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Short communication

Fabrication and characteristics of transparent conducting In_2O_3–ZnO thin films by ultrasonic spray pyrolysis

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Abstract

Transparent conducting In_2O_3–ZnO thin films were prepared by ultrasonic spray pyrolysis technique. Indium nitrate trihydrate ($In(NO_3)_3{\cdot}3H_2O$) and zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) were used as precursors and a solvent was 2-methoxyethanol. The thin films, as a function of Zn/(Zn + In) atomic ratio (abbreviated to x), were annealed at 550 °C. Oxygen gas was used as both carrier and reactor gas. From analyzing X-ray diffraction patterns, In_2O_3 phase and ZnO phase were formed at $x = 0.11$ and 0.89, respectively, while homologous phases of In_2O_3–ZnO were observed between $x = 0.5$ and 0.67. The resistivity of the thin film increased until $x = 0.33$ and then decreased to be the lowest value (1.47×10^{-2} Ω cm) at $x = 0.5$. In the range of $x = 0.6$–1, the resistivity increased again with x. The highest carrier concentration and the highest Hall mobility were 2.02×10^{19} cm^{-3} at $x = 0.6$ and 15.89 cm^2/V s at $x = 0.5$, respectively. The optical transmittance in the visible region at $x = 0.5$ was 88–92%.

Keywords: Ultrasonic spray pyrolysis; Film deposition; Indium oxide; Zinc oxide; Electrical properties; Optical properties

1. Introduction

Transparent conducting oxide (TCO) thin films have received extensive attention because of their diverse applications as transparent electrodes for optoelectronic devices such as flat panel displays and solar cells. Until now, doped metal oxides such as In_2O_3:Sn, ZnO:Al and SnO_2:F have received the most attention. Many investigations, however, have been devoted to the search for a new TCO offering similar or even better performance [1–6]. Recently, this search has been oriented toward indium–zinc oxide [7–9].

The In_2O_3–ZnO ($Zn_kIn_2O_{k+3}$) structure can be roughly visualized as a periodic intergrowth of pure InO_6 octahedra (InO_2^-) layers from a bixbyite structure in an $((In_{1/k+1}Zn_{k/k+1})O^{1/(k+1)+})$ wurtzite-type structure matrix [10].

Many techniques have been employed to produce indium–zinc oxide thin films: rf-magnetron sputtering [11], dc-magnetron sputtering [12], pulsed laser deposition [13] and chemical vapor deposition [14]. The fabrication of indium–zinc oxide by ultrasonic spray pyrolysis methods, however, has not been extensively studied.

In this study, transparent conducting indium–zinc oxide thin films have been fabricated by ultrasonic spray pyrolysis methods. The electrical and optical properties of indium–zinc oxide thin films, with various atomic ratios of Zn/(Zn + In) (abbreviated to x), have been investigated.

2. Experimental

In_2O_3–ZnO thin films were deposited by an ultrasonic spray pyrolysis method. Indium nitrate trihydrate ($In(NO_3)_3{\cdot}3H_2O$) and zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) were used as starting materials and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) was a solvent. The In–Zn starting solutions corresponding to each x value (0.11, 0.33, 0.50, 0.60, 0.67, 0.80 and 0.89) were prepared. The concentration of the total of indium nitrate and zinc acetate was fixed at 0.05 M. A bare glass (Corning Inc. 1737) and oxygen were used as a substrate and a carrier and reaction gas.

As a preliminary experiment, the thin films were deposited in various deposition conditions: temperature, time, the distance between the nozzle and the substrate, and the oxygen flow rate. As a result of comparing films deposited in different conditions,

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the optimal deposition condition was determined to be 550 °C, 90 min, 35 mm and 600 cm^3/min, respectively. Thereafter, the thin films were fabricated in the optimal deposition conditions.

The thickness of In_2O_3–ZnO thin films was examined by an ellipsometer. The thicknesses of films deposited under various compositions ranged from 60 to 70 nm. The crystallinity of the films was analyzed by an X-ray diffractometer (XRD) with Cu Kα radiation. The surface morphology of the films was investigated by a scanning electron microscope (SEM). The carrier concentration, Hall mobility and electrical resistivity of the films were measured by the Hall effect measurement system using the four-probe van-der-Paw technique. Optical transmittance and reflectance measurements were performed using an ultraviolet visible near-infrared spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of In_2O_3–ZnO thin films as a function of the x ratio. The structure of the films varied from In_2O_3 phase to ZnO phase through the homologous phases of $Zn_kIn_2O_{k+3}$, as the x ratio increased. The pattern for $x = 0.11$ indicated that the film was polycrystalline In_2O_3. For $x = 0.33$, a mixture of In_2O_3 phase and the homologous phase of $Zn_kIn_2O_{k+3}$, corresponding to $k = 2$ [15], was observed. The film for $x = 0.5$ had only a (0 0 8) peak in the $Zn_2In_2O_5$ phase. The $Zn_kIn_2O_{k+3}$ phase corresponding to $k = 4$ [16] and 5 [17] were observed in the thin films for $x = 0.6$ and 0.67, respectively. For $x = 0.8$, the $Zn_5In_2O_7$ phase coexisted with the ZnO phase. A sole ZnO phase, however, was observed for $x = 0.89$. The films had a structure assignable to cubic In_2O_3 at low Zn levels and to hexagonal ZnO at high Zn levels. In addition, the sole homologous phase of $Zn_kIn_2O_{k+3}$ was obtained in the thin films with the Zn/(Zn + In) atomic ratio ranging from 0.5 to 0.67.

