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Surface chemistry modification in ITO films induced by Sn^{2+} ionic state variation

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In this study, the surface-chemistry-dependent hydrophobicity and antibacterial properties of ITO films were examined. After annealing of the films, their surface root-mean-square roughness increased and remained the same regardless of the annealing environment. However, depending on the annealing environment (O_2, N_2, Ar, or vacuum), the contact angle increased with increasing Sn^{2+} contents in the films. Furthermore, the antibacterial effect of the annealed films decreased regardless of the annealing environment. The depth-dependent chemical state determined by X-ray photoelectron spectroscopy showed an increase in the Sn content at the surfaces of all films. In particular, the as-grown film exhibited the highest Sn content at the surface and also the strongest antibacterial effect.

1. Introduction

Sn-doped In_2O_3 (ITO) is one of the most commonly used transparent conducting oxide (TCO) electrode materials for numerous applications such as flat panel displays, organic light emitting diodes, solar cells and smart windows [1–4] owing to its high optical transparency (>80%) and low resistivity ($\rho < 10^{-4}$ Ω cm) [5,6]. Furthermore, the increased usage of touch panel displays has resulted in focus on surface characteristics of TCO films such as the chemical state, wettability and antibacterial effect [7–9], which are important parameters for potential applications.

Interestingly, surface hydrophobicity (and/or hydrophilicity) is one of the basic characteristics for examining the surface chemical state of TCOs [7]. Depending on the surface treatment methods, ITO films have been reported to have different contact angles (i.e., degree of hydrophobicity) [10–13]. Recently, Jung et al. reported the achievement of a highly hydrophilic surface (contact angle of less than 10°) of ITO films after their Ar atmospheric pressure plasma treatment [11]. In addition, So et al. reported a decreased contact angle of ITO films depending on their exposure time to UV ozone [12]. Since a hydrophilic surface promotes the surface adhesion between ITO and polymer films, it can enhance the performance of organic-light-emitting diodes [9,11]. On the other hand, the hydrophobicity of ITO films is related to the anti-fingerprint property in touch panel displays [7]. From the viewpoint of public usage of touch panels, the antibacterial effect is another important requirement for TCO applications. Metallic nanoparticles such as silver and zinc nanoparticles have been demonstrated to exhibit strong inhibition to common bacteria (e.g., *Escherichia coli* (*E. coli*)) [14,15]. However, these nanoparticles can easily deteriorate with mechanical activities such as touching and swiping, on account of the low surface adhesion [7].

Therefore, it is important to examine and understand not only the wettability but also the antibacterial effect of TCO films. In this study, we demonstrated variations in the contact angle and

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antibacterial effect of ITO films with the post-annealing environment. We explained the possible physical origin of these variations in terms of Sn segregation at the surface and the variation of the Sn^{2+} state.

2. Experiments

DC sputtered amorphous ITO films grown on glass substrates were annealed under various environment: O_2 (~3.75 × 10^5 mTorr), N_2 (~3.75 × 10^5 mTorr), Ar (~3.75 × 10^5 mTorr) and vacuum (~5 mTorr) at 400 °C for 10 min. Details of the film growth are provided elsewhere [16]. All films also examined the structure by X-ray diffraction (XRD; Empyrean, PANalytical) measurements.

The surface topography was measured by atomic force microscopy (AFM; XE-70, Park Systems) using a Pt-coated tip. The surface was scanned in the non-contact mode with a frequency of 0.2 Hz in a 1 × 1 μm^2 area. The surface and depth-dependent chemical state of the ITO films were examined by X-ray photoelectron spectroscopy (XPS; Theta Probe, Thermo Fisher Scientific). A monochromated Al $K\alpha$ ($h\nu$ = 1486.6 eV) source with a beam size of 400 μm was used for the measurements. The pass energy and step size were 50.0 eV and 0.1 eV, respectively. For determination of the depth-dependent chemical concentration, the data measured using a channel plate were resolved into 16 channels ranging from 24.875° to 81.125° in 3.75° steps. Furthermore, the UV–vis spectra (Monora-320i, Dongwoo Optron) was taken to determine the optical band-gap energy of the films.

For the contact angle measurements, a 10 μL droplet of deionized water (18 MΩ) was photographed using a CCD camera. The contact angles between the surface and the droplet were determined by fitting the droplet curvature from photographed images. Antibacterial effects of as-grown and post-annealed ITO films were assessed by measuring the cell proliferative capacity of E. Coli. Each film was prepared suitably to be seeded in a solidified agar plate. After *E. coli* cells (DH5α strain) were grown to a size of 600 nm with an optical density (OD_{600}) of 1.0, 5 μL of cells were inoculated on each ITO films seeded in the plate and further incubated in a dark chamber at 37 °C for 12 h.

