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Preparation of In doped ZnO thin Films by MOCVD using Ultrasonic Nebulization

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In this work, In doped ZnO (IZO) thin films were deposited on soda lime glass substrates at 325 °C by metal-organic chemical vapor deposition (MOCVD) using ultrasonic nebulization and the effects of In doping concentration on the structural, electrical and optical properties of In doped ZnO films were investigated. As the source precursors zinc acetylacetonate and Indium acetylacetonate were used respectively. In doping enhanced the (002) preferred orientation and crystallinity of films. The resistivity of In doped ZnO thin film was decreased with the increase of doping ratio until 4 atom%. The lowest resistivity obtained in this experiment was about 4.5×10^{-3} Ω · cm. The average optical transmittance in the visible wave length range was over 80% for all the films regardless of doping concentration. Optical band gap of In doped ZnO thin films decreased with the increase of In doping concentration.

Key words: IZO, Transparent conducting oxide(TCO), Thin Films, MOCVD.

Introduction

Transparent conducting films with an optical transmittance exceeding 80% in the visible region and a low resistivity have been widely used in a variety of applications until now. [1] Indium tin oxide film 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. [2, 3] On the other hand, ZnO film has a lot of advantages, such as low cost, non-toxicity stability in H_2 plasma atmosphere with good electrical and optical properties. [4] The addition of impurities to ZnO flim induces dramatic changes in its electrical and optical properties. Doping of ZnO is achieved by replacing Zn2+ atoms with the atoms of elements of higher valency such as Al, In, Ga, and B. The efficiency of the dopant element depends on its electronegativity and the ionic radius. [5] Usually thin films of pure or doped ZnO are made by sputtering [6] and there are some reports on the deposition by ALD [7] or PLD [8]. However there are few reports on the deposition of ZnO thin films by chemical vapor deposition (CVD) which has many advantages such as high deposition rate, uniform deposition in large area, high step coverage, etc. This seems to be due to the rarity of zinc compound applicable to CVD source. Recently we have successfully deposited the thin films of pure ZnO by MOCVD taking advantage of ultrasonic nebulization technique in carrying the Zn source precursor.

In this work, we have investigated the effect of In doping ratio range (up to 10 atom%) on structural, optical and electrical properties of indium doped zinc oxide thin films deposited by MOCVD using ultrasonic nebulization.

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Experimental

IZO thin films were prepared on soda lime glass (L.C.D TEC) at the substrate temperature of 325 °C by MOCVD using ultrasonic nebulization. The details of this method were described in our previous paper [9] and the schematic diagram of the MOCVD apparatus used is shown in Fig. 1. The source solutions were made by dissolving all the precurors for each metal component in a solvent. As the solvent the mixture of 75 vol% buthanol and 25 vol% butylacetate was used. The source reagents for In and Zn were zinc acetylacetonate (Aldrich) and Indium acetylacetonate (Aldrich), respectively. The glass substrates were washed in acetone and

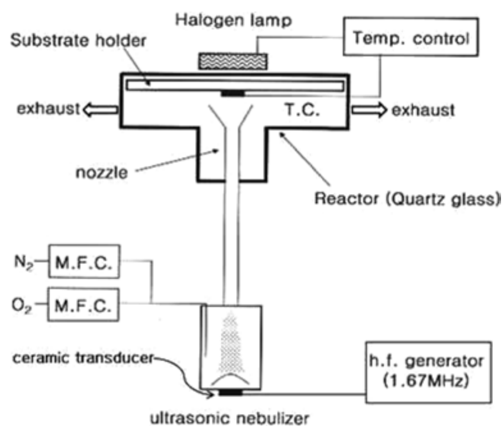

Fig. 1. Schematic diagram of MOCVD apparatus used in this experiment.

Table 1. Deposition conditions of In doped ZnO thin films.

Concentration of source solution	
Zinc acetylacetonate	0.19 ~ 0.2 M
Indium acetylacetonate	0 ~ 0.01 M
Deposition condition	
Substrate temperature	325 ^{o}C
N_2 gas flow rate	5l/min
O_2 gas flow rate	2l/min
Carrying rate of misted source solution	0.5 cc/min

methanol, and subsequently rinsed in distilled water and dried in flowing nitrogen. All the depositions were carried out at the atmospheric pressure. The deposition conditions are summarized in Table 1. The crystallographic and microstructural properties of films deposited were examined by X-ray diffraction (λ = 1.5418 Å, PANalytical, X`Pert PRO) and field emission scanning electron microscope (FE-SEM, Hitachi, S-4800). Electrical resistivity, charge carrier density and mobility of films were measured by Van der Pauw method (Ecopia, HMS-3000). The optical Transmittances were measured in the wavelength range of 200-800 nm by using UV/VIS/NIR Spectrophotometer (Agilent, Carry5000).

