Evolution of Atomically Stepped Surface of Indium Tin Oxide Thin Films Grown on Nanoimprinted Glass Substrates

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Evolution of Atomically Stepped Surface of Indium Tin Oxide Thin Films Grown on Nanoimprinted Glass Substrates

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Indium tin oxide (ITO) thin films were deposited on atomically stepped glass substrates (step height of ~0.2 nm and separation of ~80 nm) by pulsed laser deposition. The atomically stepped glass was prepared via thermal nanoimprint using an atomically stepped sapphire mold. The surface morphology of the ITO thin film definitely reflected the atomically stepped pattern of the glass substrate surface. The step height and the separation of the ITO film surface were close to those of the nanoimprinted glass surface. The fast Fourier transform analysis of the atomic force microscopy image also confirmed the periodicity of the atomic-step pattern.

Recently, organic light emitting diodes (OLEDs) have attracted much attention because of their high potential and advantages for use in display devices. Indium tin oxide (ITO) has been commonly used as anode for OLEDs because of its high electric conductivity ($\sim 10^{-4}\,\Omega\,\mathrm{cm}$), high transmittance (~90%) in the visible region, and relatively high work function. In bottom emission OLEDs, all functional organic layers are deposited on the ITO anodes, and the organic layers have a thickness of about 100 nm. Thus, the surface morphology of ITO directly affects these layers surface, and an uneven surface is not desirable for OLEDs because the instability of the organic/electrode interface is one of the reasons for degradation and formation of non-emitting areas (dark spot).[1)] Therefore, surface roughness of the ITO film is an important property for the enhancement of the stability and efficiency of OLEDs.[2–4)]

So far, researchers have been reported a significant decrease of the surface roughness of the ITO thin films grown on single crystal and glass substrates.[5–10)] The surface roughness of ITO films on single crystal substrates is considered atomically flat (RMS roughness value of 0.15 nm) given that the film surface reflects the atomically flat morphology of the substrate surface. On the other hand, there is room for improvement regarding the roughness value of the ITO films on the glass substrates because the surface roughness reaches a minimum of 0.4 nm at best.[9)]

Recently, we reported the nanoscale surface modifications of glass plates by applying a thermal nanoimprint technique in which we used self-organized nanopattern molds of oxides (NiO, α-Al_2O_3).[11,12)] The glass nanoimprinted with a stepped sapphire mold exhibited regularly arranged, straight atomic-steps (step height: ~0.2 nm), ultra flat terraces (separation: ~80 nm), and an RMS roughness value of about 0.09 nm. The use of this nanoimprinted glass substrate for ITO thin film deposition is expected to result in reduction of the surface roughness and enhancement of the uniformity possibly due to the homogenization of crystal nucleation sites and grain growth on the regularly steps and ultra flat surface.

In this study, we examined the surface morphology and the structural and electrical properties of ITO thin films deposited on the atomically stepped glasses.

An atomically stepped sapphire (α-Al_2O_3 single crystal) (0001) mold with an atomically flat terrace and periodically aligned straight atomic steps was obtained via thermal annealing of a mirror-polished sapphire substrate at 1000 °C for 3 h in air.[13)] The thermal nanoimprint of conventional soda-lime silicate glass plate (glass transition temperature of T_g, 521 °C) was conducted using the atomically stepped sapphire mold. The mold was placed in contact with the surface of the glass plate, heated at 600 °C, and pressed at 3 MPa for 5 min in a vacuum ($\sim 10^{-2}$ Torr).

We conducted the ITO film deposition on the nanoimprinted glass and the non-patterned commercial glass substrates via pulsed laser deposition (PLD) using a sintered target of 5 wt% Sn-doped In_2O_3 (ITO). The film deposition was conducted at room temperature (RT) under a 1×10^{-2} Torr O_2 atmosphere. We then annealed as-deposited films for crystallization in a vacuum (1×10^{-7} Torr) at temperatures from 200 to 400 °C for 3 h. The crystallographic characterization of the ITO films was examined via *ex situ* X-ray diffraction (XRD; Bruker AXS), and X-ray reflectivity (XRR; PANalytical X'pert MRD) studies of the films were performed for the determination of film thickness, and roughness. We investigated the surface morphology and RMS roughness with atomic force microscopy (AFM; SII SPI-3700). The electrical properties were examined by a four probe and Hall effect measurements.

Figure 1(a) shows the AFM surface image and the cross-sectional profile of the non-patterned commercial glass and the inset shows the fast Fourier transform (FFT) spectrum of the AFM surface image. The FFT provides a mathematical analysis of the AFM image, which is similar to producing a diffraction pattern. From the spectrum pattern, information on the periodicity can be obtained. The commercial glass has a relatively rough surface with some superficial spikes and the RMS roughness value of about 1.73 nm. According to the FFT spectrum, there are no periodically patterns on the surface. Figure 1(b) shows the surface morphology of the atomically stepped glass. We observed a regularly stepped morphology on the surface, which had a step height of about 0.2 nm and a separation of about 80 nm. The regularity of the atomic-step pattern was also verified from the aligned spots pattern (in the circle) of the FFT spectrum as shown in the inset of Fig. 1(b). The RMS roughness value of the nanoimprinted glass was about 0.09 nm. This value was

