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Fabrication, structural and optical characterization of In doped ZnO thin films prepared by the colloidal method

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Abstract:

Regarding to the excellent conductivity and high transparency in the visible range, the zinc oxide (ZnO) films have been widely used as transparent electrodes in optoelectronic devices, ZnO is a direct wide band-gap (3.37 eV) semiconductor. The conductivity of ZnO will be largely enhanced by doping little In, but it still keeps high transparency. So, IZO film has been widely investigated and is considered to be a promising possible alternative to ITO films.

This work consist to the fabrication and characterization of ZnO:In thin films. The sample preparation was carried out by the colloidal method. The pure and In doped ZnO thin films were deposited using a dip-coating technique on glass matrix. The optimal condition for samples fabrication has been investigated. The XRD and Raman characterizations show that the ZnO thin film crystallize with a wurtzite structure. The optical properties of ZnO thin films doped In reveal that doping changes the optical gap of ZnO.

Keywords: *ZnO thin films; Indium doping; XRD and Raman characterizations.*

1. Introduction

ZnO is a n-type compound semiconductor with a large exciton binding energy of 60 meV at room temperature and a wide direct band gap of 3.37eV, and high transmission in the visible range, which provides it the potential application in various optoelectronic applications such as optical sensors and light emitters, etc... [1,2]. During the last years, in ordre to enrich the potential application in devices ZnO has been doped with many different kinds of elements, such as Al, Ga, In, and Sb to enhance the optical/electrical properties [3-5].

In our work, we fabricated two In-doped ZnO samples, which are 0,5 and 1% IZO. Their structures were characterized in this paper. Raman scattering measurements were designed to obtain more detailed information of the structures in In-doped ZnO nanomaterials.

2. Experimental

To prepare a ZnO solution, 1.5g of zinc acetate dihydrate ($Zn(CH_3COO)_2 \, 2H_2O$) was dissolved in 30 ml of absolute ethanol at room temperature. When the solution turned milky, an equimolar amount of MEA was added drop by drop to obtain a clear and transparent solution after stirring at 60°C for 1h. The solutions were deposited by dip coating method on glass substrate. The obtained films were preheated at 100°C for 10min and the heat treatment was carried out at 500°C for 2h.

The crystal structure and phase of the samples were characterized by X-ray diffraction technique using Bruker AXS D8 Discover diffractometer, $CuK\alpha_1$ (λ=1.54056 A°), where the angle ranges within 20°-80°. Raman scattering experiments was performed at room temperature using a Raman spectroscope meter (???????????????) with the ???? nm line. The films transmittance was recorded by Shimadzu 3600 PC double beam UV-VIS-NIR spectrometer.

3. Results and discussion

3.1. Structural analysis

The figure 1 shows the X- rays diffraction pattern of two samples (0,5 and 1% Indium doped zinc oxide), and are vertically normalized for clarity.

The comparison of the observed XRD patterns with the standard JCPDS data N° 36-1451 confirms the formation of crystallites of nanometer size and hexagonal (wurtzite) [6]. No extra peak is noted in Fig. 1, suggesting no secondary phase in wurtzite ZnO.

The all investigated films have adopted a preferred orientation along the direction [002], which indicates that the films have the preferred orientation with the c-axis normal to the substrate. the Bragg position of (002) is at 34.54°, 34.3° for 0.5% and 1% indium doped ZnO respectively, and then a slight angle shift was carefully detected. Others reflection positions (2θ) and their angle shifts are listed in table1.

These results are in well agreement with those of literature [7].

It is also found that the peak (0 0 2) is less intense and sharper for 1% In, suggesting that In doping ≥1% can reduce the crystal quality, which means that the crystal quality had been improved to a certain extent.

The grain size G is given by the well-known Scherrer's formula [8],

$$G = (0.94\lambda) / (\beta.\cos\theta) \quad (1)$$

Where β is the full width at half medium of the peak, 2θ is the Bragg angle and λ is X- rays wavelength. The calculated values of G are listed in table1.

Consequently, according to all orientations, indium doping reduces the grain size. Since the radius of In^{3+} ion (0.092 nm) is larger than Zn^{2+} ion (0.083 nm) [9], the indium atoms occupying positions in ZnO lattice lead the expansion of the lattice.

Fig. 2 shows the Raman spectra of In-doped ZnO (0,5 and 1%). No Raman Peak of In2O3 appeared in the spectra of the In-doped ZnO, indicating no secondary phase in In-doped samples, which is consistent with the XRD results.

Figure 1. X-rays pattern of indium doped ZnO (0.5 and 1%), grown by dip coating process within 20°-80°.

Table 1. X-rays results of pure and indium doped ZnO

(hkl)		Bragg angle 2θ(°)	Angle Shift $\Delta 2\theta$	Grain size (nm)
(100)	ZnO pur	31,79	-	-
	0,5% In	31,81	+0,014	11,37
	1% In	31,69	-0,106	9,7285
(002)	ZnO pur	34,45	-	-
	0,5% In	34,54	+ 0,09	15,69
	1% In	34,3	- 0,15	12,46
(101)	ZnO pur	36,288	-	-
	0,5% In	36,37	+0,082	14,35
	1% In	36,19	-0,098	12,14

The wurtzite ZnO (space group C^4_{6v}) has six first-order optical modes, which are E_2^{low} , E_2^{high}, A_1(TO), A_1(LO), E_1(TO), and E_1(LO) [10].The two intensive peaks at 99 cm^{-1} and 437,5 cm^{-1} are indicated to be E_2^{low} and E_2^{high},which are the characteristic bands of the wurtzite ZnO, and the peaks at 380 and 579 cm^{-1} are known to be A_1(TO) and A_1(LO),which are also the first-order optical modes of wurtzite ZnO.

