Multi-component $ZnO-In_2O_3-SnO_2$ thin films deposited by RF magnetron co-sputtering

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Abstract

Multi-component $ZnO-In_2O_3-SnO_2$ thin films have been prepared by RF magnetron co-sputtering using targets composed of $In_3Sn_4O_{12}$(99.99%) [1] and ZnO(99.99%) at room temperature. $In_3Sn_4O_{12}$ contains less In than commercial ITO, so that it lowers cost. Working pressure was held at 3 mtorr flowing Ar gas 20 sccm and sputtering time was 30 min. RF power ratio [RF1 / (RF1 + RF2)] of two guns in sputtering system was varied from 0 to 1. Each RF power was varied 0~100W respectively. The thickness of the films was 350~650nm. The composition concentrations of the each film were measured with EPMA, AES and XPS. The low resistivity of $1\text{-}2 \times 10^{-3}$ and an average transmittance above 80% in the visible range were attained for the films over a range of δ ($0.3 \le \delta \le 0.5$). The films also showed a high chemical stability with time and a good uniformity.

1. Introduction

Transparent conducting oxides (TCO) in flat panel displays were fabricated using various binary or ternary metal oxide compounds [2]. Indium tin oxide (ITO) films prepared by a sputtering system are widely used as a TCO film for flat panel displays. Many of ITO films for practical use consist of In2O3 doped with less than about 5wt% SnO2 [3]. However, when ITO films are deposited at low temperature, the electrical conductivity and transmittance decrease as time goes by. And attainable properties of binary ITO films have often been limited in their applications because of difficulty in preparing pure materials and in controlling precisely hand gaps to optimize the performance of particular devices. For the purpose of optimizing electrical, optical and chemical properties for specialized applications, multi-component oxides composed of a combination of different oxides have attracted much attention as new materials for TCO films: Zn_2SnO_4, $ZnSnO_3$ [4], $GaInO_3$ and $Zn_2In_2O_5$ [5], In_2O_3-ZnO and In_2O_3-$InGaO_3$-Ga_2O_3 films. By controlling the composition of materials composed of various combination of the compounds, physical (optical, electrical and surface morphology) property change in the multi-component TCOs may produce more suitable characteristics. Induim is very expensive material so a quaternary compound in $ZnO-In_2O_3-SnO_2$ system can reduce cost by resulting from a lower Induim content.

We reported that highly conductive and transparent $ZnO-In_2O_3-SnO_2$, multi-component TCO films were prepared by RF magnetron co-sputtering using ITO and ZnO target. This paper also introduces physical properties of $ZnO-In_2O_3-SnO_2$, multi-component TCO films which is deposited on glass substrate at room temperature.

2. Experimental Procedure

$ZnO-In_2O_3-SnO_2$ films were deposited on glass substrates by using RF magnetron co-sputtering at room temperature. One target is ZnO (99.99%) and the other is $In_4Sn_3O_{12}$ (99.99%). These targets were placed on the facing holders. Working pressure was held at 3 mTorr flowing Ar gas 20 sccm.. RF power ratio [RF 1/(RF 1+RF 2)] of two guns in sputtering system was varied from 0 to 1. Each RF power was varied 0~100W respectively. EPMA (Electron Probe Micro-Analysis) is used for considering the composition ratio of $ZnO/(ZnO+In_2O_3+SnO_2)$ in films. The crystallinity and crystal orientation of the deposited films were investigated by X-ray diffraction (Rigaku No. D/Max-2A) using a CuK_α source. The thicknesses of the films were investigated by using alpha-step. Surface morphology FE-SEM (HITACHI S-4100). Four point probe was used for electrical properties of the films. A spectrophotometer (Shimadzu Co.) was used for measuring the optical properties of the films in the wavelength range of 200 ~ 500 nm. Surface morphology was inspected by AFM (Atomic force microscopy)

