Spin coated ($M_x, Zn_{1-x}O$), $M= Sn, Al$ nanofibers investigation

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Abstract. ($M_x, Zn_{1-x}O$), $M= Sn, Al$ nanofibers properties were investigated. Pure and M-doped zinc oxide films were fabricated onto a glass substrate by a facile and low cost spin coating route. X-rays analysis reveals that films crystallize with a wurtzite structure according to (002) orientation. The transmittance in the visible range was as high as 88 % at 550 nm. The doping increased slightly the transmittance, the as-grown films were high transparent in VIS and IR ranges. The optical band gap was a little bit changed by doping. AFM 3D-views revealed that grains were nanofibers with the size of 18.22, 18.23 and 44.27 nm respectively for pure, Al and Sn-doped ZnO films.

1 Introduction

ZnO is among a huge variety of transparent conducting oxides (TCO) which attract many researchers, due to the interesting properties such as a transparency in visible spectrum. ZnO is a wide band gap n -type semiconductor, $E_g=3.3$ eV at room temperature, with hexagonal wurtzite structure, and a large exciton binding energy of 60 meV [1-3]. In order to improve the physical properties of ZnO, many elements such as aluminum (Al), tin (Sn), indium (In) and fluorine (F) and many others have been used as dopants [1-5]. The synthesis of nanostructures has been of growing interest owing to their promising application in nanoscale optoelectronic devices, like the next generation solar cells [6-7]. The morphology of ZnO has been demonstrated to be the richest among inorganic semiconductors, and the electrical and optical properties depend considerably on both the morphology and size. In the present work we have studied the effect of cationic substitution of Zn sites by aluminum (Al) and tin (Sn), based on a purely valence considerations. Further, we report the crystalline structure, surface morphology, optical and photoluminescence properties of pure, Al and Sn-doped ZnO films grown by spin coating route and the nanofibers fabrication.

2 Experimental procedures

The films of pure, aluminum and tin doped ZnO were deposited using a sol gel spin coating process onto a glass substrate as shown in figures 1 and 2. 0.5 Molar of dihydrated zinc acetate is dissolved in an appropriate amount of 10 ml of 2-methoxyethanol. Thorough mixing is done using a magnetic stirrer for 10 min at 60°C, and the dopants aluminum nitrate nona-hydrate, Tin (II) chloride dihydrate were added, with some addition of mono-ethanolamine (MEA) as stabilizer, until the homogeneous and clear solution is obtained, then the stirring continued for 1 hour, and followed by an ageing process of 24 h. The doping ratio Al/Zn, Sn/Zn is fixed at 2 and 3% in the solution. The samples were placed onto a spin coater and rotated for one minute at chuck rotation rate of 1000 rpm (rotate per minute). After this, the sample is heated at 150 °C for 10 min. The process is repeating 5

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times and finally the films were annealed at the temperature of 400 °C for 1 h under air. Thereby, the physical properties were investigated by X-ray diffractometer, spectrophotometer and AFM microscope analysis. The photoluminescence analysis at room temperature measurements was carried out in an experimental setup consisting of a 325 nm, 15 mW He–Cd laser (Kimmon type), a 0.85 m double monochromator (SPEX, model 1404), and a GaAs photon counting photomultiplier (Hamamatsu). The selected wavelength band was of 350- 600 nm, in steps of 0.5 nm and at a speed of 0.2 s per measured point.

Fig.1. The flow chart for the preparation of sol-gel derived ZnO films

3 Results and discussions

3.1. Structural properties study

A representative X-rays diffraction pattern of our coated samples is depicted in Fig. 3. The XRD spectra indicate that all the diffraction peaks in the pattern are easily assigned to pure hexagonal phase ZnO which is known as wurtzite type with a space group of $P6_3mc$, and the lattice parameters of $a=3.247 \text{ \AA}$, $c=5.201 \text{ \AA}$. This result is in agreement with the reported standard card of JCPDS N° 36-1451. XRD pattern indicates that the ZnO film has a polycrystalline structure. A (002)-oriented hexagonal crystalline structure was confirmed by X-ray patterns. The most important orientations observed for our spin coated films are (100) (peak a), (002) (peak b) and (101) (peak c) as seen in figure 3, these orientations have been reported previously [1-2]. It is remarked that doping improves the crystalline structure and the peaks a, b and c are obviously observed specially in 3 and 2% Sn and Al-doped samples. These orientations are peaked at 31.78° , 34.44° and 36.24° as reported in previous work [1]. Similar results have been reported in literature for thin films and nanostructures [8-9]. In summary, the doping improve the main reflections, while broad and less strong peaks located within the 2θ range 44° - 69° are observed in doped-ZnO films. These peaks are attributed to the (102), (110), (103) and (112) orientations with a small angle shift due to the incorporation of cations in the host material. These obtained values are in well agreement of those found in literature [10].

Fig.2. A plot of spin coater Set up

Fig. 3. X-rays patterns of pure and M-doped ZnO films prepared by sol-gel spin coating at 1000rpm(top). Pure ZnO XRD analysis Red dash line locates the peak (002) at 34.42 °(JCPDS :36-1451) (bottom).

