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Transparent Conducting Zinc-Indium Oxides Thin Films by an Electron Beam Evaporation Method

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ABSTRACT

$ZnO-In_2O_3$ films were fabricated on Corning 1737 glass substrate by an electron beam evaporation technique and their characteristics were investigated. The composition of $ZnO-In_2O_3$ films had a marked effect on the electrical properties of the films. The $ZnO-In_2O_3$ films showed superior transparent-conducting characteristics with increase of Zn content. The resistivity and carrier concentration of the film having Zn content of 45 at% are 4.45×10^{-3} cm and 3.1×10^{19} cm^{-3}, respectively. Also, the transmittance was higher than 80% throughout the visible range. The average roughness of the film was 14.6 Å in terms of root mean square.

Key words : $ZnO-In_2O_3$ film, Electron beam evaporation, Resistivity, Carrier concentration, Transmittance

1. Introduction

Transparent Conducting Oxide (TCO) films are widely used for transparent electrode, heaters and IR reflective coatings.[1,2] The electrical and optical properties of these films were affected by the large number of parameters such as deposition parameters, microstructure, growth technique, dopant and its concentration. Although ITO is the most commonly used material for optoelectronic devices due to its excellent properties, its main disadvantage is that the indium source material is too expensive.[3,4] Recently, thin films of Zinc Oxide (ZnO) have attracted large concerns as a transparent semiconducting material because coatings of this material are relatively inexpensive and have a sharp UV cut-off. But, for practical application all undoped ZnO conducting films are not suitable because of their thermal instability as well as low electrical conductivity. Doping some elements into ZnO improves not only the properties but also the stability of ZnO films.[5-7] Up to now, the ZnO films with various doping materials have been investigated.[8-14] Among them, zinc-indium oxide is one of the promising TCO candidates exhibiting electrical and optical properties comparable to or exceeding those of many other TCOs.

In the present study, we have studied on $ZnO-In_2O_3$ system using an electron beam evaporation technique.[15] The electrical and optical properties of $ZnO-In_2O_3$ films with various compositions were investigated in this work.

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2. Experimental Procedure

$ZnO-In_2O_3$ films were prepared on Corning 1737F glass substrate at the substrate temperature of 400°C by an electron beam evaporation technique. $ZnO-In_2O_3$ pellets were fabricated as the evaporation source for $ZnO-In_2O_3$ films. The ZnO (99.9% purity) and In_2O_3 (99.99% purity) powders were weighed in specific proportions to obtain the desired compositions and were mixed in ball mill for 24 h using zirconia balls. The mixed powders were dried and pressed into compacts under the isostatic pressure of 1300 Pa. The pellets were made by sintered at 1200°C during 2 h in an air atmosphere.

The crystal phase and surface morphology of $ZnO-In_2O_3$ films was examined by X-ray diffraction and FE-SEM, respectively. Energy Dispersive Spectroscopy (EDS) was used to investigate the chemical composition of the films. The resistivity, charge carrier density and mobility of films were measured by Hall Effect Measurements (HEM-3000, EGK holdings, korea). Optical transmittance measurement was carried out using UV-visible-IR spectrophotometer. In addition, Atomic Force Microscope (AFM) was used to analyze surface roughness.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the films deposited on glass substrate at 400°C as a function of ZnO content in $ZnO-In_2O_3$ pellets. As the ZnO content in $ZnO-In_2O_3$ pellets increases, the crystallinity of the films decreases and the peaks at near $2\theta = 30°$ which is the main peak of In_2O_3 and $In_2Zn_2O_5$ was shifted as shown in Fig. 1. This seemed to be caused by the fact that $In_2Zn_2O_5$ phase be formed as ZnO was added. The films with ZnO content of 95 at% appeared

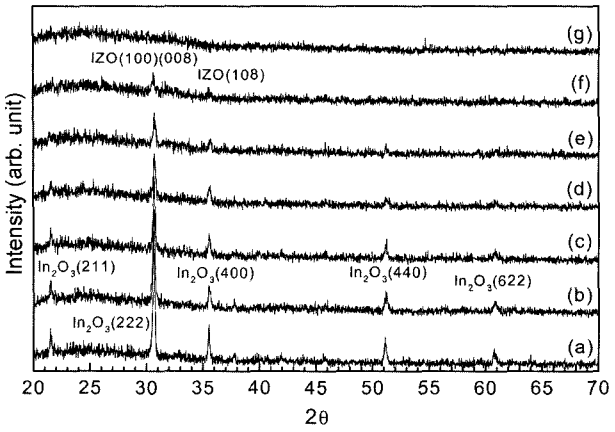

Fig. 1. X-ray diffraction patterns of the films deposited by the ZnO-In_2O_3 pellets with various ZnO contents of: (a) 33, (b) 50, (c) 67, (d) 80, (e) 86, (f) 90, and (g) 95 at%.

