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Thin Solid Films 484 (2005) 184 – 187

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Electrical and optical properties of In_2O_3–ZnO thin films prepared by sol–gel method

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Received 11 August 2004; accepted in revised form 8 March 2005
Available online 21 April 2005

Abstract

Transparent conducting indium zinc oxide (In_2O_3–ZnO) thin films were fabricated by a sol–gel method. Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and indium nitrate trihydrate [$In(NO_3)_3{\cdot}3H_2O$] were used as starting precursors, and 2-methoxyethanol as a solvent. Monoethanolamine was added as a stabilizer. The starting solution was spin-coated onto a glass substrate. Thin films at several atomic ratios of Zn/(Zn+In) were annealed at 650 °C. The minimum resistivity ($\rho \approx 1.5 \times 10^{-3}$ Ω cm) and maximum carrier concentration ($n \approx 3.0 \times 10^{20}$ cm^{-3}) were obtained for the film whose atomic ratio was 0.5. The optical transmittance in the visible region was 80–85% irrespective of atomic ratios. After the $Zn_2In_2O_5$ (a homologous compound $Zn_kIn_2O_{k+3}$ where $k=2$ and corresponds to the atomic ratio of 0.5) films were post-annealed in a reducing atmosphere, the carrier concentration increased to approximately 4.0×10^{20} cm^{-3} and the optical window was narrower, although the resistivity slightly increased.

PACS: 73.61.Le; 78.66.Li; 81.20.Fw
Keywords: Sol–gel; Indium–zinc oxide; Electrical properties and measurements; Optical properties

1. Introduction

Transparent conducting oxide (TCO) films have been extensively researched for a variety of optoelectronic devices such as displays, solar cells, and low-e windows [1,2]. Among the TCO films, ITO (Sn-doped indium oxide) is well known as the most commonly used materials with low resistivity and high optical transparency in the visible region. However, there is a growing demand for less expensive materials (e.g., ZnO, In_2O_3–ZnO, and SnO_2) because of the high cost of ITO films. In particular, the In_2O_3–ZnO system has attracted considerable interest. Moriga et al. studied the phase relations and physical properties of homologous compounds in a bulk In_2O_3–ZnO system [3]. They identified nine homologous compounds of $Zn_kIn_2O_{k+3}$ ($k=3$, 4, 5, 6, 7, 9, 11, 13, and 15), which do not include $Zn_kIn_2O_{k+3}$ ($k=1$, 2) that is unstable at the bulk phase. While In_2O_3–ZnO thin films have been prepared by metal organic chemical vapor deposition [4], sputtering [5–7], and laser deposition [8], thin films prepared by sol–gel method are rare. The sol–gel method offers many advantages such as highly homogeneous thin films, large area coating, absence of the need for vacuum, low cost, and high flexibility.

In this paper, by using this sol–gel technology, In_2O_3–ZnO thin films were fabricated and their electrical and optical properties were investigated for several atomic ratios of Zn/(Zn+In) (abbreviated as x). In addition, the effects of post-annealing condition on the properties of $Zn_2In_2O_5$ (a homologous compound $Zn_kIn_2O_{k+3}$ where $k=2$) thin film were examined for oxidizing, inert, and reducing atmospheres.

2. Experimental details

Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and indium nitrate trihydrate [$In(NO_3)_3{\cdot}3H_2O$] were separately dissolved in 2-methoxyethanol. Monoethanolamine (MEA) was added to the zinc solution as a stabilizer and the molar

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doi:10.1016/j.tsf.2005.03.007

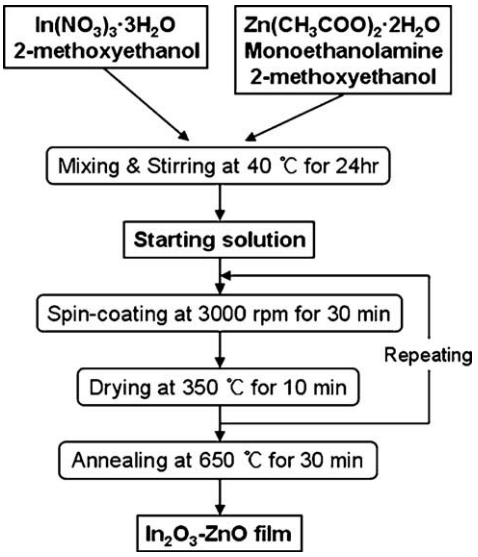

Fig. 1. The flow chart showing the procedure for preparing In_2O_3–ZnO thin films.

