Influence of Synthesis Conditions and Al doping, on structural and optical properties of ZnO:SnO$_2$ thin film

S. Benkara, N. Seghairi, S. Bouabida and H. Ghamri

Laboratory of Active Components and Materials,
Larbi Ben M'hidi University, Oum El Bouaghi, Algeria

sali_benkara@yahoo.fr

Abstract— **Zn/Sn nanocomposite deposited on glace substrate by sol gel dip-coating technic, using Zinc acetate and tin chloride as precursors and aluminium chloride as dopping source, absolute ethanol and monoethanolamine (MEA) were used as the solvent and stabilizer, respectively. The quantity of tin in the solution was 0; 25; and 40 at.% Sn, and of aluminium was 0; 0,5; 2; and 4 at.% Al. The films are deposited at two dipping speeds: 100 mm/min and 50 mm/min, and used two dipping cycles: 10 and 5.**

The structure, optical properties and morphology of nanofilms and the influence of experimental parameters as withdrawal speed and dipping cycles on deposition of ZnO films were studied using X-Ray Diffraction (XRD), UV–vis spectroscopy and optical microscope. The crystalline phase determination from XRD confirmed that the films are composed of hexagonal wurtzite ZnO and tetragonal rutile SnO$_2$ without compound impurities. The doping and dipping speed and cycles effect on optical bandgap is estimated by transmittance spectra.

I. INTRODUCTION

Coupling two semiconductors with different band gap widths have attracted considerable attention, because this way allows to assemble the best properties of the two oxides and obtain unique properties not exixted in single semiconductor.

ZnO-based composites have shown excellent optoelectronic properties due to the electronic coupling between ZnO and other oxide phases [1-3]. ZnO-SnO$_2$ nanocomposite has been widely studied. J.-C. Li et al. [4] have obseved in their ZnO-SnO$_2$ nanocomposite an enhancement in the conductivity, A. Hamrouni et al. [5] found that the photoefficiency of the ZnO–SnO$_2$ samples was superior to that of pure ZnO or SnO$_2$. Highly transparent ZnO–SnO$_2$ thin films were prepared by team of D.Y. Torres Martínez et al. [6] and shown an improuvement in photocatalytic activity.

To obtain high quality ZnO-SnO$_2$ nanocomposite films, a various synthesis can be used as Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD) [7] and magnetron sputtering [8], these methods require sophisticated and expensive equipment; very high vacuum, high temperature, etc. Sol- gel technic has been successfully used in preparation of thin flms, given its advantages as simplicity, safety, low cost of the apparatus, easily control, which the films thickness can be easily controlled by number of coating layers [9].

This paper demonstrates the preparation of ZnO-SnO nanocomposite films doped with aluminuim varied at 0.5 at%, 2.0 at% and 4 at% by sol gel dip coating. The effect of Al doping concentrations, withdrawal speed and number of dipping on the crystallinity, surface morphology, optical, and transparency of deposited Al doped ZnO-SnO$_2$ thin films have been studied in detail.

II. EXPERIMENTAL DETAILS

Tree solutions were prepered by sol gel dip coating method. Solution 1 present by Al-doped ZnO thin films was obtained by mixing Zinc acetate (Zn (CH$_3$COO)$_2$) and aluminium chloride (AlCl$_3$), using 1 and 3 % Al-doping concentration, were dissolved in a mixture of ethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate was maintained at 1.0 and the concentration of zinc acetate was 0.1 M. The solutions was stirred at 60°C for 2 h to yield a clear and homogeneous solution.

The synthesis of the ZnO–SnO$_2$ (Solution 2) represented in adding a 0.1 M ethanol solution of $Zn(CH_3COO)_2 \cdot 2H_2O$, previously prepared at 60 °C under vigorous stirring, to solution of $SnCl_2 \cdot 2H_2O$. The amount of $SnCl_2 \cdot 2H_2O$ solution was opportunely determined in order to obtain thin films with molar ratio ZnO/SnO$_2$ equal to 1/0.25 and 1/0.4.

Solution 3 obatained from solution 2 which doped by 2% Al. Then the same conditions are followed.

