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Transparent conducting indium zinc tin oxide thin films with low indium content deposited by radio frequency magnetron sputtering

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ABSTRACT

Indium zinc tin oxide (IZTO) thin films were deposited on glass substrate by radio frequency magnetron sputtering at various substrate temperatures. The indium content of the IZTO targets was reduced from 60 at.% to 30 at.% and replaced with equal amounts of zinc and tin (20, 25, 30, and 35 at.%). The crystallinity of the as-deposited films improved with increasing substrate temperature. For all IZTO films, the onset of crystallization began at above 100 °C. The IZTO films deposited at higher substrate temperature showed better optical transmittance and lower electrical resistivity than those deposited at lower temperatures. The minimum electrical resistivity of approximately 8.0×10^{-4} Ω·cm was observed in the IZTO films prepared deposited at 400 °C from targets containing 20 at.% Zn and 20 at.% Sn. The optical transmittance was above 80% for all IZTO films. On the other hand, higher co-doping resulted in amorphous films, which slightly impaired the electrical properties. The deterioration in the electrical properties of IZTO films, however, was compensated for by the higher optical transparency. Therefore, reduced-indium IZTO films are promising alternatives for some transparent conducting oxide applications.

1. Introduction

Transparent conducting oxide (TCO) thin films are used widely in flat panel displays, plasma displays, organic light emitting diodes, and dye-sensitized solar cells (DSSCs) [1,2]. The most important issue in TCO thin films is high electrical conductivity and high optical transparency [3]. Indium tin oxide (ITO) is the most popular TCO material owing to its low resistivity (as small as 1×10^{-4} Ω·cm) and high optical transmittance (>80% in the visible spectra) [4,5]. On the other hand, the need to reduce the heavy dependence on ITO in TCO applications has encouraged many researchers to develop alternative materials. Multi-component oxide In–Sn–Zn–O (Indium Zinc Tin Oxide/IZTO) thin films are considered possible alternative materials, with the advantages of high electrical conductivity and optical transparency, good chemical stability, and low temperature deposition capability [6,7]. These films have also been acknowledged for practical TCO applications, such as the TCO layer in DSSCs [8,9].

In the case of multi-component systems, the solubility of the dopants is important. The same amounts of Zn and Sn substitution for In ions in In_2O_3 was reported to extend the solubility limit up to 40 at.% [10,11]. Based on previous studies, crystalline IZTO thin films with a reduced indium content of up to 60 at.% showed comparable properties to ITO and might be a possible alternative to ITO films [12–14]. On the other hand, amorphous TCO thin films are beneficial for applications with polymer substrates, which could be obtained by increasing the number of co-doping components, i.e. Zn and Sn, in the system [15].

This paper discusses the properties of as-deposited IZTO thin films with decreasing indium content of up to 30 at.% under a range of deposition conditions. Radio frequency (RF) magnetron sputtering was applied because of its ability to obtain uniform and good quality films over a large area [16]. The amount of zinc and tin co-doping was kept the same to allow an increase in the solid solubility by the co-doping technique, and to observe any possible changes in the properties of IZTO thin films with decreasing indium content. Both crystalline and amorphous films with low-indium contents grown under various deposition conditions were investigated. The effects of increasing co-doping or decreasing indium content on the structural, optical and electrical properties of IZTO thin films are discussed.

2. Experimental details

IZTO thin films were deposited glass substrate by RF magnetron sputtering. Ceramic IZTO targets with four different nominal compositions, i.e. IZTO20, IZTO25, IZTO30, and IZTO35, where the zinc and tin contents were 20, 25, 30, and 35 at.%, respectively, were employed as the sputtering sources using the conventional mixed-oxide ceramic process. Prior to deposition, glass substrates, 15 mm × 15 mm in size, were cleaned ultrasonically in acetone, ethanol, and de-ionized water

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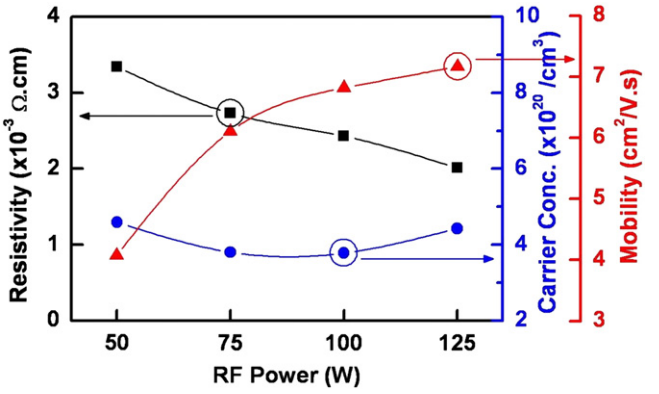

Fig. 1. Resistivity, carrier concentration and mobility of the IZTO20 films deposited at room temperature as a function of the RF power from 50 to 125 W.

for 15 min each. This was followed by drying on a hot plate to remove any remaining moisture.