3. Results and Discussion

Structural Analysis. The composition ratio of deposited film was analyzed by EPMA. Figure 1 shows that δ lineally increases as RF 1 (ZnO target side) powers up when let δ be Zn / (Zn+Sn+In). It is also shown that Zn content increases as δ is expended in Fig. 2. Amorphous phases are shown in range $0 \leq \delta \angle 6$, but ZnO (002) peaks appear in $\delta > 6$. That is Zn content is enough to be oriented to (002) direction. At δ = 0.788 , ZnO (002) peak is shifted due to amorphous phases including In and Sn. After that, ZnO (002) peak is shown at 34.4 degree because ZnO content is much more than In and Sn content. Nevertheless, at δ=1, the growth of ZnO other direction was supposed out of considerable for the decrease of (001) direction.

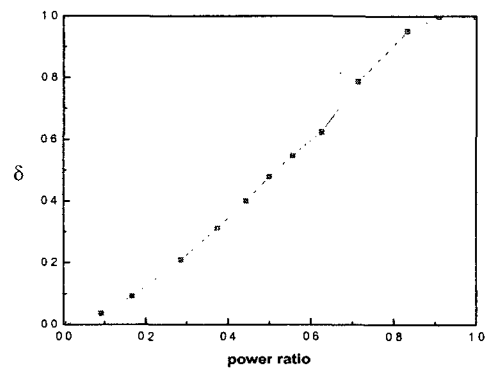

Fig. 1. δ-power ratio graph when let δ = Zn / (Zn + Sn+ In) (wt%), power ratio = RF1 / (RF1 + RF2)

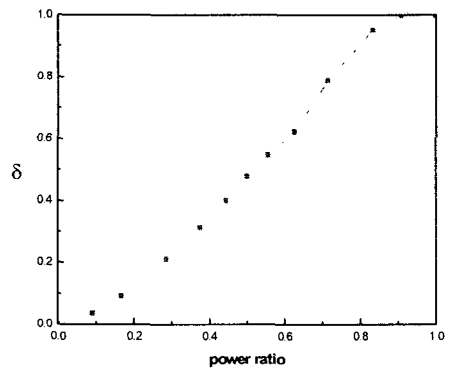

Fig. 2. Fig.2. XRD spectrum for the deposited thin films as a function of δ.

Electrical and Optical properties.

Figure 3 shows the resistivities of the films as a function of δ. The lowest resitivity of films was 1.86×10^{-3} [Ω•cm] as δ was 0.479, that is, the weight percent of Indium oxide, tin oxide and zinc oxide were 32.55, 27.39, 40.06 respectively. As shown fig. 5, carrier concentration and mobility were measured by Hall measurement. Although , at δ=0.788, carrier concentration was -1.38×10^{20} more than -9.1×10^{19} [cm^{-3}] at δ=0.479, mobility was 4.49 and 17.4 [cm^2/V•sec] respectively. Therefore the resistivity of film at δ=0.479 was lowest.

Figure 4 shows the optical transmittance spectra of the films. An average transmittance above 80% in the visible range was obtained for films.

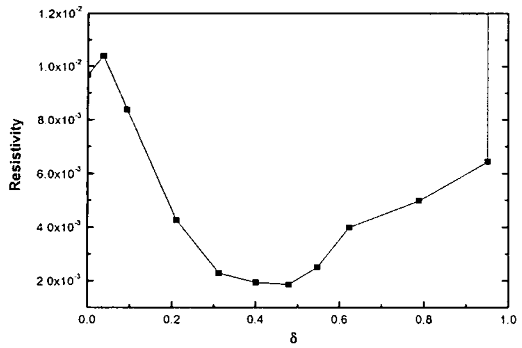

Fig. 3. Resistivity as a function of δ.

