Atomic-Scale Pattern Control of Surfaces on Functional Oxide Thin Films and Glass Plates*

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Atomic-scale surface modification of silicate glass plates was demonstrated by applying a thermal nanoimprint technique using self-assembled oxide nanopattern molds, which were atomically stepped sapphires (α-Al2O3 single crystal) (step height of about 0.2 nm and terrace width of about 100 nm) or originally developed multiple nanogrooved NiO thin films (groove depth, width, and separation of about 25, 70, and 150 nm, respectively). Atomically stepped or nanowire patterns were successfully formed on the nanoimprinted glass surface. The former surface-modified glass has atomic steps (step height of about 0.2 nm) and atomically smooth terraces (RMS roughness of about 0.10 nm). The stepped pattern on the nanoimprinted glass (glass transition temperature of 521°C) disappeared after annealing at temperatures above 600°C. In addition, glass nanoimprint on the atomically stepped glass plate using graphite molds (highly oriented pyrolytic graphite (HOPG)) was examined preliminarily.

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I. INTRODUCTION

There has been great interest in nanoscale modification of the surface and structure of functional oxides and glasses for a wide range of applications, including nanoelectromechanical systems, patterned nanostructures for nanoimprint lithography, optical waveguides, and optical storage devices [1–4]. The development of nanoscale processing techniques has enabled fabrication of novel nanostructures of scientific and applied interest.

There have been studies on the fabrication of magnetic and semiconductor nanowires, nanodots, and nanogrooves of oxides such as (Mn0.5Zn0.5FeO12, Fe2O4, and NiO [5–11]) via self-assembly phenomena along the atomic steps of the vicinal surface of stepped sapphire (α-Al2O3 single crystal) substrates [12]. The sapphire substrate has atomically flat terraces with 0.2-nm-high atomic steps, which are formed by atom migration to reduce the surface energy during thermal annealing. NiO is an attractive wide-bandgap p-type semiconductor. NiO:Li is a promising material for various applications such as high-performance thermoelectric devices and cathodes of molten carbon fuel cells [13–15].

Nanoimprint lithography has attracted much attention as a useful fabrication technique for simple, low-cost, and high-throughput nanopatterning [16–19]. Lately, nanoscale modification of oxide glass plates by applying thermal nanoimprint was researched. The atomically stepped sapphire substrates and nanogrooved NiO thin films are considered suitable as thermal nanoimprint molds for oxide glasses, partly because of their high thermal stability and durability against oxidation and mechanical stress. On the other hand, graphene is a single atomic planar sheet of graphite [20–22]. Atomic-scale patterning on glass surface can be performed by using graphene in the form of graphite consisting of graphene sheets as the nanoimprint mold. In addition, there is a possibility of achieving a novel transparent electrode by attaching a single layer graphene sheet on the glass plate.

In this study, we report the surface control of sapphire plates and NiO:Li thin films by self-assembled phenomena, and the atomic-scale patterning of oxide glasses by nanoimprint technique. Thermal nanoimprint for oxide glasses using self-assembled oxide molds and graphite was carried out to control the oxide glass surface at an atomic scale. We also investigate the thermal durability of the nanopattern on the nanoimprinted glass plates.

II. EXPERIMENTAL

An atomically stepped sapphire (0001) substrate with atomically flat terraces and periodically aligned straight atomic steps was obtained by thermal annealing of a mirror-polished sapphire substrate at 1000°C for 3 h in air [12]. Li-doped NiO thin film was deposited on the sapphire substrate by pulsed laser deposition (PLD) using a KrF excimer laser (wavelength of 248 nm, pulse duration of 20 ns, repetition of 5 Hz, energy density of 3.0 J/cm²) and a sintered target of 10 mol% Li-doped NiO [11]. The substrate temperature and the atmosphere were fixed at room temperature of 20°C (RT) and 1.0×10⁻⁵ Torr O₂, respectively. Prepared NiO:Li epitaxial film was annealed at 800°C in air for 3 h to form nanogrooved stripes on the surface.

Thermal nanoimprint of conventional soda-lime silicate glass plates (glass transition temperature of T₉: 521°C) was carried out using the atomically stepped sapphire or nanogrooved NiO molds. The molds were put in contact with the surface of the glass plates, heated at 600°C, and pressed at 3 to 10 MPa for a few minutes in vac-
FIG. 1: AFM surface images (1×1 μm²) of (a) stepped sapphire mold and (b) glass nanoimprinted with the stepped-sapphire mold. Insets show FFT spectra of the AFM surface image.

FIG. 2: AFM surface image (1×1 μm²) of nanoimprinted glass after annealing at 600°C. Inset shows FFT spectrum of the AFM surface image.

