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Grain-size effect on the electrical properties of nanocrystalline indium tin oxide thin films

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ABSTRACT

In this paper, we demonstrate the electrical properties, depending on grain size, of nanocrystalline indium tin oxide (ITO) thin films prepared with a solution process. The size distributions of nanometer-sized ITO film grains increased as the post-annealing temperature increased after deposition; the grain sizes were comparable with the calculated electron mean free path. The mobility of ITO thin films increased with increasing grain size; this phenomenon was explained by adopting the charge-trapping model for grain boundary scattering. These findings suggest that it is possible to improve mobility by reducing the number of trapping sites at the grain boundary.

1. Introduction

The most important transparent conductive oxide (TCO), indium tin oxide (ITO; In_2O_3:Sn doped with 5–10 mol% Sn^{4+}), has a wide range of applications in the electronic device industry, such as touch panels, light-emitting diodes, photovoltaics, and flat panel displays [1–3]. ITO thin films have been deposited using vapor transport deposition techniques, such as the chemical vapor deposition system, magnetron sputtering, and vacuum evaporation method [4–6]. An optimum resistivity of $10^{-4}\,\Omega$ cm, transparency of over 80%, and sheet resistance of 10 Ω/sq can be achieved using the vacuum deposition technique [7]. However, printing techniques (e.g., ink-jet, silk-screen, or offset printing) using solution precursors are preferred for use in actual devices in order to reduce cost and time [8,9]. These methods have some advantages such as a large area and high-throughput process. A few research groups have reported the preparation of ITO materials by using the solution methods and described the effects of environmental conditions, such as an annealing temperature and the time duration of a thermal treatment [10–16]. The role of oxalic acid as an additive in a sol–gel process was treated and the influence of thermal annealing and pyrolysis temperature on physical properties was demonstrated [11,13,14]. The dependence on the Sn composition of transport properties in ITO materials prepared by the solution methods has also been treated [16,17]. Although the low resistivity of ITO thin film grown by a vacuum deposition method has been reported [18], the achievement of good electrical properties in ITO materials prepared using a solution method is difficult due to various difficulties in controlling grain size, doping level, relative composition, etc. Specially, the study on the transport properties of ITO materials depending on the grain size is essential to prepare high quality materials, because it is basic information for improving the quality of related materials. However, there is a lack of research on the grain size effect for ITO materials prepared by a solution method.

Resistivity is affected by two parameters: carrier concentration, affected substantially by oxygen vacancy and Sn composition in ITO thin film, and mobility, influenced by strong scattering centers with free carriers, grain boundaries, acoustical phonon, surface, etc. [19–21]. Some of research groups have reported that the mobility of TCO thin films with large grain sizes (approximately several tens of nanometers) is affected more by ionized impurity scattering than by the grain boundary scattering at the different levels of carrier concentration in the thin films [22,23].

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The main purpose of this study is to understand the microstructural and electrical properties of ITO thin films prepared by a solution-based method. Insights gained at the microscopic level regarding how the microstructural and electrical properties of ITO thin films depend on post-annealing temperature are essential for the development of an efficient process for applicable ITO films. Therefore, a detailed study of the structural and electrical characteristics of ITO thin films was carried out based on transmission electron microscope observation and Hall effect measurement.

2. Experimental

Indium (III) nitrate hydrate (0.3 M) and tin acetate (0.03 M) were dissolved in 2-methoxyethanol, and acetylacetone (0.33 M) was injected into the mixed solution as a chelating agent. In the mixed solution, the atomic ratio between indium and tin was 9:1. The solution was stirred at 60 °C for 3 h, after which the solution was purified using a 0.2 μm-diameter syringe filter. Using a spin coating technique, the ITO solution was coated onto a silicon oxide layer prepared thermally on a Si substrate. The spin coating process was conducted at 3000 rpm for 30 s. The coated sample was heated at 200 °C for 10 min to remove solvent. To increase the thickness of the ITO thin films, the spin coating process was repeated five times. Finally, the prepared films were annealed at different annealing temperatures to investigate the effects of post-thermal annealing temperature on the structural and electrical properties of ITO thin films; the films were annealed at 300–700 °C in ambient air for one hour. To exclude the effects of deposition parameters other than post-thermal annealing temperature, the annealing environments were carefully maintained during the process. The crystalline properties of the ITO thin films were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The microstructural properties of the ITO thin films were evaluated using various TEM techniques, such as bright-field (BF) and high-resolution (HR) TEM micrographs and selected area electron diffraction (SAED) patterns. The carrier concentration and mobility of the ITO thin films were systematically investigated at room temperature using the Hall effect measurement system.