Prior to deposition, glass substrates were cleaned with acetone, ethanol, and distilled water. The substrates were dipped into the prepared solutions and withdrawn at a constant speed of 100 and, 50 mm/min, respectively.

After each dip-coating process, all films were pre-heated at 200 °C for 10 min in a furnace prior to evaporating the solvent and organic residuals. To obtain the desired film thickness, this coating/drying procedure was repeated for ten and five times and finally the resulting thin films were annealed at 500 °C in air for 1 h.

The X Ray Diffraction curvs were obtained with X Ray diffractometer (ARL) Equinox 100, using Cu K_α radiation (Cu K_α = 0.15406). The UV measurements were carried out at room temperature using Jasko V-750 visible spectrophotometer (JASCO International Co. Ltd., Tokyo, Japan). Morphological structure of the samples were obtained using Optical Microscope (OM) euromex CMEX5000 (ME2660 and 2665).

S. BENKARA is with Electrical Engineering Department, Larbi Ben M'hidi University, Oum El Bouaghi, Algeria. And Laboratory of Active Components and Materials, Larbi Ben M'hidi University, Oum El Bouaghi, Algeria; (e-mail: sali_benkara@yahoo.fr).

N. Seghairi, was with Physic Department, Larbi Ben M'hidi University, Oum El Bouaghi (e-mail: nassima.seghairi@yahoo.fr).

S. Bouabida is with Electrical Engineering Department, Larbi Ben M'hidi University, Oum El Bouaghi (e-mail: bouabida.seddik@univ-oeb.dz).

H. Ghamri is with Physic Department, Hadj Lakhdar University, Batna1, Batna, Algeria; (e-mail: ghamri_houda@yahoo.fr).

III. RESULTS AND DISCUSION

XRD patterns of the undoped, Al-doped ZnO and Al doped Zn/Sn films are shown in Figure 1. Diffraction peaks are observed at 31.8°, 34.5°, 36.0°, and 56.5° in the undoped and Al-doped ZnO films (figure 1(a) and (b)), which can be indexed as diffractions of (100), (002), (101), and (110) planes of wurtzite structured ZnO.
while in the figure 1 (c), the peaks can be indexed as a mixture of the hexagonal wurtzite ZnO and tetragonal rutile SnO_2 according to standard SnO_2 cards.
It can be observed in curvs of doped ZnO, the intensity of (0 0 2) increases which confirmed the improvement in preferential orientation growth along (0 0 2) direction.
ZnO phase peaks are clearly sharp and intense due to its lower crystallization temperature than SnO_2. [10,11]

The average grain sizes of the various samples were determined by using the diffraction peaks (0 0 2) for ZnO and (1 1 0) for SnO_2. The valeus obtained of undoped ZnO, 2% Al doped ZnO and 2% Al doped Zn/Sn are respectively: 21.66 nm; 19.74 nm and 15,43 nm.

The crystallinity degree of the films decreased with dopping and much more for nanocomposite Al doped Zn/Sn. This is in agreement twith previous results obtained for coupled ZnO/SnO_2 [12,13].
In most studies, the mean sizes of ZnO and SnO_2 were larger in the single oxides than in the mixed ZnO–SnO_2 samples. Mixing two different oxides usually limits the growth of both. [12,14]
The addition of SnO_2 caused a reduction of the main crystallite size of ZnO according to results obtained in literature [12,14, 15].

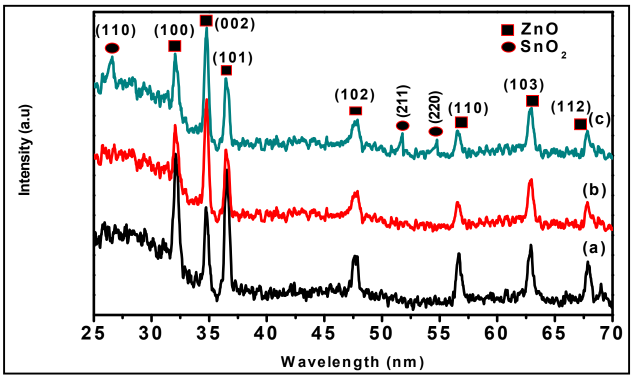

Figure 1. XRD patterns of (a) undoped ZnO; (b) 2% Al doped ZnO; (c) 2% Al doped Sn/Zn nanocomposite.

