JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 2, February 2008, p. 33 9 - 343

On the optical properties of heat-treated multilayered Zn/In thin films

G. G. RUSU, A. P. RÂMBU, M. RUSU*
"Al.I. Cuza" University, 11 Carol I Bd., 700506 Iasi, Romania

Zn/In multilayered thin films (d = 70 – 110 nm) were deposited in vacuum onto unheated glass substrates, by staked layer technique. Metallic Zn and In were evaporated from independent and separated between them sources, maintained at 723 K for Zn and 570 K for In, respectively, during deposition. After preparation, the samples were heat-treated by annealing in air with a rate of 12 K/min from room temperature to 550 K. The as deposited samples present a polycrystalline hexagonal Zn (002) textured structure. The heat-treatment determines the formation of the hexagonal ZnO structure with highly (002) oriented crystallites. The optical transmittance in the wavelength range 380-1400 nm of the treated samples is about 85%. The optical band gap for respective samples is 3.18 eV.

(Received September 25, 2007; accepted February 7, 2008)

Keywords: Multilayered film, Optical properties, XRD, SEM

1. Introduction

In the last years there is an increasing interest in the obtaining and study of the behavior of transparent conducting oxides (TCO) in thin films, due to their multiple applications in thin-film devices technology: transparent electrodes, gas sensors, photodiodes, wave guides, window materials for displays, solar cells, etc.[1-6]. Among other TCO thin films, the zinc oxide (ZnO) thin films are intensively studied because they exhibit attracting properties, such a good mechanical, chemical and thermal stability, high electrical conductivity, high optical transmittance in the visible spectral domain, it is inexpensive, highly resistant to deoxidation, etc. [1, 7-9]. These characteristics explain the large number of the applications of ZnO thin films. Moreover, by doping of ZnO films with different chemical elements, important changes of their electrical and optical properties, useful for improving of the device performance, can be obtained. Thus, by doping with 3rd group elements (Al, In, Ga, B, etc), on can prepare ZnO film having a lower electrical resistivity and a better optical transmittance in visible and near-infrared region in comparison with non-doped ZnO films [10-13]. A variety of techniques, including magnetron sputtering, spray pyrolysis, pulsed laser deposition, chemical vapor deposition, sol-gel, electrodeposition, etc, have been reported for preparing of doped ZnO thin films [10-17]. An important problem in obtaining the doped ZnO films is the control of the uniform doping of the film. A deposition technique that can assure a uniform doping of the films is the multi-staked layer (MSL) method.

In this paper, In-doped ZnO films are prepared by such method. A comparative study of electrical and optical properties of In-doped ZnO thin films (obtained by annealing of as-deposited Zn/In multi-layered thin films) and of non-doped ZnO thin films, (obtained by thermal oxidation of evaporated metallic Zn films) is presented.

2. Experimental

To obtain In doped ZnO thin films, multi-layered Zn/In were deposited onto unheated glass substrates in standard vacuum equipment (10^{-5} Torr) by MSL method. A schematic view of the used experimental set-up is shown in Fig. 1.

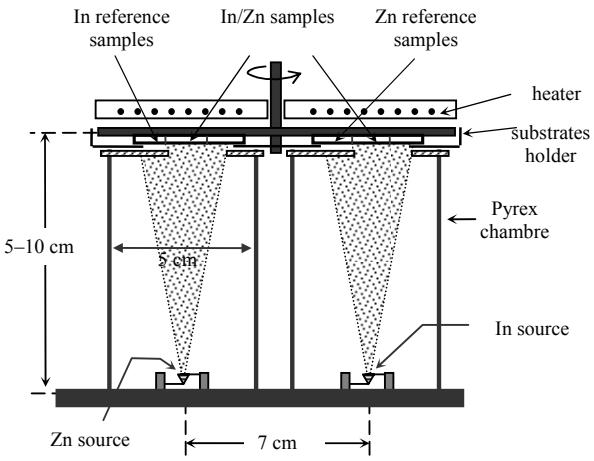

Fig. 1. Experimental set-up for the deposition of the Zn/In film

An aluminum disc with pits for the substrates is used as a substrate holder. A mask with an appropriate form, fixed over all substrates permits to prepare six identical samples simultaneously. Before or during film deposition, the substrate holder could be resistively heated via a special heater up to temperature of 700 K. The metallic Zn and In were evaporated from independent and separated between them sources, maintained during deposition at 723 K for Zn and 570 K for In. A set of vertical Pyrex tubes with different highs can be used to vary the evaporator-substrate distance and to close the space