3.2. Surface morphology investigation

Atomic force microscope images are depicted in figure 4. AFM images reveal that grains were nanofibers. As indicated in micrographs, the doping increases the nanofibers size. The measured size of nanofibers assigned by red arrow in AFM images are 156, 347, 208, 190, 1000 nm respectively as listed in table 1. Nanofibers are so smooth and doping change the roughness (RMS) as indicated in table 1. Based on X-ray pattern, ZnO films are preferentially oriented along the c-axis. This latter, is the (002) plane of ZnO which possesses a minimum surface energy. This result is in well agreement with AFM observations. As seen in figure 4, red arrow demonstrates the fiber growth along the c-axis. Yaakob et al. have succeeded the ZnO nanofibers fabrication by electrospun method [11].

208 nm

Fig.4. AFM 3D-views of pure and M-doped ZnO films. The grain size is indicated on the nanofiber (right) and measured size is shown by two red arrows in the image (left)

3.3. UV-VIS-IR spectrophotometer study

The transmittance in the visible range was as high as 86 % at 550 nm. However, the films are high transparent in VIS and IR ranges. Both the pure and doped ZnO films exhibit a drastic increase of

transmittance in UV spectrum and attain a maximum as indicated by an arrow in figure 5 (UV band-down). A slight increase is observed in VIS-IR bands. At the IR band edge, the transmittance of as-grown films is the highest (>90%) as sketched in IR band in figure 5 (down). Sn and Al ions decrease a little the optical property in visible range of the as-synthesized ZnO films. It is also reported that ZnO film presented a high transmittance around 83% [12].

Fig. 5. Transmittance dependence on photon wavelength of pure and M-doped ZnO films (up), UV, VIS and IR bands are sketched (down).

The optical band gap E_g (eV) is systematically deduced from the following expression,

$$(\alpha h\nu)^2 = h\nu - E_g \quad (1)$$

Where α is the absorption coefficient, h is Planck's constant, ν is the photon frequency, E_g is the band gap energy. The direct energy gap of the coated films has been calculated by extrapolating the linear part of $(\alpha h\nu)^2$ plot as a function of the photon energy to the energy axis as shown in figure 6. As can be observed from the recorded data in table 1 ZnO film reveals a wide band gap (E_g) of 3.74 eV, while E_g decreases slightly with doping level. This result agrees with transmittance spectra.

Table 1. Optical band gap, high transmittance in visible range, RMS and grain size.

Material	T (550nm) (%)	Band gap (eV)	RMS (nm)	Grain size (nm)
ZnO	86.44	3.74	25	156
2% Al: ZnO	85.58	3.72	52	347
3% Al: ZnO	81.55	3.65	61	208
2% Sn: ZnO	84.31	3.67	45	190
3% Sn: ZnO	84.54	3.56	35	1000

Fig. 6. Plot of $(\alpha h\nu)^2$ against photon energy of pure and M-doped ZnO films, E_g is determined by extrapolation.

3.4. Photoluminescence investigation

The photoluminescence (PL) of as-deposited films at room temperature is sketched in figure 7. Doping affects the photoluminescence intensity as seen in figure 7. Except weak UV emission for the Sn-doped ZnO no emission, originating from the near-band edge, was detected. While some PL emissions are revealed in visible band, among them we can observe the strong and narrow violet and yellow emissions (442 and 588 nm) respectively. Probably, both the preferential orientation and abundant grain boundaries in the as- grown ZnO film might cause the presence of the violet emission at 442 nm. The similar violet peaks have been detected by Liang et al. [13]. In addition, the cause of

yellow emission in the range 570–610 nm in ZnO was due to extrinsic impurity or defects, some authors found the same behavior for Si-doped ZnO films [14]. Furthermore, lesser emission peaks are respectively blue emission (501 and 508 nm) and green emission (533 and 538 nm). The green peaks ~ 538 nm presence is due to the concentration of defects responsible of deep level in ZnO as-grown films as reported in literature [13]. The calculated energy (eV) of these PL peaks (A, B, C, D, E and F), by using $1240/\lambda$ (nm), is 2.81, 2.47, 2.44, 2.32, 2.30 and 2.1 eV respectively. No significant peak shift is observed but an important decrease in PL emission intensity, caused by doping level, is revealed particularly within the range 450–525 nm as indicated in fig 7a and 7b. It is noted that PL emissions reveal crystalline structure and presence of defects and anion vacancies in the lattice. However, blue emission correspond to surface defects in samples, green peaks might ascribe to oxygen vacancies.

Fig.7. Photoluminescence plot of pure and M-doped ZnO films. Gaussian deconvolution is shown (orange curves) (up). A plot of PL in restricted range of wavelength of 450–525 nm is sketched figures a and b (down).

Conclusion

In summary, nanofibers of pure and M-doped ZnO films are successfully synthesized by spin coating route @ 1000 rpm. A (002)-oriented hexagonal crystal structure was confirmed by X-ray patterns. Additionally, X-ray pattern reveals that the nanofibers are preferentially growing along the c-axis orientation, which is in agreement with AFM views. ZnO nanofibers are wide band gaps > 3 eV. A PL investigation reveals a strong VIS emission and a weak UV emission. By PL spectra, nanofibers present a strong violet (~440 nm) and yellow (~588 nm) emissions, defects and vacancies presence is indicated. Owing these promising qualities, ZnO films are considered as the ideal materials for the

microelectronic devices fabrication, such as the short-wavelength optoelectronic devices like UV and visible lasers, violet and yellow light-emitting diodes and photoconductive detectors.

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