Variations of the carrier concentration, Hall mobility and the electrical resistivity of In_2O_3–ZnO thin films are plotted in Fig. 2 as parameters of the x ratio. The carrier concentration was decreased as the x ratio increased up to 0.33. As the zinc oxide was incorporated into the In_2O_3 host, the carrier concentration decreased by means of p-type doping. For $x = 0.5$, however, the carrier concentration increased because of the formation of a sole $Zn_2In_2O_5$ phase, in which conduction electrons originated from donor sites associated with oxygen vacancies [18]. The carrier concentration of the film for $x = 0.6$ increased to a value of 2.02×10^{19} cm^{-3}, which was the highest value in the $Zn_kIn_2O_{k+3}$ phase. On the other hand, as the Zn/(Zn + In) atomic ratio exceeded 0.6, the carrier concentration decreased. Such a decrease in the carrier concentration, with the increase of the k value, was also reported in bulk $Zn_kIn_2O_{k+3}$ [19].

Hall mobility is known to be mainly influenced by the change in the texture and the structure of film, while the carrier concentration is influenced mainly by oxygen vacancies [18]. Except for pure In_2O_3, as the x ratio increased from 0.11 to 0.33, the mobility decreased. This was probably due to an increase of scattering followed by a mixture of the In_2O_3-type structure and the $Zn_kIn_2O_{k+3}$ structure. For $x = 0.5$, the mobility was 15.89 cm^2/V s, which was the highest value. The mobility decreased as the x ratio increased from 0.5 to 0.67.

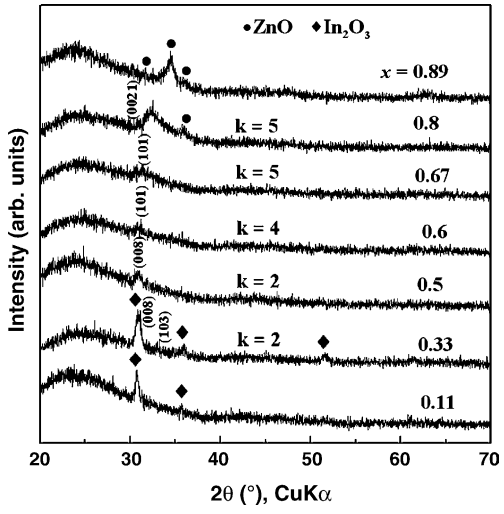

Fig. 1. XRD patterns of In_2O_3–ZnO thin films deposited at 550 °C for 90 min as a function of x: k represents the $Zn_kIn_2O_{k+3}$ phase that is observed at each x ratio. Miller indices of the $Zn_kIn_2O_{k+3}$ phases are marked. The symbols ♦ and ● indicates In_2O_3 phase and ZnO phase, respectively.

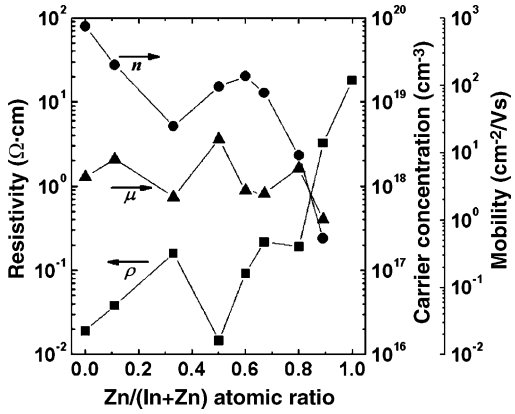

Fig. 2. Carrier concentration (●), Hall mobility (▲) and resistivity (■) as functions of the Zn content (Zn/(Zn + In)) of In_2O_3–ZnO thin films.

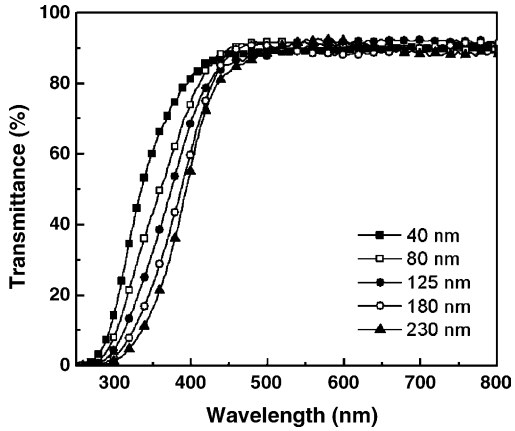

Fig. 3. Optical transmittance spectra of In_2O_3–ZnO ($x = 0.5$) thin films with the thickness variation.