between each source and substrate holder. During film deposition, the substrate holder can be rotated with constant rate ranged from 0 to 200 rpm, passing over the top opening of each cylinder. A special mask situated between substrate holder and cylindrical tubes permits to obtain separated Zn and In reference sample, simultaneously with Zn/In films. The thickness of the individual sub-layers of the deposited multi-layered system can be estimated by taking into account the rotating speed of the substrate, the deposition time and the thickness of the corresponding reference samples. By varying both the source temperatures and the rotating frequency of the substrate holder, multi-layered films with different structure and compositions can be obtained. The main advantage of this method is the possibility to assure the uniform doping and to control the sub-layer thickness of each component, hence the dopant content.

After deposition, the as-grown both Zn/In films and Zn reference samples were heat-treated under ambient atmosphere by annealing with rate of 12 K/min from room temperature to 550 K, followed by a cooling down to room temperature with the same rate.

The film thickness, d, measured with an interferometric microscope, ranged between 70 nm and 110 nm.

The surface morphology and the structural characteristics of the studied samples were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

The optical transmittance measurements, recorded in the 380-1400 nm wavelength range, corrected from the effect of the glass substrate, were used to calculate the absorption coefficient, α, and the optical energy band-gap, E_g.

3. Results and discussion

Figs. 2 and 3 show the typical diffraction patterns of as-deposited Zn reference sample and Zn/In multi-layered film, respectively, before and after their heating up to 550 K. As it results from Figs. 2a and 3a, the respective samples are polycrystalline with Zn wurtzite-type (hexagonal) structure [18]. It may be observe that the presence of In atoms in the Zn/In multi-layered sample influences the preferential orientation of the crystallographic planes. Whereas the Zn reference sample presents a crystalline structure like to those of bulk Zn, with a light (002) orientation of crystallites, the as-deposited Zn/In thin films present a strongly (002) orientation. The sharp diffraction peak at 2θ = 36.3º from Fig. 3a corresponds to the (002) plane of the hexagonal Zn structure and indicates that in respective film, the crystallites grow with their c-axis normally to the substrate. The calculated data, summarized in Table 1, confirm the above conclusion. In the table, the relative intensities, I_{hkl}, of different diffraction peaks for the two typical as-deposited samples (A1 and A2, respectively) normalized to the maximum line for each pattern are indicated. The standard intensity for Zn powder are also presented. The value of 100% for I_{002} corresponding to the single Zn peak from Fig. 3a, greater than the standard value of 53%, proves the strongly (002) orientation of as-deposited Zn/In films. The weak diffraction peak at 2θ = 33.1º, from the same figure, corresponds to the reflection on (101) plane of indium trigonal phase [19] and indicates the presence of In microcrystallites in respective sample.

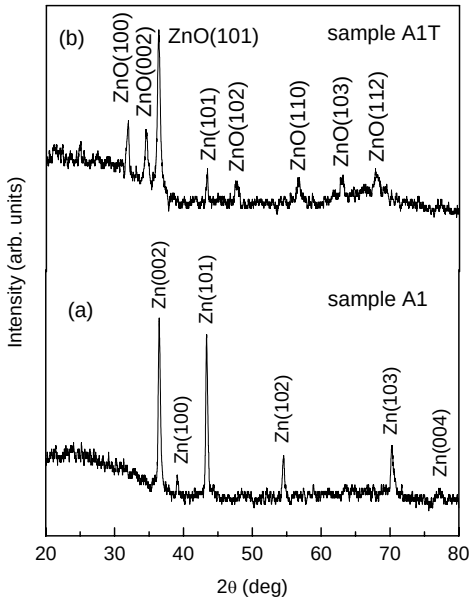

Fig. 2. The XRD patterns for evaporated reference Zn thin films: (a) as-deposited; (b) heated at 550K.