The optical transmission of Al doped Zn/Sn prepared with different doping percentage of Al are plotted in figure 2. The films show transmittance more than 95% in the visible region. It can be seen from these curves that the increase in the aluminum content decreases the transmission in the visible range.

The decrease in transmission at higher doping concentrations of Al can be attributed to the increased scattering of photons by crystal defects created by doping. [16,17].

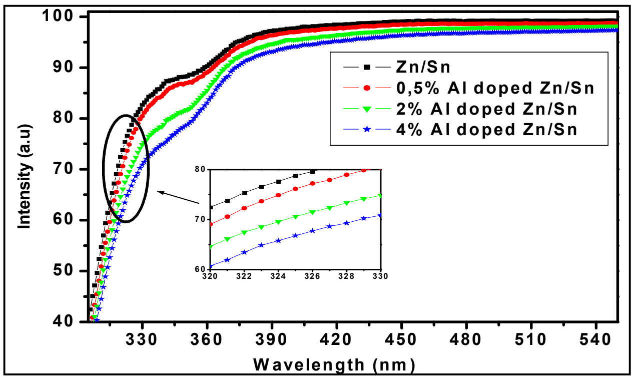

Figure 2. Transmittance curvs of Sn/Zn nanocomposite at different Al concentration.

Optical gap (Eg) is determined by tansmittance derivative and calculates from the following relationship: [18]

$$E_g = \frac{1243}{\lambda_{max}}$$

Where λ_{max} corresponds to the maximum value of the derivative.
The values of the band-gap energy with different doping concentrations are shown in figure 3.

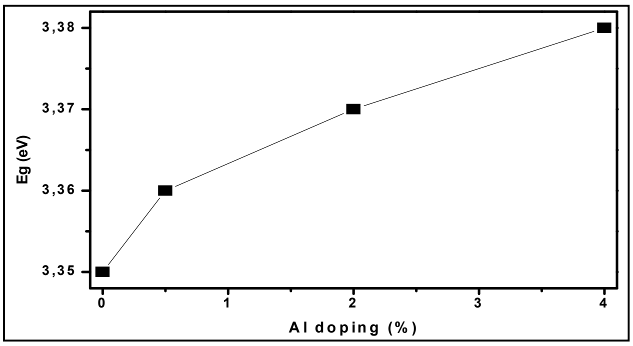

Figure 3. Eg variation versus the Al-doping concentration.

Fig. 4 shows spectra transmittance of Zn/Sn nanocomposite (40% Sn) deposited at dip-coating speed of 100 and 50 mm/min.

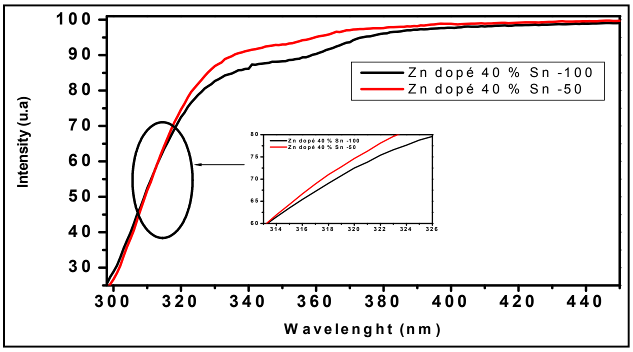

Figure 4. Transmittance curv of Sn(40%)/ ZnO nanocomposite at different dip-coating speeds

The films were transparent with an average optical transmittance greater than 95% in the visible spectral region.

The maximum transmittance is correspond to lower withdrawl speed (50 mm/min). Acording to S.M. Salaken et al. [19], the decrease in transmittance may be due to the increase in diffusion caused by the increase in grain boundary density in porous films.

