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The effect of annealing treatment on microstructure and properties of indium tin oxides films

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Abstract

Indium tin oxide (ITO) thin films were prepared by radio frequency (r.f.) magnetron sputtering system with high-density ITO target (90 wt.% In_2O_3 and 10 wt.% SnO_2). The microstructure of the thin films at various processing parameters was measured using an X-ray diffractometer (XRD) method. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to observe the microstructure and surface morphology of the thin films. The composition of the thin films was measured by energy dispersive X-ray (EDX). The result shows that the as-deposited ITO film is amorphous-like and includes some round shaped particles in the matrix. The transformed temperature of amorphous to crystal is the range of 150–250 °C. The resistivity is increased sharply at 250 °C with the film fine grain and minimum optical band gap. We could get the minimum resistivity of 3.5×10^{-4} Ω cm and over 80% of the average transmittance in a visible region at the optimum condition of our deposition technique.

Keywords: Indium tin oxide; Annealing treatment; Transmission electron microscope (TEM); Sputtering; Crystallization; Electrical properties; Optical properties

1. Introduction

Transparent conducting oxide (TCO) thin films are widely used as electrodes owing to their excellent transmittance (∼90%) in the visible light wavelength region and electrical conductivity (∼10^{-4} Ω cm) [1]. TCO thin films have been applied as anti-static electricity shielding coatings, heat reflecting mirrors, solar cells, liquid crystal displays (LCDs), sensors, and organic light emitting devices (OLED). These thin films also play an important role in the general performance of opto-electronics devices [2]. Currently the major concept for application of TCO thin films is to emphasize how to satisfy the minimum resistivity requirement and overcome the problems of response time and resistivity of the devices [3].

Various techniques have been used to deposit the ITO thin films, and studies have been concentrated on how to obtain the excellent properties of the thin films, especially in the effect of the processing related parameters of the grown oxidation films and the incorporation of Sn [4,5]. ITO thin films can be prepared by various techniques [2,6–9], such as chemical vapor deposition (CVD), thermal evaporation deposition, direct current (dc), and radio frequency (r.f.) magnetron sputtering, electron beam evaporation, spray pyrolysis, pulse laser method, and the sol–get method. It is suitable for various substrates with larger areas, and so, magnetron sputtering technique is widely used for the manufacturing of the thin films. In the preparation of the ITO thin films using the magnetron sputtering method, the loss of Sn concentration as well as the roughness of the thin films can easily affect the performance of the devices. A high quality ITO film, with low electric resistivity and high optical transmittance are generally fabricated by a magnetron sputtering method. It is interesting for us to understand that the resistivity change depends on the microstructure of ITO films on annealing treatment in an argon atmosphere. The microstructure of ITO film is observed by transmission electron microscope (TEM) and the samples are prepared by various methods reported on pervious researchers [10–12]. For these reports, the ITO films deposited at room temperature are almost amorphous. The crystallization temperature is roughly beyond 150–250 °C [10,13]. The crystallized processs are not yet reported in detail. As previous reports show [13–16], the properties of ITO depend on its oxidation state and

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impurities content. Hence, oxidizing or reducing atmospheres during deposition can modify the oxygen vacancy content, thus modifying the carrier density. Heat treatment of ITO films can modify these structural characteristics and improve the electrical and optical properties. In this paper, we demonstrate to concentrate the annealing effect to the change of ITO microstructures, electrical properties and optical transmission properties.

2. Experimental detail

ITO thin films were prepared by r.f. magnetron sputter with a target composite of the mixture of 90 wt.% indium oxide (In_2O_3) and 10 wt.% tin oxide (SnO_2). In order to perform TEM observation of the ITO fines structures, the deposition is carried out on carbon thin film mounted on a copper grid. For the measurements of an XRD, optically transparent and electrical conducting properties, the ITO films are deposited on Coining 7059 glass substrates at room temperature.

Initially, all the substrates were ultrasonic ally cleaned in an acetone, alcohol solution and de-ionized water used to remove all the organic contaminants. Before sputtering, the background pressure in the vacuum chamber was reduced to below 10^{-6} Torr. Three sputtering targets each had a diameter of 76.2 mm. The films were sputtered in the atmosphere of pure argon at work pressure of 3×10^{-3} Torr at 100 W and the substrates are unheated. Annealing treatment of TEM samples is carried out in an argon atmosphere at a specified temperature for 15 min.

