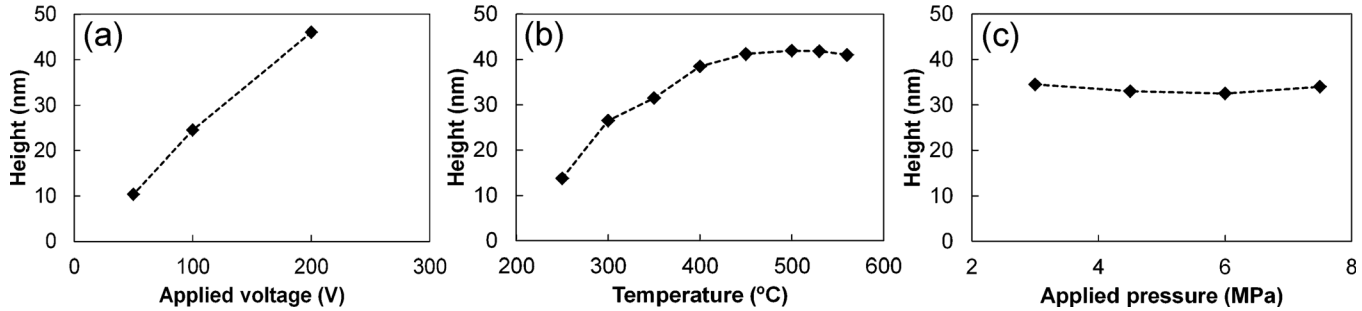

FIG. 4. Dependence of imprinted structure height on (a) applied voltage for 60 s (temperature = 450 °C, pressure = 3 MPa for 180 s), (b) temperature (applied voltage = 200 V for 60 s, pressure = 3 MPa for 180 s), and (c) applied pressure (temperature = 450 °C, applied voltage = 200 V for 60 s).

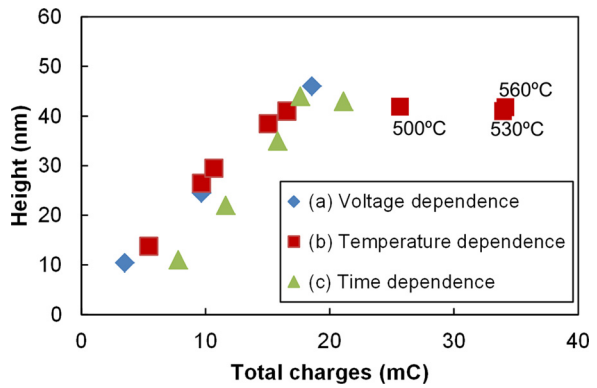

FIG. 5. Imprinted structure heights as a function of total charge. The height is shown using results from Figs. 3(b), 4(a), and 4(b). The total charges are estimated from the time integration of the measured current values in each experimental data.

anodic surface layer during the electric imprint. Furthermore, the alkali-deficient area should be in a low-density state, engendering surface deformation below T_g because of a collapse for densification. Therefore, the structural formation mechanism by the proposed electrical nanoimprint is entirely different from the conventional thermal imprint process. Recently, we have reported the fabrication of antireflective subwavelength structures on the glass surface using a conventional thermal imprint.[12,14] The imprint pressure over 5 MPa and the temperature exceeding T_g of the glass were required to obtain the effective structure height for the antireflection. Such high pressure and temperature shorten the mold life time. By contrast, the electrical nanoimprint and subsequent chemical etching enabled the formation of fine structures on the glass surface under a low pressure and temperature because the Na^+ was enough migratable in the glass even if below 250 °C. This curious characteristic should accelerate the fabrication of future optically functional devices.

The electrically imprinted glass surface was chemically etched in the KOH solution. Figure 7 shows changes of SPM surface profiles depending on the etching time. The imprinted alkali deficient area was removed preferentially by etching. Such selective etching might be attributable to the higher acidity and/or lower density of alkali deficient area than those of other areas. Remarkably, the structure height reached up to 280 nm (Fig. 8) after etching for 12 h, but only 40 nm before etching. Therefore, the diffusion depth of Na^+ was much deeper than the structure height formed by the electrical imprint alone, which suggests that a structure with