3. Results and discussion

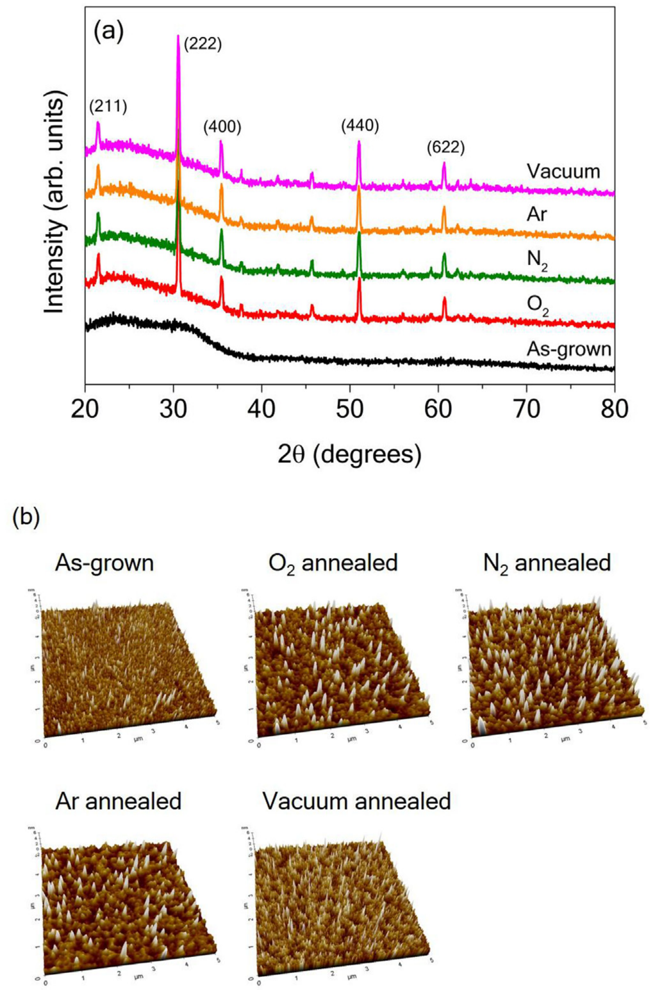

Fig. 1. (a) XRD patterns of the as-grown and annealed (under O_2, N_2, Ar and vacuum environments) ITO films. (b) Surface topography of as-grown, O_2 annealed, N_2 annealed, Ar annealed and vacuum annealed ITO films.

Fig. 1 shows the XRD patterns and AFM images of as-grown and annealed ITO films. For the as-grown films, there was no structural ordering based on XRD measurements (Fig. 1(a)), suggesting the film formed amorphous structure. On the other hand, annealed films showed polycrystalline bixbyite structure (ICSD #50848) regardless of annealing environment. Furthermore, the crystalline size of the annealed films using (222) peak was estimated using Sherrer equation [17] and listed in Table 1. The calculated crystalline size of all the annealed ITO films remained ~29 nm range, suggesting that there were no noticeable structural variation depending on the annealing environments. Fig. 1(b) shows the surface topography of the as-grown and post-annealed ITO films. The surface of the as-grown ITO film showed grains approximately ~10 nm. The surface of films post-annealed under O_2, N_2 and Ar environment showed larger grains than that of the as-grown film. On the other hand, the grain size of the film annealed under vacuum remained unchanged after annealing. The RMS roughness values of the as-grown and post-annealed ITO films were obtained from the surface profile (Table 1). The as-grown film showed an RMS roughness of ~0.6 nm. After annealing, a slight increase in the RMS roughness was observed (~0.8 nm) regardless of the annealing environment, suggesting that after annealing, no significant effects such as surface degradation and improvement occurred.

The annealing-environment-dependent surface wettability of the ITO films was examined. Fig. 2 shows the contact angles of the as-grown and post-annealed ITO films. All films exhibited a hydrophilic surface, since the contact angle was lower than 90° [18]. In general, the contact angle depends on the surface roughness [19]. The as-grown film was expected to show the highest contact angle and the post-annealed films were expected to show no variation of the contact angles since there were no noticeable differences in their RMS roughness. However, the measured contact angles of the post-annealed films (also listed in Table 1) varied according to the post-annealing environments. Specifically, the film annealed under the O_2 environment exhibited the lowest contact angle (~71.6°), whereas the film annealed under the vacuum environment exhibited the highest contact angle (~76.9°). To gain physical insight into this trend, the chemical states of the films were examined by XPS, since the surface energy variation (which is related to the contact angle) might be associated with the surface chemical state [20].

Fig. 3 shows the survey scan of X-ray photoelectron spectra of the as-grown and post-annealed ITO films. The spectra show that all films exhibited clear peaks of C, Sn, In and O regardless of annealing environment and that no additional surface contamination occurred during the annealing process. Furthermore, the amount of carbon reduced after annealing, indicating that the annealing process resulted in removal of the initial carbon