Table 1. Relative intensity, I_{hkl}, of XRD peaks for two typical as-deposited samples (the data for the A1 and A2 samples have been normalized relative to the maximum intensity peak for each pattern).

Sample	I_{hkl} (%)				
	(002)	(100)	(101)	(102)	(103)
A1 (as-deposited Zn reference sample)	100	14.2	95.2	28.5	31.4
A2 (as-deposited Zn/In)	100	–	–	–	–
Zn hexagonal phase [18]	53	40	100	28	25

The XRD patterns for the same two typical samples, recorded after their heating up to 550 K are presented in Figs. 2b and 3b.

The well defined diffraction peaks at 2θ = 31.9º, 34.4º, 36.3º, 47.6º, 56.6º and 67.8º from Fig. 2b, are characteristic for polycrystalline structure of bulk ZnO [20] and indicate the formation of respective compound. The additional peak at 2θ=43.2º in the same diffraction pattern corresponds to the reflection on (101) plane of hexagonal Zn structure and indicates that at heating temperature of 550 K the Zn oxidation process is not yet

finished. In the case of the Zn/In film heated up to the same temperature of 550 K, the respective XRD pattern presents only a single sharp diffraction peak at 2θ = 34.4º corresponding to the reflection on (002) plane of hexagonal ZnO structure (Fig. 3b). No diffraction peaks associates with metallic In, Zn or other compounds were observed. This shows that the respective film presents a single phase, with highly oriented ZnO crystallites with the (002) plane parallel to the substrate.

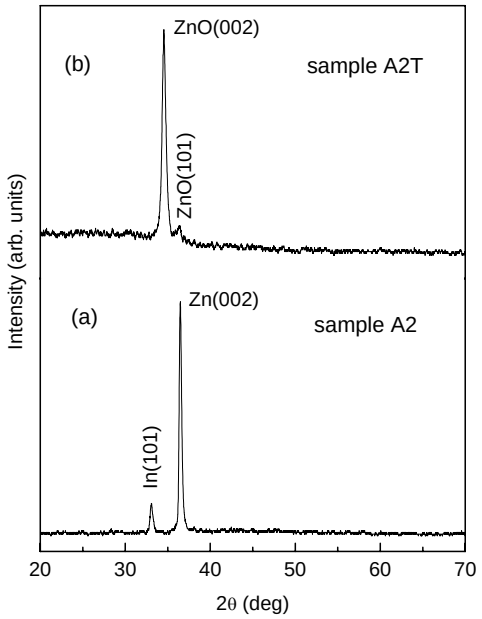

Fig. 3. The XRD patterns for multilayered Zn/In thin films: (a) as-deposited; (b) heated at 550 K.

The values of average grain size, D, calculated using Debye-Scherrer formula [21] relative to the main maxima of XRD patterns for ZnO films obtained both by thermal oxidation of evaporated Zn films (sample A1T) and by thermal oxidation of Zn/In multi-layered films (sample A2T) are indicate in Table 2.

Table 2. Some physical parameters of the typical studied samples: D – average crystallite size; σ_c – electrical conductivity at room temperature; E_g – optical band gap.

Sample	D (nm)	σ_c ($\Omega^{-1}m^{-1}$)	E_g (eV)
A1T (ZnO) (A1 sample heat-treated)	13.6	$2.6x10^{-1}$	1.19
A2T (ZnO) (A2 sample heat-treated)	13.2	$1.8x10^{2}$	1.18

The relative lower values of grain size obtained for both heat-treated typical samples indicate that these films are characterized by a nanocrystalline structure and that the indium atoms influence only the growth orientation of the ZnO crystallites but not their sizes.

A typical SEM image of surface morphology for the heat-treated Zn/In thin films is presented in Fig. 4. The presence of the ZnO grain with nano-whisker shapes can be observed on the film surface. Similar grain shapes was reported by K. Sreenivas et al [22] for post-deposition annealing at 300-400 ºC of multilayered ZnO/Zn/ZnO structure.