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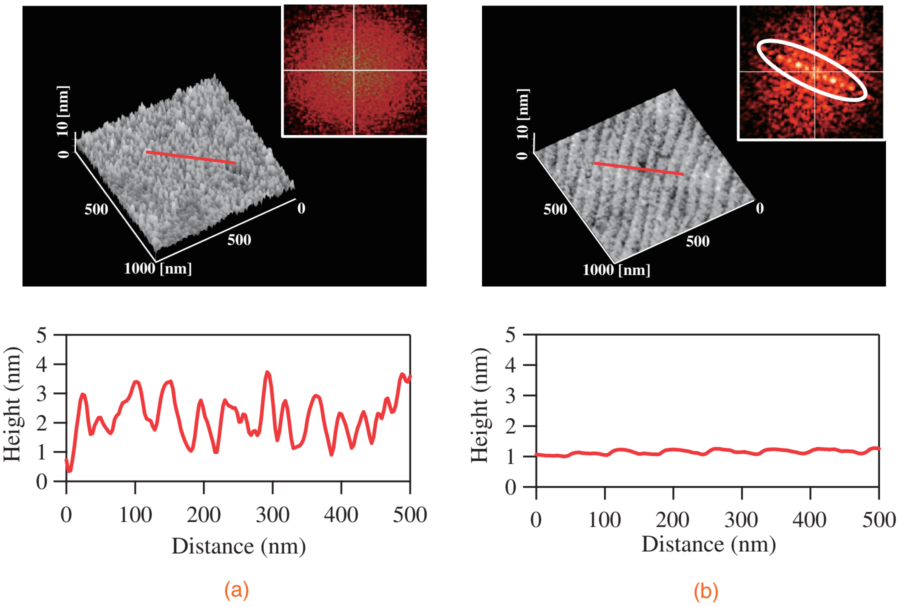

Fig. 1. AFM surface images ($1 \times 1\,\mu m^2$) and cross-sectional profiles of (a) non-patterned commercial glass and (b) atomically stepped glass. Insets show the FFT spectra of the AFM surface images.

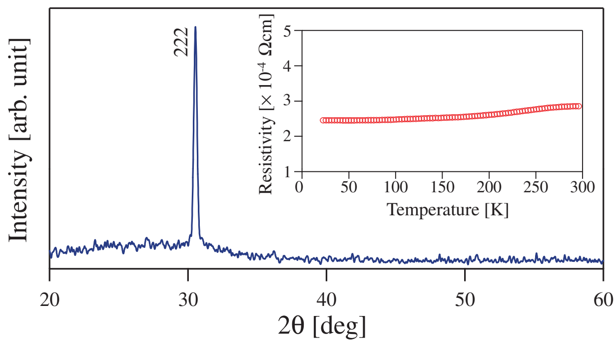

Fig. 2. XRD pattern of 2θ–θ scan of the ITO film annealed at 200 °C after being deposited on the nanoimprinted glass. Inset shows the temperature dependence of the resistivity of the ITO film.

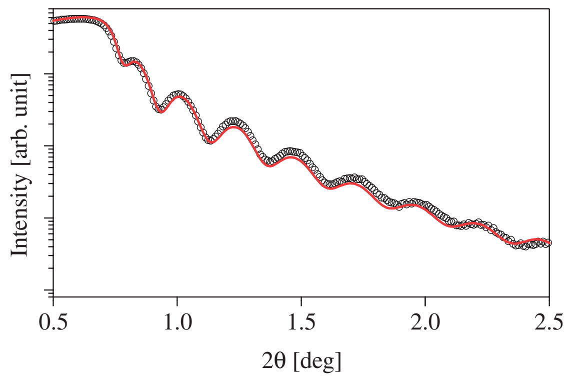

Fig. 3. XRR pattern of the ITO film annealed at 200 °C after being deposited on the nanoimprinted glass. Solid line and circles show the simulation and experimental results, respectively.

about twenty times less than that of the non-patterned commercial glass.

Figure 2 shows the XRD pattern of 2θ–θ scans measured for the ITO thin film annealed at 200 °C after being deposited on the nanoimprinted glass substrates, and inset shows the temperature dependence of the resistivity of the ITO film. We verified from the 2θ–θ pattern that the film exhibits strongly (111) oriented polycrystalline growth because 211 and 440 peaks from integrated peak intensities (data not shown) were observed. From the rocking curve measurements around 222 peak, the full width at half maximum (FWHM) value of the film on the nanoimprinted glass and on the commercial glass was 11.4 and 15.1°, respectively. The FWHM value of the film on the nanoimprinted glass was about 25% less than that on the commercial glass. Thus, it was confirmed that the (111) orientation of the film on the nanoimprinted glass was stronger than that on the commercial glass. From the inset, the resistivity at RT of the film on the nanoimprinted glass was $2.8 \times 10^{-4}\,\Omega\,cm$. The ITO film on the nanoimprinted glass yielded a carrier concentration and Hall mobility of $1.3 \times 10^{21}\,cm^{-3}$ and $17.5\,cm^2\,V^{-1}\,s^{-1}$, respectively. Despite the high carrier density of the film, transmittance in visible region of the film was above 88%. The high carrier density of the film is because of the oxygen defect from annealing in high vacuum ($\sim 10^{-8}$ Torr). Further experiments should optimize the fabrication of ITO thin films with low resistivities.