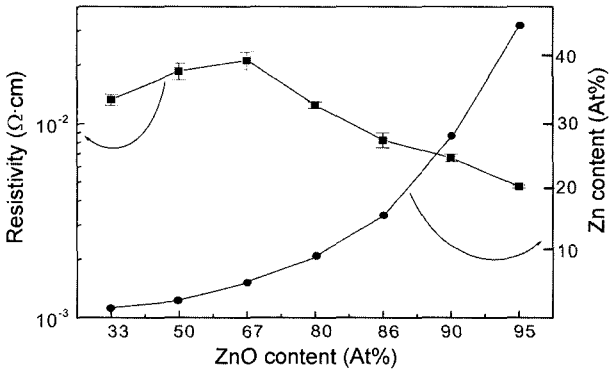

Fig. 2. Resistivity and Zn content of ZnO-In_2O_3 films as a function of ZnO content of the pellets.

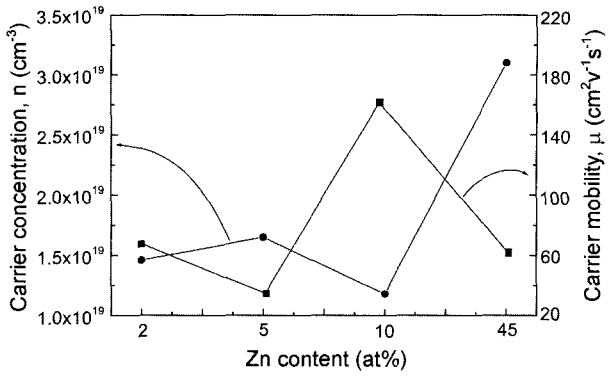

Fig. 3. Carrier concentration and hall mobility of the ZnO-In_2O_3 films as a function of Zn content.

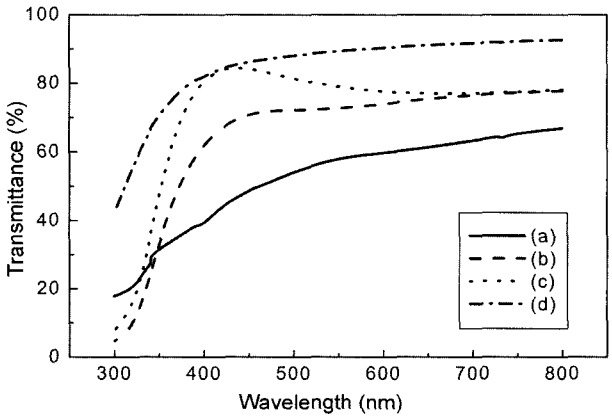

Fig. 4. Optical transmittance spectra of the ZnO-In_2O_3 films with various Zn contents of: (a) 2, (b) 5, (c) 10, and (d) 45 at%.

to have amorphous phase.

Fig. 2 shows Zn content and variation of resistivity of the film as a function of ZnO content in ZnO-In_2O_3 pellets. The Zn content in ZnO-In_2O_3 films is much lower than that in the pellets. This means that In_2O_3 and ZnO have different equilibrium vapor pressure. It can be observed from this figure that the big change of resistivity didnt appeared until to 5 at% Zn content in the film as the ZnO content increased. It means that there is little difference between carieer concentration and hall mobility as shown in Fig. 3. When the Zn content of ZnO-In_2O_3 films is higher than 5 at%, the resistivity decreases sharply. This result may be explained by increasing either the carrier concentration or the carrier mobility. At 10 at% of Zn content, ZnO-In_2O_3 film has the highest hall mobility value despite nearly unchangeable the carrier concentration as shown Fig. 3. At 95 at% of ZnO content in ZnO-In_2O_3 pellets, ZnO-In_2O_3 film with about 45 at% Zn content has the value of resistivity 4.45×10^{-3} cm. In our case, the carrier concentration mainly influenced by oxygen vacancies while the mobility, as we will show, may be influenced by change in microstructure of the films.

Fig. 3 shows the variation of carrier concentration and hall mobility of ZnO-In_2O_3 films as a function of Zn content. The carrier concentration increases with Zn content changes from 10 to 45 at%. Maximum carrier concentration is reached for 45 at% Zn content. This increase in carrier concentration has been attributed to increase free electron. The amount of Zn content provides a large number of free electrons in the film. The free electrons in these films are supplied from donor sites associated with oxygen vacancies or excess metal ions by homologous phase. As the Zn content changed from 5 to 10 at%, the hall mobility increased. This seemed to be caused by crystallinity and decrease in grain boundary barrier potential in these films.[16] In the case of Zn contents higher than 10 at%, the hall mobility continuously decreases. It may be seen due to formed homologous phase such as $ZnIn_2O_4$, $Zn_2In_2O_5$, and $Zn_3In_3O_6$ in crystalline, which appear amorphous film as shown in Fig. 5(d).

Fig. 4 shows the spectral dependence of transmission for ZnO-In_2O_3 films. As the Zn content increases, transmittance property was improved and absorption edge shift slightly towards shorter wavelengths. This shift of absorption means band-gap wideness in ZnO-In_2O_3 films. In the case of Fig. 4(d), the transmittance is greater than 80% throughout the visible range.