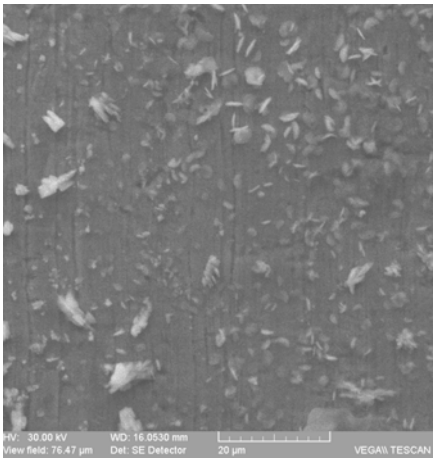

Fig. 4. Surface morphology of the heat-treated Zn/In films (sample A2T) as revealed by SEM

It is well known that the doping with group III donor elements such as Al, B, Ga, In, determines an important improvement of the electrical properties of ZnO films [11-13, 23, 24]. In order to investigate this effect of the donor dopant in the case of our heat-treated Zn/In films, the comparative measurements regarding the temperature dependence of the electrical conductivity, σ, for the two typical studied samples were performed, using surface type cells. In Fig. 5, the obtained results are presented.

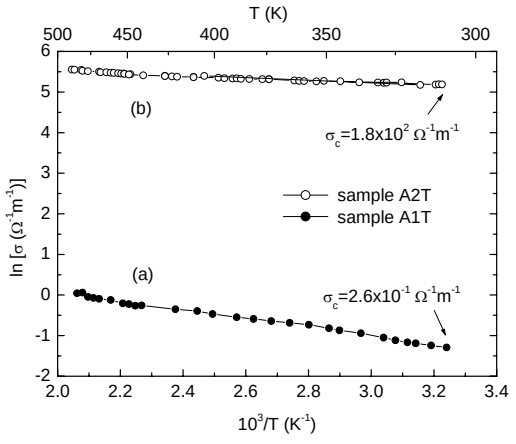

Fig. 5. Typical temperature dependence of electrical conductivity: (a) ZnO thin film obtained by thermal oxidation of Zn film; (b) ZnO thin film obtained by heat-treating Zn/In multilayered thin film.

As it can be observed, the electrical conductivity of ZnO films obtained by thermal oxidation of as-deposited Zn/In multi-layered films is about three orders of magnitude higher than that of the ZnO films obtained by thermal oxidation of evaporated Zn sample. This increase in conductivity can be attributed to the increase of free carrier concentration as consequence of In doping. A decrease of resistivity by Al doping of ZnO films grown by spray-pyrolysis was also reported by A.El Manouni et al. [13] and was attributed to the increase of carrier concentration as a result of electrons coming from the donor Al^{3+} ions incorporated as substitutional ions in Zn^{2+} cation sites or as interstitial positions [13, 23]. The same explanation can be valuable in the case of our results, the role of Al^{3+} donors being taken by In^{3+} donors.

Fig. 6 shows optical transmittance spectra at room temperature for studied un-doped and In doped ZnO films. It can be seen that ZnO sample (A2T) prepared by thermal oxidation of Zn/In multi-layered films are characterized by a sharp absorption edge and a constant higher transmittance values in the all wavelength range 400-1400 nm, whereas the un-doped ZnO sample (A1T) presents a broadening in the absorption edge. The increasing in transmittance for sample A2T can be correlated with their better crystallinity and greater electrical conductivity in comparation with those of sample A1T as it results from Fig. 3b and 5. This assumption is in concordance with the results reported by K. Ramamoorthy et al. [25] which revealed that the deposited by pulsed laser deposition ZnO films with textured better aligned microstructure have superior transmission to randomly oriented and an improved electrical conductivity.

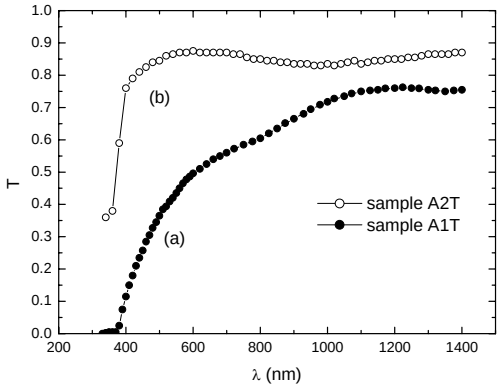

Fig. 6. Typical transmission spectra for studied films: (a) ZnO thin film obtained by thermal oxidation of Zn film; (b) ZnO thin film obtained by heat-treating Zn/In multilayered thin film.