The film thickness was measured using α-step (TENCOR INSTRUI/MA-1450 200 type). The structure of ITO films at various processing parameters was measured using an X-ray diffractometer (XRD) method. The crystallography is measured by θ–2θ XRD using Cu Kα radiation, with a scan speed of 4°/min and scan range of 20–80°. Transmission electron microscopy and scanning electron microscopy (SEM) were used to observe the microstructure and surface morphology of the thin films. The composition of the thin films was measured by energy dispersive X-ray (EDX). Four-point probes (Model RT-70, NAPSON, Japan) were used to measure the sheet resistivity of the thin films. All values of film thickness and electrical properties in the study were averaged from several measurements at different positions on the samples. Optical transmittance and absorbance were measured by UV–vis/NIR spectrophotometer (spectrophotometer, Hitachi U4001) with the wavelength range of the spectrum between 300 and 1100 nm. The transmission percentages were calculated by dividing the measured percent transmission of corresponding bare substrates.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows an XRD analysis of a 150 nm thick film. It indicates that the ITO film is amorphous at 150 °C, and ITO film becoming crystalline after 250 °C. The recrystallization temperature is in the range 150–250 °C. However, the experimental results herein indicate that ITO films have a crystallized structure in the range 150–250 °C, the result is similar that of Morikawa et al.'s reported investigation [12]. A higher temperature of annealing is well known to provide a stronger driving force of the nucleation and growth of ITO films. The as-deposited film is amorphous-like (or nano-crystalline) but has a polycrystalline structure after it is annealed above 250 °C. The ITO film tends to grow in the directions (2 2 2) and (4 0 0). Therefore, the annealing processing makes the ITO film crystalline and denser. XRD analysis revealed none of the phases Sn, SnO, or SnO_2, so no phase separation was present. At 250 °C, the intensity ratio of (2 2 2) plane and (4 0 0) plane increased, and the preferred orientation of the crystal is derived from (2 2 2) plane. The energy obtained from the particles is higher at even higher temperature. XRD pattern of crystallization phenomena is even significant with the elevation of temperature. When the temperature is continuously raised to 450 °C, the crystallization is almost completely accomplished. XRD patterns clearly indicate complete crystallization of the ITO film; the major intensified peak also appeared. The crystallization of the thin film was even improved with the elevation of annealing temperature.

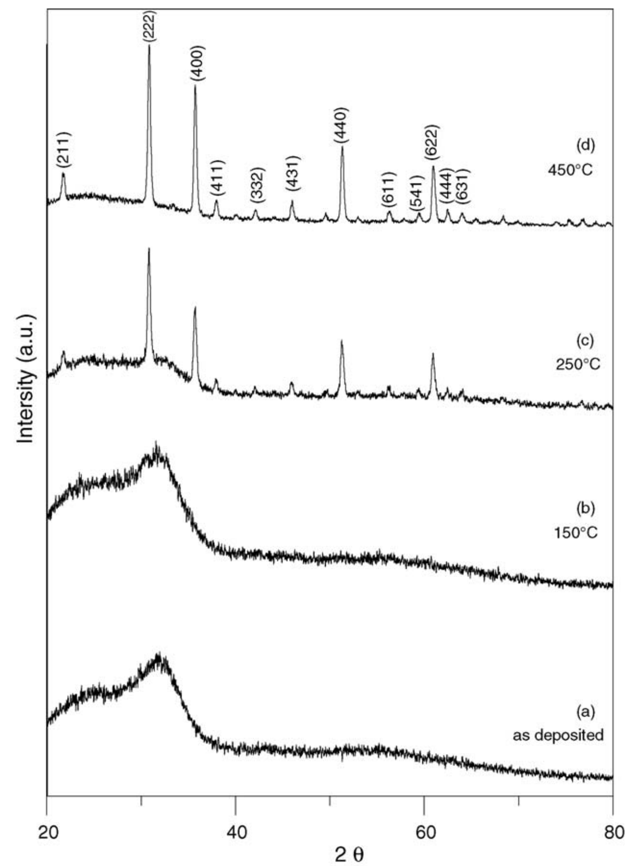

Fig. 1. XRD diffraction patterns for ITO films heat treatment at various temperatures and time of 15 min: (a) as-deposited; (b) 150 °C; (c) 250 °C; (d) 450 °C.

Fig. 2 shows the surface morphology of the ITO films annealed at different temperatures. It can be seen from the images that the films are dense and the grain size along sample surface increases as the annealing temperature is increased. It shows the films prepared below 150 °C have non-uniform particles (or clusters), the films annealed at 250 °C has both small