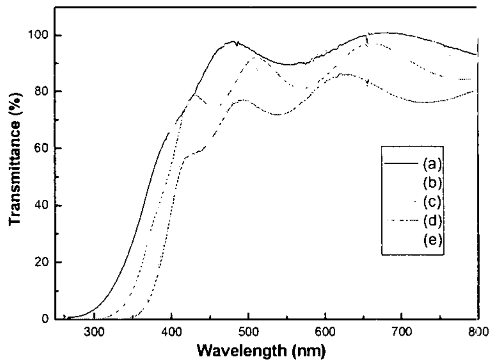

Fig. 4. Optical transmittance spectra of the films : (a) δ=0, (b) δ=0.21, (c) δ=0.479, (d) δ= 0.788 and (e) δ=1

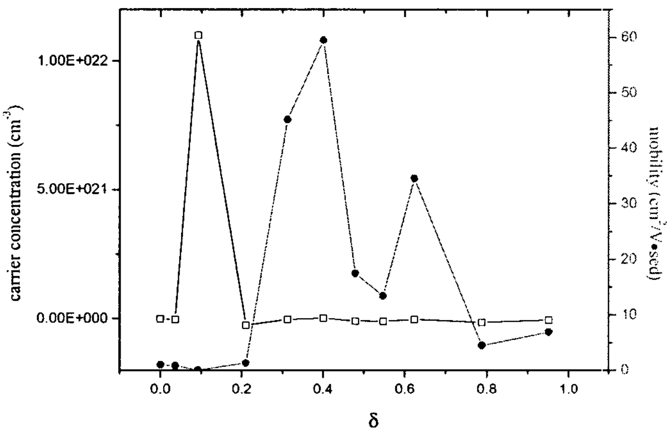

Fig. 5. Carrier concentration and mobility as a function of δ

Figure 6 show the ternary diagram and SEM images of films. Roughness was also measured by AFM. The rms value of films were 40.5, 30.9 and 67.7 Å at δ=0, δ=0.479 and δ= 0.951 respectively

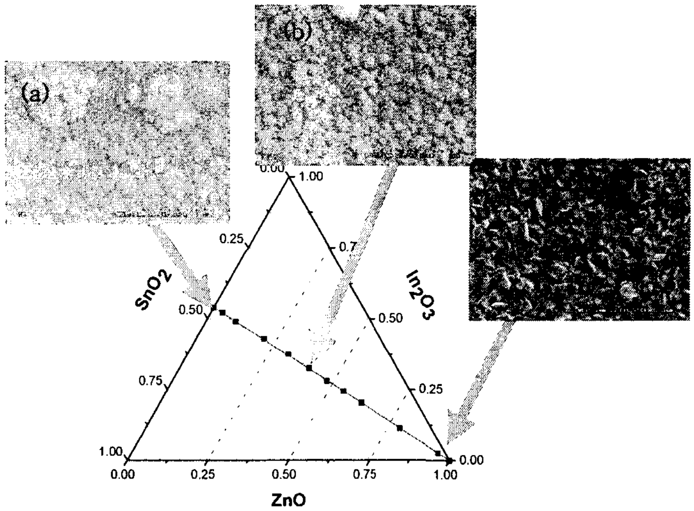

Fig. 6. Ternary diagram and SEM images of the films : (a) δ=0 , (b) δ=0.479 and (c) δ=0.951

4. Conclusions

New multi-component ZnO-In_2O_3-SnO_2 thin films have been prepared by RF magnetron co-sputtering using targets composed of $In_3Sn_4O_{12}$(99.99%) and ZnO(99.99%) at room temperature. The low resistivity of 1.86×10^{-3} [Ω•cm] and an average transmittance above 80% in the visible range were attained for the films in composition of In_2O_3: SnO_2: ZnO = 32.55 : 27.39 : 40.06 (w%). The roughness value was 30.09 Å. The carrier concentration and mobility were -9.1×10^{19} [cm^{-3}] and 17.4 [cm^2/V•sec] respectively. The films also showed a high chemical stability with time and a good uniformity. $In_3Sn_4O_{12}$ contains less In than commercial ITO, so that it lowers cost.

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