Deposition was carried out in an argon gas atmosphere. The chamber was pumped down to below 2.66×10^{-3} Pa. To evaluate the effect of the RF power on the film properties, deposition was conducted at room temperature with different RF powers (50 to 125 W). During deposition, the substrates could also be heated to various temperatures up to 400 °C, while the substrate holder was rotated at a steady speed of 75 rpm. The working pressure and argon gas flow rate were kept at 0.67 Pa and 20 sccm, respectively. The deposition time was fixed to 25 min regardless of the RF power and substrate temperature used, with the IZTO film thickness ranging from 150 to 350 nm. The substrate to target distance was kept at around 10 cm for better control in film crystallinity.

The crystallization and phase evolution behavior was observed by X-ray diffraction (XRD, Rigaku D-500) using Cu Kα radiation (λ = 1.5405 Å) and the scanning angle 2θ was varied in the range between 20 and 80°. The surface roughness and morphology were examined by atomic force microscopy (NanoScope IIIa) operated with contact mode and field emission scanning electron microscopy (FESEM, Hitachi S-4800) operated at 15 kV. The film thickness was determined using a stylus profilometer (Alpha-step, Dektak 3). The optical transmittance in the visible region was characterized by ultraviolet–visible spectrophotometry (UV/Vis/NIR spectrophotometer, Cary5000). The electrical properties, i.e. carrier concentration, mobility and resistivity, were analyzed using a four-point probe and Hall measurements (Ecopia, HMS-5000).

3. Results and discussion

The room temperature deposition of IZTO20 thin films containing 60 at.% indium and 20 at.% each of zinc and tin at an RF power ranging from 50 to 125 W resulted in an amorphous structure. This is in good agreement with previous studies where the energy from RF power is insufficient to obtain crystalline films [8,15,17–19]. Although there was no noticeable difference in microstructure, increasing the RF power apparently affected the electrical resistivity and optical transmittance of these films. The optical transmittance of the IZTO20 films with different RF powers barely exceeded 80%. Higher RF power also induced a higher growth rate and yielded thicker IZTO20 films due to the more energetic ion bombardment, which decreased the optical transparency [20]. The IZTO20 film thickness increased from 150 to 270 nm with increasing RF power. A higher RF power improved the electrical properties with increased mobility values and lowered the electrical resistivity, as shown in Fig. 1. In an argon atmosphere, increasing the RF power should have released more target atoms and also left oxygen deficiencies in the films, which would show up as a high carrier concentration [21]. The increasing mobility was attributed to the increase in film thickness with increasing RF power. The films showed increasing mobility but a similar carrier concentration despite the different thicknesses [22,23]. In this study, the lowest resistivity of 2×10^{-3} Ω·cm was obtained from IZTO20 film deposited at a RF power of 125 W at room temperature. Therefore, a constant RF power of 125 W was used for all subsequent experiments.

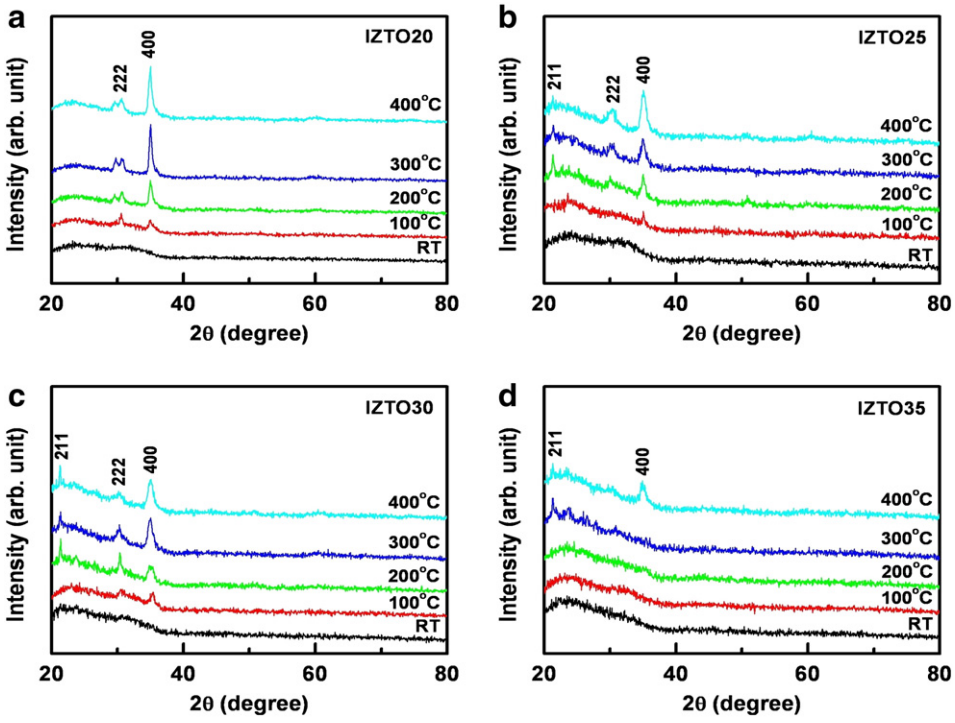

Fig. 2. X-ray diffraction patterns of (a) IZTO20, (b) IZTO25, (c) IZTO30 and (d) IZTO35 films deposited onto glass substrates at various substrate temperatures from room temperature to 400 °C.

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