FIG. 3: AFM surface images (1×1 μm²) of (a) nanogrooved NiO thin film mold and (b) glass nanoimprinted with the nanogrooved NiO mold.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the AFM surface image of the stepped sapphire (0001) substrate and the inset shows fast Fourier transform (FFT) spectrum of the AFM surface image. Here, we observe a regularly stepped morphology on the surface, which has steps height of about 0.2 nm and a terrace width of about 100 nm. This regularity of stepped morphology on the surface is also verified by the FFT spectrum, as shown in the inset. The RMS rough-
ness value of the flat terrace was about 0.08 nm. Thus, the stepped sapphire substrate has an atomically smooth terrace and uniformly aligned steps on the surface. The terrace width could be changed by varying the miscut angle of the substrate surface, and the angle of this sapphire substrate as shown in Fig. 1(a) was estimated to be about 0.12°.

Figure 1(b) shows the AFM surface image of the glass plate nanoimprinted with the stepped sapphire mold shown in Fig. 1(a). The inset shows the FFT spectrum of the AFM surface image. The nanoimprinted glass plate was 10 mm×10 mm. The surface morphology of the stepped sapphire mold was successfully transferred to the glass surface, and regular atomic steps and terraces were observed on the surface, as seen in Fig. 1(b) and in the FFT spectrum shown in the inset. The step height and terrace width of the nanoimprinted glass surface were about 0.2 nm and about 100 nm, respectively. The RMS roughness value of the terrace was about 0.10 nm. The nanoimprinted glass had uniform atomic steps and atomically smooth terraces on the surface.

To investigate the thermal durability of the nanoscale pattern developed on the glass, we annealed the nanoimprinted glass, as shown in Fig. 1(b). Figure 2 shows an AFM surface image of the nanoimprinted glass after annealing at 600°C, and the inset shows the FFT spectrum of the AFM surface image. The regular step and terrace morphology disappeared after annealing, as shown in the FFT spectrum. The RMS roughness value of the glass surface was about 0.29 nm. The surface roughness of the annealed glass was more than that of the nanoimprinted glass. This can be proved to be related to the softening behavior of the nanoimprinted glass, which might occur from the step edge of the nanostep pattern, resulting in the undulated surface near the step sites.

Figure 3(a) shows the AFM surface morphology of the nanogrooved NiO:Li thin film post-annealed at 800°C for 3 h in air. The nanopattern, consisting of parallel nanogrooves, is clearly seen over the substrate. The depth, width, and separation of the nanogrooves were estimated to be about 25, 95, and 170 nm respectively. It was also confirmed that straight nanogrooves formed over the entire surface of the NiO thin film. Figure 3(b) shows the AFM surface morphology of the glass plate nanoimprinted with the nanogrooved NiO film mold shown in Fig. 3(a). The straight nanogroove pattern of the NiO mold transferred inversely onto the glass surface. As shown in the AFM image of Fig. 3(b), the height, width, and interval between the nanowalls were estimated at about 18, 125, and 170 nm respectively. The height (18 nm) and width (125 nm) of the nanowalls in Fig. 3(b) were lower by about 30% and wider by about 25% compared to the depth (25 nm) and width (95 nm) of the nanogrooves in Fig. 3(a). This is probably related to the viscous flow of the glassy nanowall, which is a relaxed phenomenon characteristic for amorphous glass near Tg. Therefore, it is considered that the height of the nanowall decreased, and its width became greater than those of the pristine nanowalls on the nanoimprinted glass.

Figure 4(a) shows the AFM surface image of HOPG; atomically hexagonal and trigonal carbon ring images were observed on the HOPG surface. Figure 4(b) shows the AFM surface image of the glass plate nanoimprinted with the HOPG mold in air; the atomic image of graphite was observed on the nanoimprinted glass. But, this image might be developed due to the part of graphene sheets attached eventually to the nanoimprinted glass surface. Further experiments are now in progress to achieve the transfer of the HOPG atomic pattern onto the glass plate.

IV. CONCLUSIONS

The atomic-scale modification of silicate glass plates was demonstrated by applying a thermal nanoimprint technique using self-assembled oxide molds, which were atomically stepped sapphire or nanogrooved NiO thin films. The atomically stepped or nanowire patterns were...
formed successfully on the glass plate, and the stepped glass had atomically smooth terraces on the surface. The stepped-pattern glass had atomic steps and atomically smooth terraces. The stepped pattern of the nanoimprinted glass disappeared after annealing at temperatures higher than 600°C. In addition, glass nanoimprint on an atomically stepped glass plate using a graphite mold (HOPG) was examined preliminarily.

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