Results and discussion

Fig. 2 shows the X-ray diffraction (XRD) patterns of the In doped ZnO films with various In doping concentration. In all the films, intensity of (002) peak was much stronger than that of (101) peak which is the main peak of ZnO power diffraction. This indicated that the most of the crystallites became have [001] preferred orientation perpendicular to the substrate surface. According to the increase of indium doping concentration, the relative intensity (002) peak decreased and that of (101) peak increased. Similar behavior has been reported in many other works [11-13].

The (002) peak and (101) peak were shifted to lower values of 2θ with the increase of indium concentration. It is noted that the ionic radius of In^{3+} (0.81 Å) is larger than that of Zn^{2+} (0.74 Å). [14] Based on the Bragg's law, the Bragg angle shifts to lower angles, due to the larger lattice constant induced by In incorporation. The grain size of the films was calculated using the Debye-Scherrer formula. $D = (0.9)\lambda/(\beta\cos\theta)$, where D is diameter of the crystallites forming the film, λ is the wavelength of CuKα line, β is FWHM in radians and θ is the Bragg angle. Fig. 3 shows the variation of the grain size. It was found that the grain size decreased up to the Indium concentration of 6 atom%. This may be due to the fact that indium prevents the orderly arrangement and increases number of nucleation centers. However, at the In content of over 6 atom%, the grain size increased.

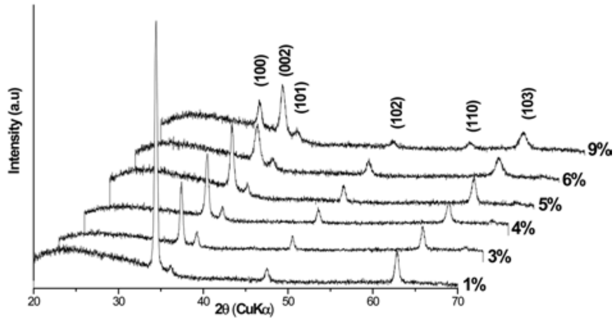

Fig. 2. X-ray diffraction patterns of the indium doped ZnO thin films with In doping concentration.

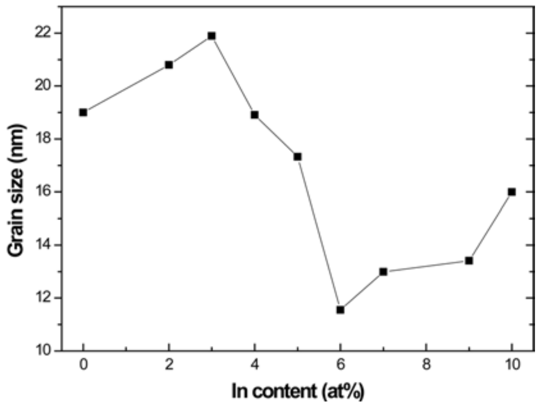

Fig. 3. Grain size for different indium doping concentration.

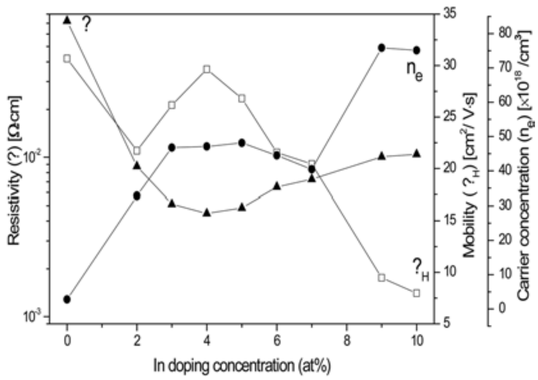

Fig. 4. FE-SEM micrographs of the surface and fractured cross-section of the IZO thin films with In doping concentration of (a) 1 atom%, (b) 4 atom%, (c) 6 atom% and (d) 9 atom%.

Fig. 4 shows the FE-SEM micrographs of the surface and fractured cross section of the IZO thin films with various doping concentration from 0 atom% to 10 atom%. It was reported that the textured morphology was a consequence of the nucleation of oriented c-axis grains that grew geometrically. When the doping concentration becomes over 2 atom%, the surface shows needlelike geometry up to 7 atom%. Kim et al. proposed that the IZO thin films deposited by RF magnetron sputter show the needlelike geometry. It is thought that the indium lies distributed randomly on the ZnO film, thus preventing an orderly arrangement. [15]

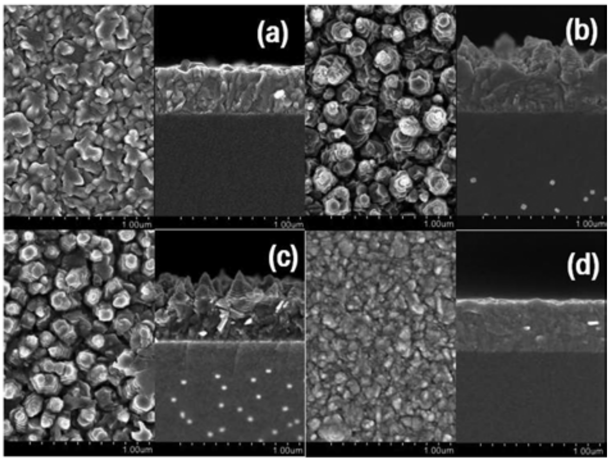

Fig. 5. Variation of resistivity, carrier concentration, and mobility as a function of In doping concentration.