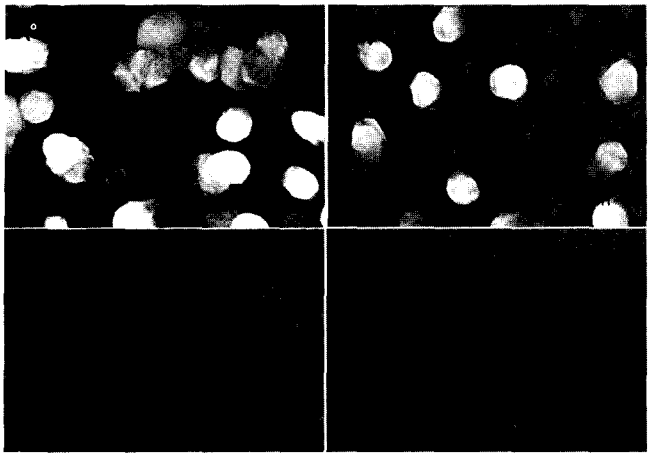

Fig. 5. SEM photographs of the $ZnO\text{-}In_2O_3$ films with Zn contents of : (a) 2, (b) 5, (c) 10, and (d) 45 at%.

Figs. 5 and 6 show the change in surface morphology of the films as a function of Zn content in $ZnO\text{-}In_2O_3$ films. As the Zn content is lower than 10 at%, the In_2O_3 phase is formed and obtain $ZnO\text{-}In_2O_3$ phase without second phase as shown in Fig. 5(a), (b), and (c), respectively. In the case of Fig. 5(d), we observed amorphous phase. When the Zn content increases, the roughness of $ZnO\text{-}In_2O_3$ films was decreased as shown in Fig. 6. The value of rms roughness with Zn content of 45 at% was 14.6 Å.

4. Conclusions

$ZnO\text{-}In_2O_3$ films have been prepared on glass substrate at 400°C by electron beam evaporation. $ZnO\text{-}In_2O_3$ films with various Zn content (such as at 2~45 at%) were investigated. Zn content in the $ZnO\text{-}In_2O_3$ films has a significant effect on the characteristics of the films. From the XRD result, Zn content in the $ZnO\text{-}In_2O_3$ films affected the change of the crystallinity. At 45 at% of Zn content, the value of resistivity is 4.45×10^{-3} cm. The carrier concentration and hall mobility are 3.1×10^{19} cm^{-3} and 62 $cm^2V^{-1}s^{-1}$, respectively. Also, the transmission is greater than 80% throughout the visible range. The surface morphology of the films observed amorphous phase. The value of rms roughness was 14.6 Å.

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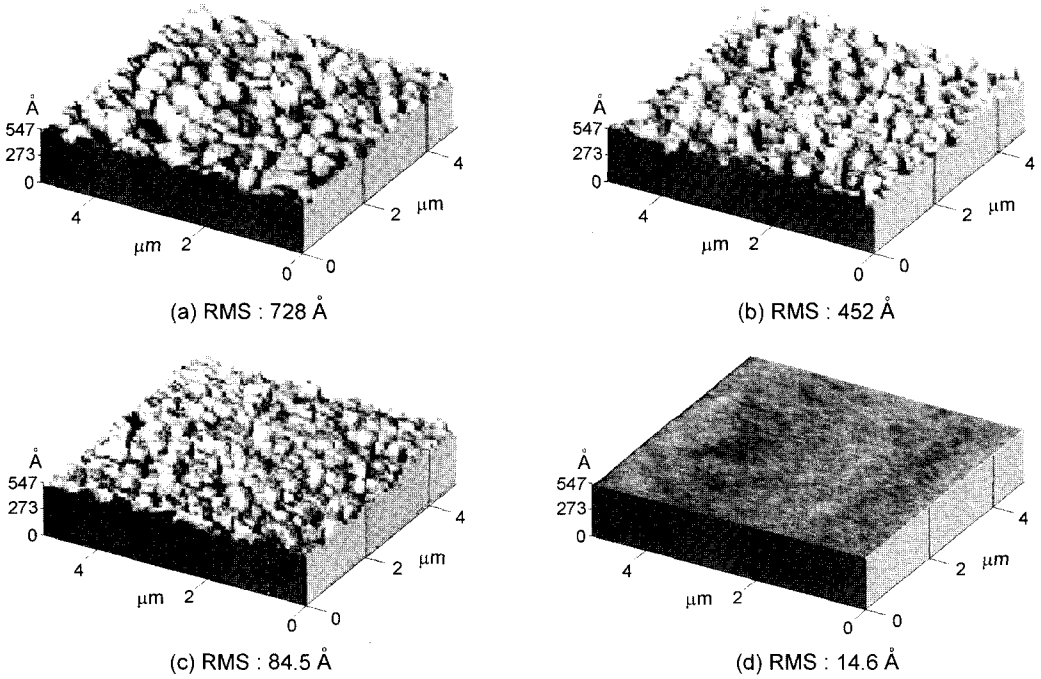

Fig. 6. AFM image of the $ZnO\text{-}In_2O_3$ films with Zn contents of : (a) 2, (b) 5, (c) 10, and (d) 45 at%.

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