From the optical transmittance spectra, the optical band gaps, E_g , for the heat treated typical samples (A1T and A2T, respectively) were estimated by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ *vs* $h\nu$ to α=0 (Figs. 7, 8). We have found no net increase of the band gap due to In doping. Both the typical samples are characterized by the about the same values of the E_g, around 3.2 eV. These values are lower than the usually 3.3 eV for ZnO thin films and can be attributed to the greater density of donor states near the conduction band determined by the oxygen vacancies and the indium doping [15].

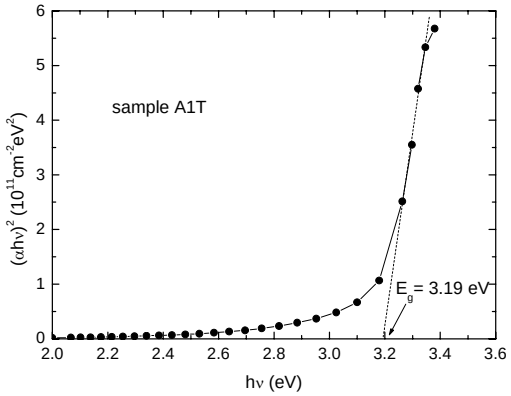

Fig. 7. The dependence $(\alpha h\nu)^2 = f(h\nu)$ for ZnO thin film obtained by thermal oxidation of Zn film.

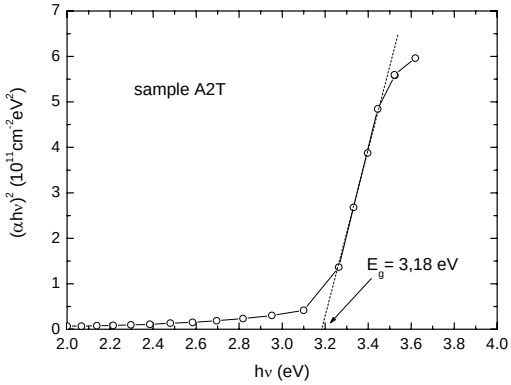

Fig. 8. The dependence $(\alpha h\nu)^2 = f(h\nu)$ for ZnO thin film obtained by heat-treatment of the Zn/In multilayered thin film

A value of around 3.2 eV for optical band gap of annealed ZnO films, deposited at 350ºC on fused quartz by metal-organic chemical vapor deposition, was also reported by S.T. Tan et al. [26].

4. Conclusions

A comparative study of some electrical and optical properties both of In doped and non-doped ZnO samples was performed. The ZnO doped samples were obtained by heating in air up to 550 K of the evaporated multilayered Zn/In thin films. The non-doped ZnO samples were obtained by heating in air up to 550 K of the evaporated metallic Zn thin films.

The XRD studies revealed that the non-doped ZnO films present a polycrystalline hexagonal structure whereas those In doped sown a (002) preferred orientation

with c-axis normal to the substrate. The average crystallite size for both typical films is of about 13 nm.

The electrical conductivity at room temperature of the In-doped ZnO samples is about 1.8×10^{2} $\Omega^{-1}m^{-1}$, greater than about 2.6×10^{-1} $\Omega^{-1}m^{-1}$ for non-doped ZnO samples.

The values of the band-gap evaluated from $(\alpha h\nu)^2 = f(h\nu)$ dependence in the region of the fundamental absorption edge both for non-doped and In doped ZnO films are of about 3.2 eV.

The obtained results revealed that the multi-staked method used for preparation of Zn/In thin films and the post- deposition heat-treatment of such structures can be a promising method to obtain ZnO transparent conducting thin films for different technological applications.

Acknowledgements

Part of this work is part of the researches of the Grant CEEX 89/2006, CNCSIS, Romania and under financial support of this.

We wish to thank to A.V. Sandu for the SEM micrographs.

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*Corresponding author: mirusu@uaic.ro