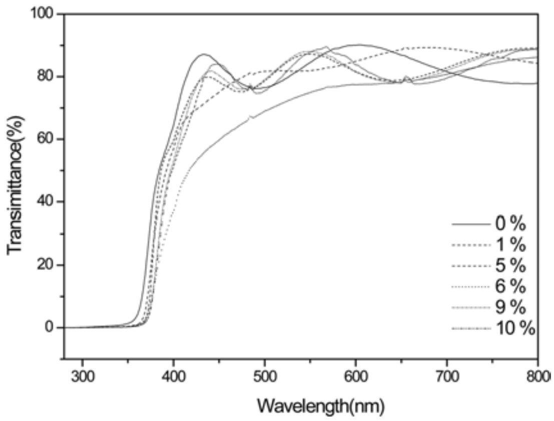

Fig. 6. Optical transmittance of the indium doped ZnO thin films with various In doping concentration.

Fig. 5 shows the dependence of the resistivity, carrier concentration, and mobility of IZO films on In doping concentration. The resistivity of pure ZnO film was about 0.1 Ω · cm. This resistivity might be due to the formation of metal rich films. The resistivity of IZO films decreased with the increase of doping concentrations up to 4 atom%. At the doping concentration of 4 atom%, the lowest resistivity of 4.5×10^{-3} Ω · cm was obtained. This decrease of resistivity was due to the increase of charge carrier concentration and mobility. The charge carrier concentration increased abruptly up to 3 atom% and then gradually increased. This increase of the carrier concentration was due to the substitutional incorporation of In^{3+} ions into the Zn^{2+}site [16] Thus, one free electron was produced by the replacement of one Zn atom. However, the resistivity of the IZO films gradually increased as In doping was further increased up to 10 atom%. The grain size was found to be decreasing with increase of doping concentration. Hence grain boundary scattering might have increased. The effect of grain boundary scattering would have dominated in the higher doping region leading to an increase in resistivity.

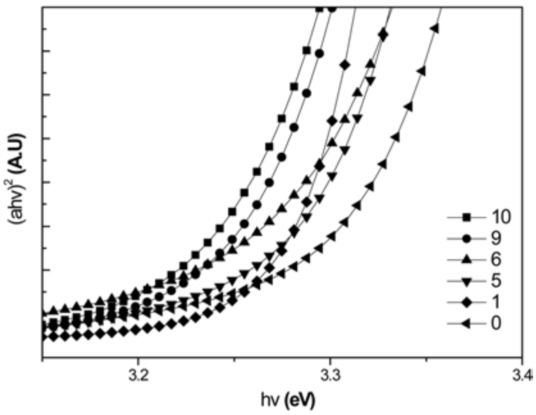

Fig. 7. Optical absorption plots of the Indium doped ZnO thin films with various In doping concentration.

Fig. 6 shows the optical transmittance spectra in the wavelength range of 300 ~ 800 nm at 325 ºC temperature of the IZO thin films with various In doping concentration. All the films were highly transparent and had the average transmittance of over 80% in the visible wave length range. The transmittance is found to decrease at high doping level. In transparent metal oxides, metal to oxygen ratio decided the percentage of transmittance. A metal rich film usually exhibited less transparency. Hence the decrease in optical transmittance in doped samples might be due to the increase in metal to oxygen ratio, (Zn + In)/O. The large decrease in transmittance in the infrared ray (IR) region might be due to the free-carrier absorption, since the doped sample were showing high electrical conductivity. Optical band gap of the IZO films was calculated using the Tauc's plot shown in Fig. 7. The band gap of undoped ZnO film was 3.28 eV. It has observed that the absorption edge slightly shifts to the shorter wavelength as doping level increase, This is mainly attributed to the Burstein-Moss effect. [17]

Conclusions

IZO thin films could be successfully deposited on glass substrate at 325 ºC by MOCVD using ultrasonic nebulization. As the doping concentration of In was increased, the [002] preferred orientation was decreased and the grain size of the films was decreased also. These resulted in the increase of mobility of charge carrier. Charge carrier concentration in the films increased largely up to the doping concentration of 9 atom% and then gradually. The lowest resistivity of indium doped ZnO thin film obtained in this research was 4.5×10^{-3} Ω · cm at the In doping concentration of 4 atom%. The average transmittance in the visible wave length range was over 80% for all the films. Optical band gap of IZO thin films decreased with the increase of Indium doping concentration.

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