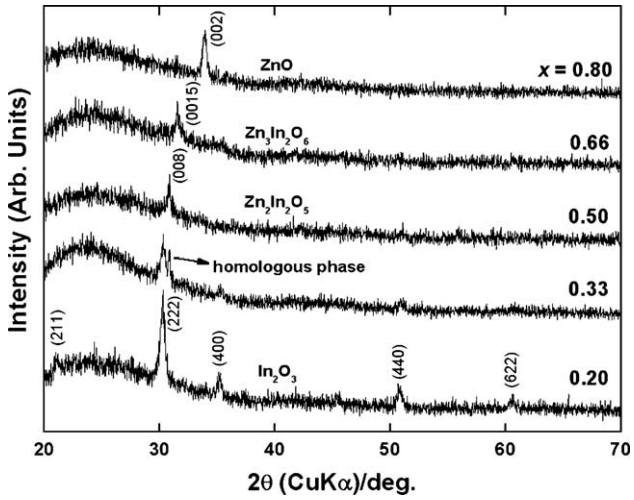

Fig. 2. XRD patterns of In_2O_3–ZnO thin films of several atomic ratios annealed at 650 °C for 30 min; the atomic ratio of Zn/(Zn+In) is abbreviated to x.

ratio of MEA to Zn ion was maintained at 1.0. To prepare a 0.2 M starting solution, two solutions were mixed and stirred at 40 °C for 24 h on a hot plate. The thin films were coated for 2 days after the starting solution was prepared.

The starting solution was dropped onto a substrate and rotated at 3000 rpm for 30 s. A $15 \times 15 \times 1$ mm bare glass (Corning Inc. 1737) was used as the substrate. The substrate was cleaned in an ultrasonic bath with acetone, ion-exchanged water, and ethanol successively. After deposition by spin coating, the films were dried at 350 °C for 10 min on a hot plate. The procedure from coating to drying was repeated until the thickness of the sintered films was approximately 100 nm. The films were then annealed in an electric furnace at 650 °C for 30 min. In this way, films of $x=0.20$, 0.33, 0.50, 0.66, and 0.80 were fabricated. $Zn_2In_2O_5$ thin films corresponding to $x=0.50$ were post-annealed in O_2, N_2, and $N_2+5\%H_2$ atmosphere at 500 °C for 30 min. Fig. 1 shows the flow diagram for In_2O_3–ZnO thin films prepared by the sol–gel process using the spin-coating method.

The structural characterization of the films as a function of x was analyzed using X-ray diffractometer (XRD) with CuKα radiation operated at 30 kV and 30 mA. The carrier concentration, Hall mobility, and electrical resistivity of the films were determined by Hall measurements using a four-probe van der Paw technique. Optical transmittance measurements were carried out using an ultraviolet visible near-infrared spectrophotometer. The surface morphology of the $Zn_2In_2O_5$ thin film was examined by scanning electron microscopy (SEM).

3. Results and discussions

Fig. 2 shows how the XRD patterns of In_2O_3–ZnO thin films varied with x. At $x=0.20$, the XRD pattern was In_2O_3 peak, where the preferred orientation along the (222) plane was observed. As x increased to 0.33, showing a new peak at 30.9°, it was assumed that the In_2O_3 bixbyite phase coexisted with a homologous phase. The peak of homologous phase of $Zn_kIn_2O_{k+3}$ appeared clearly in the films of $x=0.50$ and 0.66. The peak (30.9°) at $x=0.33$ appeared at about the same angle as the (008) peak of $Zn_2In_2O_5$ phase at $x=0.50$. At $x=0.66$, a diffraction peak corresponding to $k=3$ ($Zn_3In_2O_6$) was observed. As the amount of Zn in the film was increased to $x=0.80$, the XRD pattern showed a peak of (002) plane of ZnO.

The results of Hall effect measurements are presented in Fig. 3. Hall mobility is mainly affected with changes in the crystal structure of the film, while carrier concentration is principally dependent upon the number of oxygen vacancies. The Hall mobility of the film was about 18.0 cm^2/V s at $x=0.20$ and decreased as x increased to be about 8.0 cm^2/V s, which was probably due to the increase of scattering

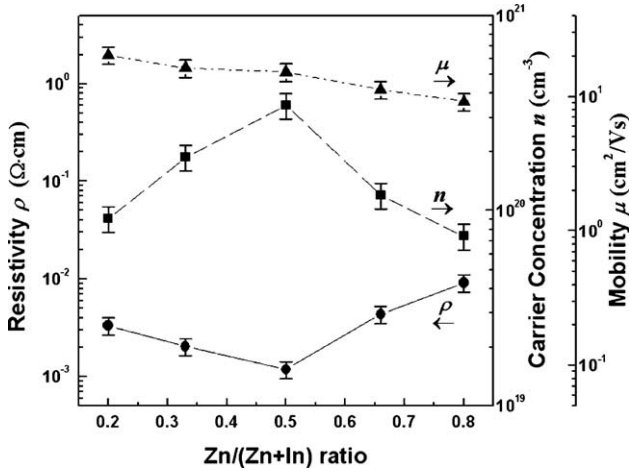

Fig. 3. Electrical resistivity, carrier concentration, and Hall mobility of In_2O_3–ZnO thin films as the variation of Zn/(Zn+In) ratio; resistivity is abbreviated to ρ (●), carrier concentration to n (■), and mobility to μ ().