3. Results and discussion

The BFTEM images shown in Fig. 1(a)–(c) were taken under many beam conditions, including transmitted and diffracted beams, and provide cross-sectional views of the ITO thin films annealed at 300, 500, and 700 °C, respectively. The thicknesses (97–106 nm) of the ITO thin films were very uniform, regardless of the annealing temperature (Fig. 1(a)–(c)). All of the ITO thin films exhibited a smooth surface that was not dependent on the annealing temperature. Although not shown in this article, the result was also confirmed by the scanning electron microscope images observed at low magnification. Smooth and flat surfaces have many advantages in the fabricating process of electronics devices [24]. The Sn composition was determined by energy-dispersive X-ray spectroscopy (EDS) analysis, and the quantification values were calculated as the average of five different positions on the surface of each sample. The Sn compositions of the all ITO films were approximated to 12.7 (±0.5) atomic percent. As shown in Fig. 1(a)–(c), the grain size of the ITO thin films increased with increasing post-annealing temperature. The size distribution of nanometer-sized grains was measured using BFTEM. The projected area of each individual grain was manually determined in the BFTEM image, and the diameter of the grains was calculated as $d = 2 \times (A/\pi)^{1/2}$. To minimize errors in the statistical analysis, we selected individually complete grains that had no overlapping areas with neighboring grains. The distribution of grain sizes for the ITO thin films was fitted to a Gaussian distribution (Fig. 1(d)). As the annealing temperature increased from 400 to 700 °C, the grain sizes of the ITO thin films also increased; the exact values were 2.5 (±0.74), 2.7 (±0.83), 5.7 (±1.91), and 6.5 (±2.07) nm at 400, 500, 600, and 700 °C, respectively. The amorphous phase was observed in the ITO thin films annealed in 300 °C, but the crystallization was revealed at 400 °C. Up to 500 °C there was simple growth by slightly increased grain size, but over 600 °C the grain size increased rapidly. This phenomenon could be explained by coalescence between grains to be recrystallization. Similar result was reported in the nanocrystal growth by showing rapid increase of grain sizes [25]. SAED patterns were taken from the ITO thin films to identify the crystalline properties. The SAED pattern shown in Fig. 1(e) of the ITO film annealed at 300 °C is free from any diffraction spots or rings, which indicates that the film is an amorphous phase. The SAED pattern shown in Fig. 1(f) of the ITO sample annealed at 700 °C shows diffraction rings, concentric circles around the transmitted spot, indicating that the film is a polycrystalline structure; the ring patterns are indexed sequentially as (2 1 1), (2 2 2), (4 0 0), (4 3 1), (4 4 0), and (6 2 2).

To obtain global information about the crystalline properties, an XRD analysis was conducted on the ITO thin films (step = 0.05° and dwell time = 4 s/step); the results are shown in Fig. 2. No characteristic diffraction peaks in the XRD spectrum taken from the ITO thin film annealed at 300 °C are visible, which indicates that the film is an amorphous phase. This observation is consistent with the result of the SAED analysis shown in Fig. 1(e). On the other hand, the XRD spectra taken from the ITO thin films annealed at higher temperature (above 400 °C) show characteristic diffraction peaks from (2 1 1), (2 2 2), (4 0 0), (4 3 1), and (4 4 0) planes, which confirms that the ITO thin films prepared in the experiments have a bixbyite structure. In addition, all of the spectra are free from diffraction peaks from impurity phases, such as SnO_2, which supports that the Sn^{4+} atoms were successfully incorporated into the In^{3+} lattice sites. The inset in Fig. 2 shows that the peak intensity from the (2 2 2) diffraction increased slightly with the increase in post-thermal annealing temperature. The relative increase of the peak intensity in the XRD spectra is related to the crystalline quality of the thin film. As shown in Fig. 3, it was impossible to detect amorphous regions in amorphous areas of the polycrystalline ITO thin films, even at grain boundaries. In addition, as mentioned above, the thicknesses of the ITO thin films were uniform, regardless of the annealing temperature. Therefore, we deduced that the increase in the peak intensity from the (2 2 2) diffraction originated from the larger grain size and the relatively reduced area of the grain boundary.

To evaluate the electrical properties, the ITO thin films, annealed at 300–700 °C, were examined by Hall effect measurement using the Van der Pauw method; the results are shown in Table 1. Here, carrier concentration approximated a 10^{20} cm^{-3} in all of the ITO thin films, and the mobility increased as the post-thermal annealing temperature increased from 4.03 cm^2 V^{-1} s^{-1} at 400 °C to 11.30 cm^2 V^{-1} s^{-1} at 700 °C. As a result of the improved mobility, the resistivity of the ITO thin film decreased from 1.79×10^{-2} Ω cm (1700 Ω/sq) at 400 °C to 5.42×10^{-3} Ω cm (526 Ω/sq) at 700 °C. However, the ITO thin film annealed at 300 °C could not be measured using Hall effect measurement. The carrier concentration levels in the ITO thin film were similar, about $10^{20}/cm^3$, which is comparable with the previous report [26]. However, the resistivity is slightly higher resistance, $\sim 5.42 \times 10^{-3}$ Ω cm (grain size = 6.5 nm), when is compared with the ITO thin film prepared by the optimized vacuum deposition, $\sim 10^{-4}$ Ω cm (grain size = 30 nm) [27]. This result may be associated with the small the grain size and random orientation of the ITO thin film prepared in our experiment. The electrical properties in the porous thin film were considered to use filling factor [28]. In our results, the thickness of ITO thin films