The peak observed at 332 cm^{-1} is attributed to $E_2^{high}-E_2^{low}$, which are second order features caused by multi-phonon processes [11].

The board band at 980–1465 cm^{-1} is conjectured to be associated with intrinsic lattice defects and often arise by the doping [12].

The shift of the E2 mode can give the information on stress. Previous investigations have shown the relation between stress and E_2(high) mode: under a compressive stress the

E_2(high) up shifts, where as a tensile stress will lead to its downshift [13]. Compared to the E_2(high) mode of the standard ZnO (437 cm^{-1}), a up shift of 0,5 cm^{-1} was observed for the E_2(high) mode of the two ZnO:In films. This shift indicates that a slight compressive stress existed in the In doped ZnO films. This shows that doping In atoms into a ZnO films will cause its compressive lattice distortion.

3.2. Optical characterization

Transmission spectra for indium doped ZnO thin films are shown in Fig.3a. The average optical transparency is higher than 90% in the visible region (400–700nm) of spectrum for all the films, which gives the thin ZnO films the character of transparency in the visible region and makes this material a potential candidate for optoelectronic applications.

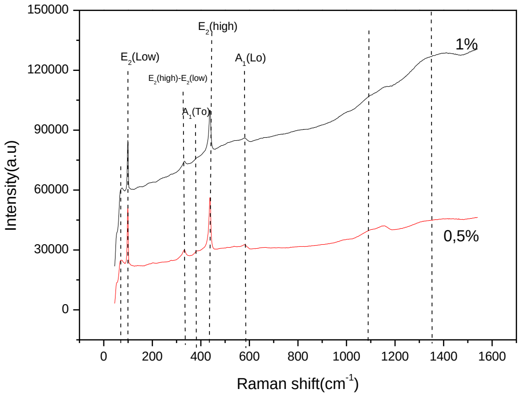

Fig 2. Raman spectra of two samples of In-doped ZnO (0,5 and 1%).

Compared to pure ZnO film, the UV absorption edge is blue-shifted for IZO film, indicating broadening of the optical band gap due to In doping. In general, a blue shift of the absorption edge is associated with an increase in the concentration of carriers blocking the lowest states in the conduction band, known as the Burstein–Moss effect [14]. In doping increases the Fermi level of the films into the conduction band, making the films completely degenerate, which shifts the absorption edge to energies higher than the actual band gap of the material.

For direct-transition semiconductors, the optical band- gap Eg can be calculated according to :

$$(\alpha h\nu)^2 = D(h\nu - Eg)^{1/2} \qquad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy and D is a constant [15,16]. We assume that $\alpha=(1/d)\ \ln(1/T)$, where d is the film thickness and T is the transmittance.

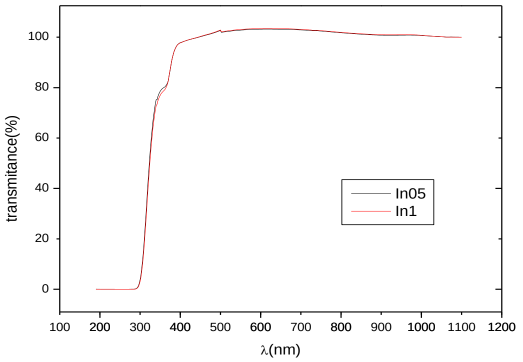

Fig-3.a: transmittance of In doped ZnO (0.5% and1%) and pure ZnO.

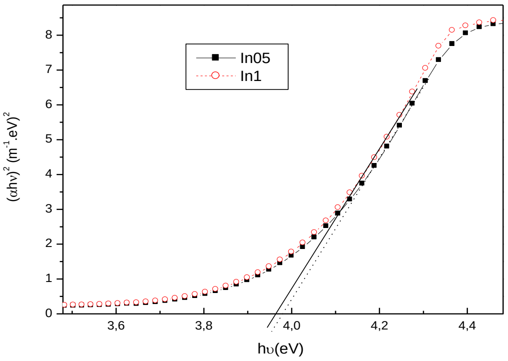

Fig-3.b: UV-visble spectroscopy of In doped ZnO (0.5 and 1%)

A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 3b. Eg can be determined by extrapolation to the energy axis at $(\alpha h\nu)^2=0$. We obtained Eg values of 3.97 and 3.96 eV for 0,5% and 1% indium doped ZnO thin film; these values are greater than Eg for pure ZnO thin film (3.37 eV).

In figure 3b, it can be seen that the influence of the concentration of Indium on the gap is weak.

This observation is similar to this of Ayouchi et al. [17], who had obtained values of Eg higher than those of stoichiometric massive ZnO and thus observed a decrease of Eg. This phenomenon was attributed to the reduced grains size in the thin layers of ZnO prepared and to the oxygen deficiency.

4. Conclusion

Indium doped ZnO thin films were prepared on glass matrix by colloidal method, with different concentrations. The XRD spectrum of the all thin films have a crystalline structure with the preferential orientation of (0 0 2). The raman spectroscopy result is consistent with the XRD one. UV-visible spectroscopy shows that the In changes the optical gap of ZnO (shift of optical gap to higher energies (blue shift)).

The results obtained by different characterization reveal that the introduced of Indium as a dopant for different ratio (0.5, 1%), who is an isoelectonic with ZnO, have not make a free electron. This results indicated that Indium has formed a composite ZnO/In.

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