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New transparent conducting $ZnO–In_2O_3–SnO_2$ thin films prepared by magnetron sputtering

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Abstract

New multicomponent $ZnO–In_2O_3–SnO_2$ system and new $In_4Sn_3O_{12}$ transparent conducting oxide thin films have been prepared by RF magnetron sputtering. The $In_4Sn_3O_{12}$ films, or $In_2O_3–SnO_2$ films with a Sn/(In + Sn) atomic ratio around 0.5, showed a resistivity of $3–4 \times 10^{-4}$ Ω cm and an average transmittance above 80% in the visible range when they were prepared at substrate temperatures of room temperature to 350°C. In addition, the electrical properties of multicomponent $Zn_2In_2O_5–ZnSnO_3$ films changed monotonically as the $ZnSnO_3$ content was varied. © 1998 Elsevier Science S.A.

Keywords: Thin films; Magnetron sputtering; Oxide

1. Introduction

Transparent and conductive indium–tin oxide (ITO), films are widely used as transparent electrodes for flat panel displays. Many of the ITO films for practical use have been prepared by magnetron sputtering using an oxide target composed of In_2O_3 and SnO_2: 5 to 10 wt.% SnO_2 in content. As a result, studies have been focused on ITO materials consisting of In_2O_3 doped with less than about 10 wt.% SnO_2 [1].

On the other hand, multicomponent oxides composed of binary and/or ternary compounds have recently attracted much attention as new materials for transparent conducting films [2–4]. As a result of changes in physical properties brought about by controlling the composition of materials in the binary or ternary compounds, these multicomponent transparent conducting oxide thin films may exhibit properties which are suitable for specialized applications. In addition, ternary compounds may possibly improve attainable properties [5–11]. However, thin films of multicomponent oxides composed of In_2O_3 and SnO_2, $In_2O_3–SnO_2$ system thin films, have been not reported.

This paper describes the preparation of highly transparent and conductive multicomponent oxide films by RF magnetron sputtering using $ZnO–In_2O_3–SnO_2$ targets. A new transparent conducting $In_4Sn_3O_{12}$ film is demonstrated. In addition, transparent conducting $Zn_2In_2O_5–ZnSnO_3$ system thin films have also been prepared.

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2. Experimental

Films were prepared by conventional RF planar magnetron sputtering using powder targets. A mixture of In_2O_3 (purity, 99.99%) and SnO_2 (purity, 99.99%) powders calcined at 1000°C in an argon (Ar) atmosphere for 5 h was used as the target: stainless steel holder, diameter of 80 mm. Substrates of Corning 7059 glass were placed parallel to the target surface at a distance of 35 mm. Sputtering deposition was carried out at sputter gas pressures of 0.1 to 1 Pa in a pure Ar gas or a mixture of Ar and oxygen (O_2) gases with a RF power of 40 W. The O_2 gas content in the $Ar + O_2$ gas atmosphere was varied from an O_2 partial pressure of 0 to 8%. Substrate temperatures were varied from room temperature (RT) to 350°C. Although the substrate at RT was not intentionally heated, the surface temperature reached about 180°C after a sputter deposition of 30 min. The deposition rate varied from 10 nm/min for a In_2O_3 target to 15 nm/min for a SnO_2 target; it was about 11 nm/min for a target with a Sn content (Sn/(In + Sn) atomic ratio) of 0.5. Film thickness was measured using a conventional surface roughness detector with stylus. Electrical resistivity and Hall mobility were measured using the van der Pauw method. Optical transmission through the film was measured in the visible wavelength

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range, 300 to 800 nm. The composition of deposited films was measured by electron probe microanalysis (EPMA).

3. Results and discussion

3.1. Preparation of In_2O_3–SnO_2 thin films

When In_2O_3–SnO_2 films were prepared by RF magnetron sputtering using In_2O_3–SnO_2 targets with a Sn content of 0 to 1.0, two peaks of carrier concentration were observed depending on the Sn content. The electrical properties as functions of the Sn content are shown in Fig. 1 for In_2O_3–SnO_2 films prepared on substrates at RT and 350°C. The sputter deposition was carried out at a sputter gas pressure of 0.25 Pa in an $Ar + O_2$ (2%) gas atmosphere. It is well known that the first peak of carrier concentration in films prepared with a Sn content around 0.05 results from the doping effect of Sn into In_2O_3, i.e., ITO [1]. In addition to the maximum carrier concentration, films prepared with a Sn content around 0.05 exhibited the minimum resistivity. The second peak was obtained in films prepared using a target with a Sn content around 0.5, regardless of the substrate temperature. In contrast, the second minimum resistivity of films prepared at RT was obtained using a target with a Sn content of 0.5, but that of films prepared at 350°C was obtained with a Sn content of 0.6.

The obtainable resistivity was dependent on the O_2 gas content introduced into the Ar sputter gas. The electrical properties as functions of the O_2 gas content are shown in Fig. 2 for films prepared on substrates at RT and 350°C using a target with a Sn content of 0.5. The optimal O_2 gas content was about 2%, regardless of the substrate temperature. Films at the second peak exhibited resistivities and carrier concentrations comparable to those of ITO films at the first peak. A minimum resistivity of 3.5×10^{-4} Ω cm was obtained for a film prepared at a substrate temperature of 350°C.