Figure 3 shows the XRR spectrum (circles on the figure) with a simulation (solid line) of the ITO film annealed at 200 °C after being deposited on the nanoimprinted glass. A simulated pattern exhibited good agreement with the experimental results, indicating excellent homogeneity of the film deposited on the atomically stepped glass substrate. From the fitting pattern, the thickness, surface roughness and film density of the film were estimated to be 31 nm, 0.2 nm, and $7.11\,g\,m^{-3}$, respectively. The thickness of the film was in good agreement with that of the stylus method. The ITO film on the nanoimprinted glass has an extremely flat surface in macroscopic scale.

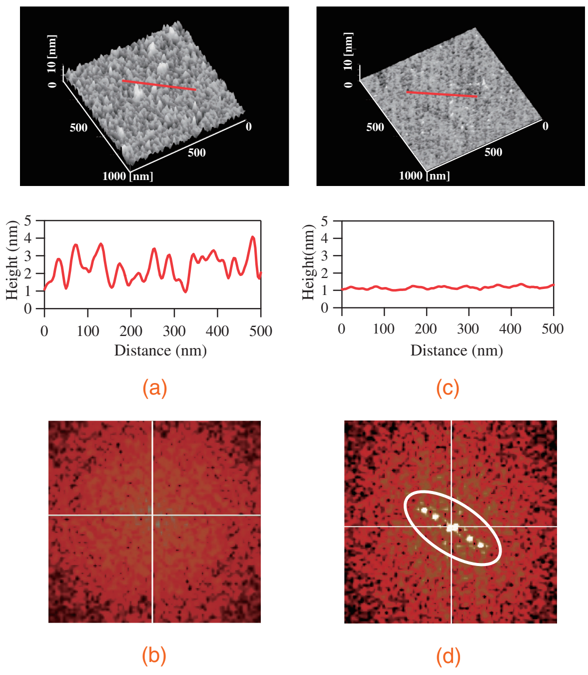

Fig. 4. (a) AFM surface image (1 × 1 μm^2) and cross-sectional profile of the ITO film annealed at 200 °C after being deposited on the commercial glass and (b) the FFT spectrum of the AFM surface image. (c) AFM surface image (1 × 1 μm^2) and cross-sectional profile of the ITO film annealed at 200 °C after being deposited on the nanoimprinted glass and (d) the FFT spectrum of the AFM surface image.

Figure 4(a) shows the surface morphology of the ITO thin film annealed at 200 °C after being deposited on the commercial glass. The ITO film had some spikes on the surface, and the RMS roughness value was of about 1.55 nm. Figure 4(b) shows the FFT spectrum of the AFM surface image of the ITO film on the commercial glass [see Fig. 4(a)]. There were no spot patterns on the FFT spectrum, indicating the ITO film on the commercial glass had an irregular surface.

In contrast, extremely flat surface morphology was observed on the ITO film annealed at 200 °C after being deposited on the atomically stepped glass as shown in Fig. 4(c). The surface morphology of the ITO film on the nanoimprinted glass definitely reflected the atomically stepped pattern of the nanoimprinted glass substrate surface [see Fig. 1(b)], and the step height and the separation of the ITO film were about 0.2 nm and about 80 nm, respectively. The RMS roughness value of the ITO film on the atomically stepped glass was about 0.18 nm, which was about ten times less than that of the film on the commercial glass. Even for the relatively thick film with thickness of about 200 nm on the nanoimprinted glass, the flatness of the surface morphology was found to be maintained. Additionally, we clearly observed periodic spot patterns in the circle of the FFT spectrum of the AFM surface image as shown in Fig. 4(d), indicating that the ITO film had a periodic pattern on the surface.

Furthermore, the surface roughness of the crystallized film on the nanoimprinted glass was found to be independent of the annealing temperature from 200 to 400 °C. As the polycrystalline ITO film was obtained from the amorphous film via solid-phase growth by thermal annealing, the surface morphology of the crystallized film on the nanoimprinted glass was thought to reflect well the smooth surface of the amorphous film before annealing. In addition, the grain-size distribution of the crystallized film on the nanoimprinted glass was found to be less than that of the film on the commercial glass from the point of less FWHM value of the XRD rocking curve for the film on the nanoimprinted glass. The homogeneous nucleation and crystallization on the nanoimprinted glass substrate might be also related to formation of the ultra smooth surface of the ITO film.

In summary, the ITO thin film was deposited on the atomically stepped glass substrate by PLD. The ITO thin film reflected well the step pattern of the nanoimprinted glass substrate surface with an RMS roughness value of about 0.18 nm. The step height and separation of the atomically stepped ITO film were about 0.2 nm and about 80 nm, respectively. We also confirmed the periodicity of the ITO film via FFT analysis from the AFM image.

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