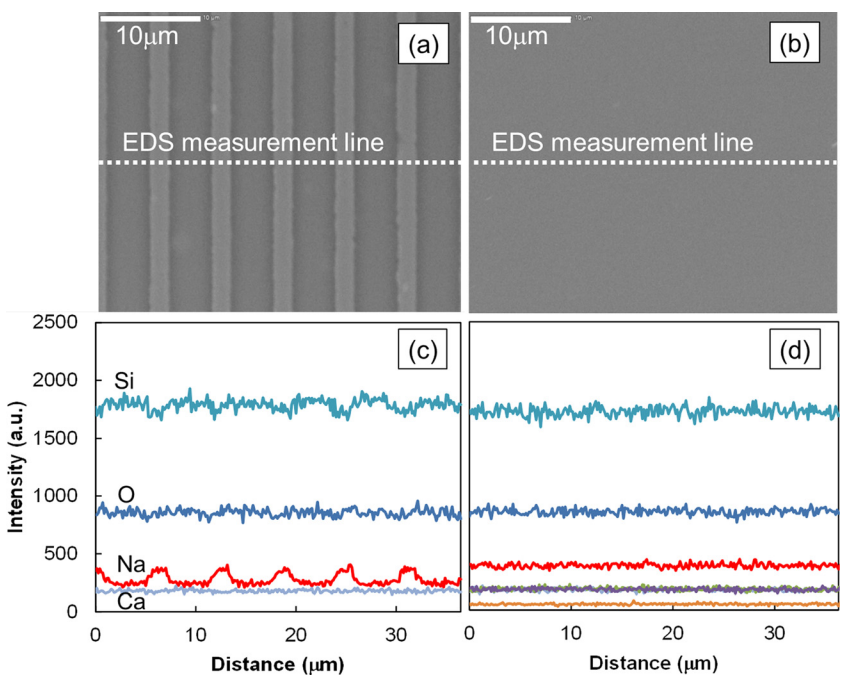

FIG. 6. SEM images and EDS elemental profiles of (a), (c) soda lime glass imprinted at 450 °C, 200 V, 3 MPa, (b), (d) pristine glass.

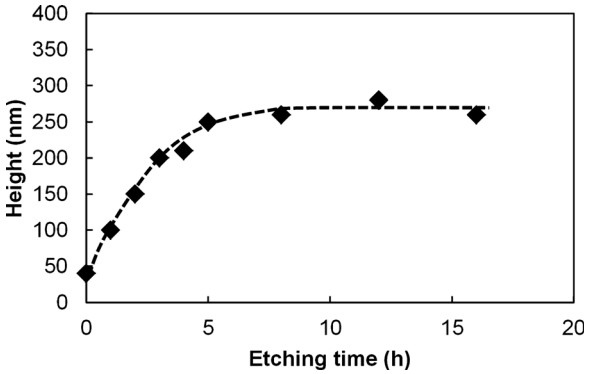

FIG. 7. Enhancement of the imprinted structure height by chemical etching. The soda lime glass was imprinted at 450 °C, 3 MPa with 200 V for 60 s, then etched using KOH.

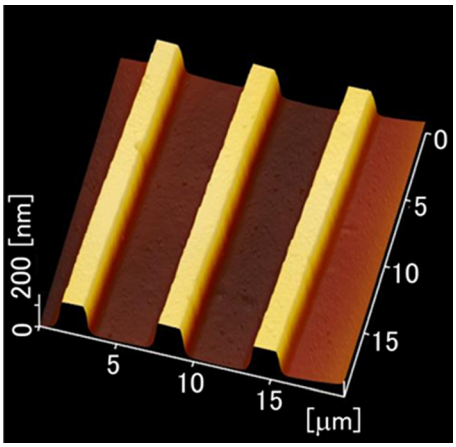

FIG. 8. SPM image of the structure on the glass surface obtained from etching for 12 h following imprinting at 450 °C, 3 MPa with 200 V for 60 s.

a higher aspect ratio should be obtained by adjusting the glass composition with larger alkali mobility enhancing the selective acidity and/or density changes in the alkali-deficient area.

IV. CONCLUSION

One-dimensional surface relief patterns were imprinted on a soda lime glass surface using superimposed DC voltage below its T_g. The origin of the surface deformation was attributed to mechanical compression of the Na^+ deficient areas formed depending on the mold pattern. Chemical etching using KOH solution was effective for the selective removal of Na^+ deficient areas. The etching rate was enhanced by seven times compared with that for the pristine glass. Such rapid etching might result from the higher acidity and/or lower density of alkali deficient area than those of other areas.

The electric field assisted nanoimprint is a practical and useful microfabrication process relative to the conventional thermal imprint process. Because the advantageous characteristics such as low temperature and low pressure extend the life time both of the equipment and the mold, and saves the energy consumption, resulting the low-cost microfabrication. Furthermore, the further optimization of glass composition and wet processing condition should enable the large scale formation of fine structure with high aspect ratio, which is strongly desired for next generation optical elements and solar cells.

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