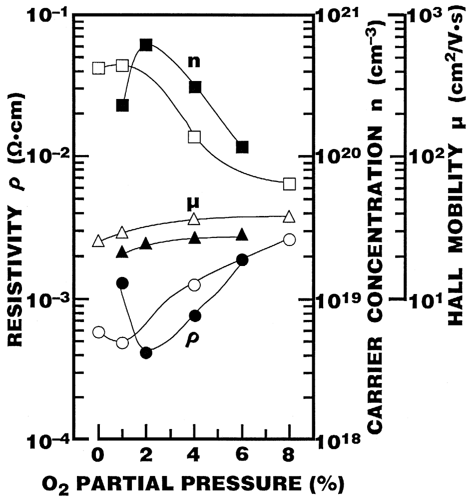

Fig. 2. Resistivity (○, ●), Hall mobility (△, ▲) and carrier concentration (□, ■) as functions of O_2 gas content for films prepared at RT (solid) and 350°C (open) with a Sn content of 0.5.

3.2. Preparation of $In_4Sn_3O_{12}$ films

From an EPMA of the prepared films, it was found that the Sn content in the films was approximately equal to that present in the target. In addition, the fact that films prepared using targets with a Sn content around 0.5 exhibited a peak of carrier concentration and a minimum of resistivity, as mentioned above, may suggest the existence of a ternary compound composed of In_2O_3 and SnO_2. The films prepared using targets with a Sn content around 0.5 were identified as $In_4Sn_3O_{12}$ [12] by the X-ray diffraction analysis shown in Fig. 3, whereas the powder targets with

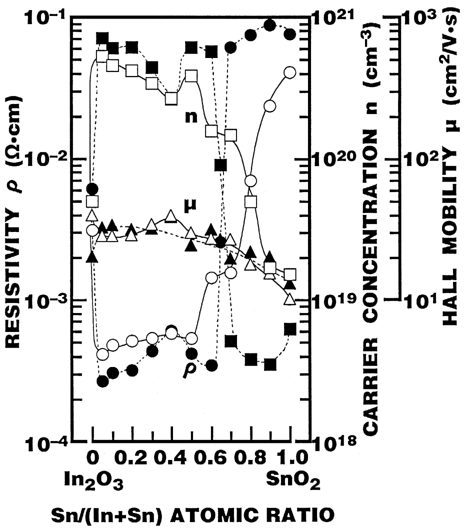

Fig. 1. Resistivity (○, ●), Hall mobility (△, ▲) and carrier concentration (□, ■) as functions of Sn content for In_2O_3–SnO_2 films prepared at RT (open) and 350°C (solid).

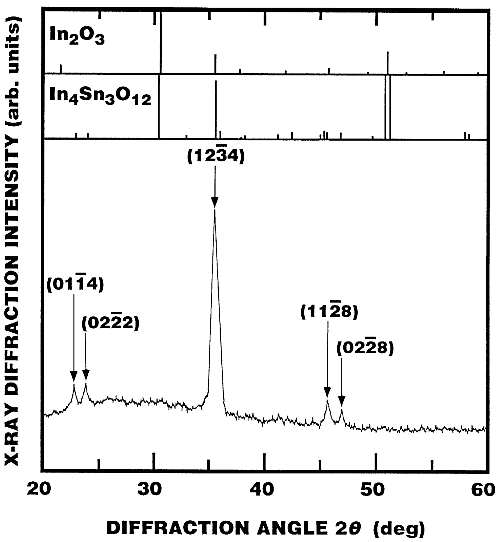

Fig. 3. X-ray diffraction profile for film prepared with a Sn content of 0.5.

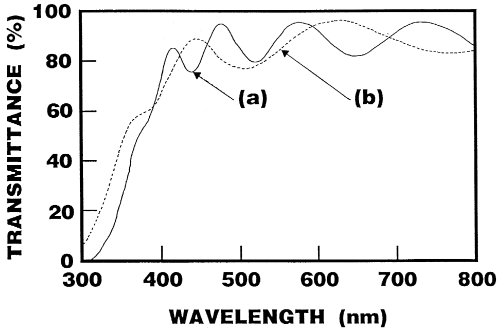

Fig. 4. Optical transmission spectra for $In_4Sn_3O_{12}$ films prepared at RT (a) and 350°C (b).