Similarly, using the above formula, we determined the values of optical gap Zn/Sn layers prepared at the different withdrawal rates, we find 3,35 eV and 3,34 eV respectively correspond to the speed 100 and 50 mm/min. Eg values increase with the speed, the same behavior is seen by S. Aydemir. [20].

Fig. 5 shows the transmittance spectra of Zn/Sn nanocomposite (25% Sn) prepared at different number of dipping: 5 and 10. The film with 5 cycles shows higher transmittance reaches 95% at 380 nm wave length. From these spectra, it is obvious that the transparency varies with the thickness of thin layers which is controlled by the number and time of dipping.

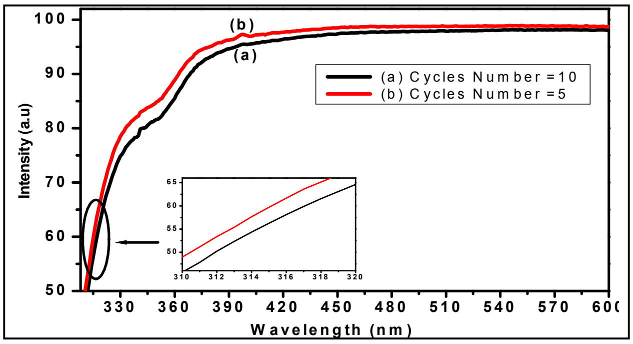

Figure 5. Transmittance curv of Sn(25%)/2% Al doped ZnO nanocomposite at different dipping cycles.

Fig. 6 shows the optical microscope images of Sn(40%)/ZnO nanocomposite deposited at different dipcoating speed.

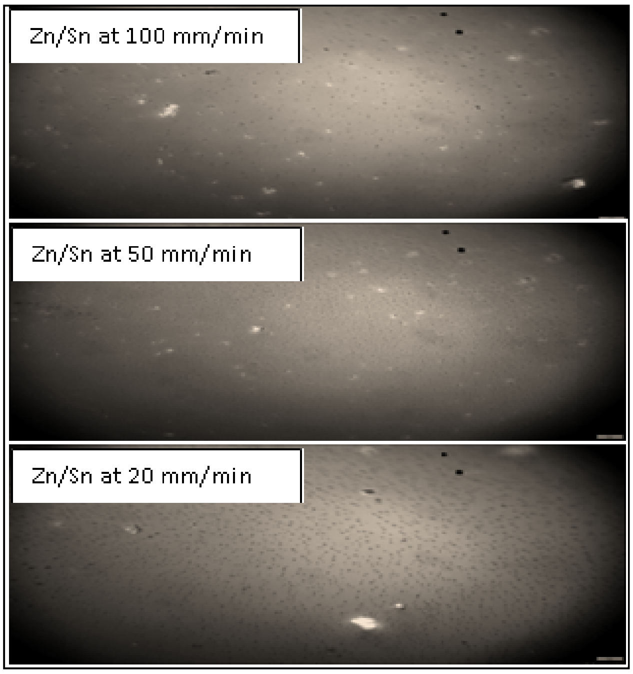

Figure 6. OM images of Sn(40%) doped ZnO nanocomposite at different dip coating speed.

These images revealed that the surface of all samples is homogeneous, and contains pores.

IV. CONCLUSION

Al-doped ZnO and Al doped Zn/Sn films are prepared by sol–gel dip coating technique at varying doping concentration, withdrawal speed of substrate and dipping cycles.

The films were dipped five and ten times, withdrawn at speeds of 100 and 50 mm/min and calcined at 500 °C in air for 1 hour.

The films were found to be highly c-axis oriented. The transmittance was decreased in the visible region with increase of Al doping and withdrawal speed. The decrease in transmission at higher doping concentrations of Al can be attributed to the increase in diffusion caused by the increase in grain boundary density in porous films.

The influence of Al doping and experimental parameters represented by dip-coating speed and dipping cycles on *Eg* was investigated. Their values were about 3.35–3.38 eV as Al dopant varied from 0,0 % to 4 % , and Eg decreased from 3,35 eV to 3,34 eV at withdrawal speed of 100 and 50 mm/min, respectively.

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