a Sn content around 0.5, calcined at 1000°C, were a In_2O_3 and SnO_2 powder mixture. Enoki and Echigoya [12] have recently reported $In_4Sn_3O_{12}$ as a new material in the In_2O_3–SnO_2 system; $In_4Sn_3O_{12}$ was identified from an electron diffraction analysis of powder composed of $2In_2O_3$ and $3SnO_2$, annealed at 1227°C. Although the X-ray diffraction profile from $In_4Sn_3O_{12}$ is very close in that from In_2O_3, as seen from the ASTM [1] and the Enoki and Echigoya data indicated in Fig. 3, there is a clear difference at 2θ between 20° and 25°: the diffraction profile from $In_4Sn_3O_{12}$ shows two peaks, but that from In_2O_3 is single. As can be seen in Fig. 3, the diffraction profile from films deposited at RT with an O_2 gas content of 2% using targets with a Sn content of 0.5 exhibited two peaks. It should be noted that the X-ray diffraction profile was strongly dependent on preparation conditions such as the O_2 gas content, the sputter gas pressure and the substrate temperature. In addition to the two peaks in the X-ray diffraction profile, the angle of the observed diffraction peaks coincided well to the $In_4Sn_3O_{12}$ data [12]. Therefore, it can be concluded that a polycrystalline $In_4Sn_3O_{12}$ film with a resistivity as low as 3×10^{-4} Ω cm was prepared by RF magnetron sputtering using targets with a Sn content around 0.5.

Fig. 4 shows optical transmission spectra for $In_4Sn_3O_{12}$ films prepared at a substrate temperature of RT and 350°C. The $In_4Sn_3O_{12}$ films were prepared at a sputter gas pressure of 0.25 Pa with an O_2 gas content of 2% using targets with a Sn content of 0.5. The thicknesses of films prepared at RT and 350°C were 580 and 330 nm, respectively. An average transmittance above 80% in the visible range was obtained for these $In_4Sn_3O_{12}$ films. The band-gap energy is roughly estimated to be about 3.5 eV and the refractive index to be about 2.1 for $In_4Sn_3O_{12}$ films [10].

3.3. Properties of multicomponent $Zn_2In_2O_5$–$ZnSnO_3$ films

We have reported previously that highly transparent and conductive films were realized by $Zn_2In_2O_5$ [10] and $ZnSnO_3$ [7], both ternary compounds composed of ZnO and In_2O_3 or SnO_2. Now, multicomponent $Zn_2In_2O_5$–$ZnSnO_3$ films have been prepared using ZnO-In_2O_3–SnO_2 targets. The electrical properties as functions of the $ZnSnO_3$ content are shown in Fig. 5 for multicomponent $Zn_2In_2O_5$–$ZnSnO_3$ films prepared on substrates at RT. The sputter deposition was carried out at a sputter gas pressure of 1.2 Pa in a pure Ar atmosphere. It was found that the electrical, optical and chemical properties of the $Zn_2In_2O_5$–$ZnSnO_3$ films changed monotonically as the $ZnSnO_3$ content was varied. In In_2O_3–SnO_2 system films, the etching rate in acid solutions such as HCl decreased as the Sn content was increased. In contrast, the etching rate of $Zn_2In_2O_5$–$ZnSnO_3$ system films was improved by the introduction of Zn. The etching rate of $Zn_2In_2O_5$–$ZnSnO_3$ system films in HCl solutions decreased as the $ZnSnO_3$ content was increased; the films prepared with a $ZnSnO_3$ content above 30 at% were hardly etched in 0.2 M HCl solution.

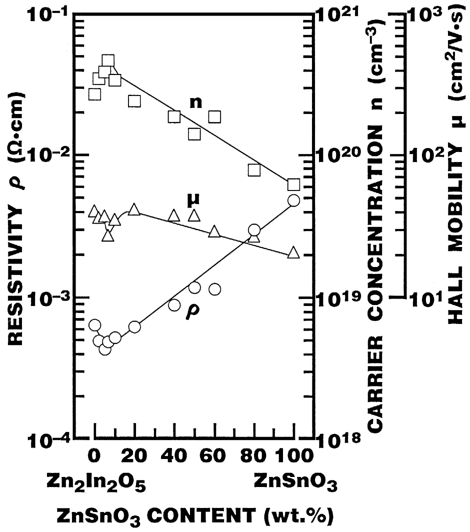

Fig. 5. Resistivity (○), Hall mobility (△) and carrier concentration (□) as functions of $ZnSnO_3$ content for $Zn_2In_2O_5$–$ZnSnO_3$ films prepared at RT.

4. Conclusions

Transparent conducting multicomponent oxide thin films have been prepared by RF magnetron sputtering using ZnO–In_2O_3–SnO_2 targets. When films were prepared using In_2O_3–SnO_2 targets with a Sn content (Sn/(In + Sn) atomic ratio) of 0 to 1.0, two peaks of carrier concentration were observed depending on the Sn content. In_2O_3–SnO_2 films prepared with a Sn/(In + Sn) atomic ratio around 0.5 were identified as $In_4Sn_3O_{12}$. A resistivity of 3–4×10^{-4} Ω cm and an average transmittance above 80% in the visible range were obtained in $In_4Sn_3O_{12}$ films prepared at substrate temperatures of room temperature to 350°C. In addition, multicomponent $Zn_2In_2O_5$–$ZnSnO_3$ films were prepared using ZnO–In_2O_3–SnO_2 targets. The

[1] ASTM X-ray Powder Diffraction File, Inorganic, No. 6-0416.

electrical properties of the multicomponent oxide films changed monotonically as the $ZnSnO_3$ content was varied. This new material, $In_4Sn_3O_{12}$, is promising as a transparent conducting oxide film because of its low cost in comparison with ITO films with a high In content.

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