SYNTHESIS OF Al-doped ZnO NANOSTRUCTURED FILMS BY SCS METHOD

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***Abstract**: Nanostructured films of ZnO and Al-doped ZnO have been deposited using a successive chemical solution (SCS) method. The as-deposited nanostructured films were subjected to photothermal annealing at the temperature of 300℃ for 5 minutes. The morphological, structural, vibrational and chemical proprieties were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), micro-Raman spectroscopy and EDX techniques. Dopant incorporation was demonstrated by the EDX measurements of Al-doped ZnO nanostructured films.*

***Keywords:** ZnO, Nanostructures, Chemical synthesis, Oxides.*

1. Introduction

We are in a threshold of new era of materials, nano and micro semiconducting materials, which have attracted a great deal of attention for their nano-size dependent proprieties and wide range of applications.

ZnO is one of the most interesting semiconducting materials. It has the band gap energy of 3.37 eV at room temperature, a large free-exciton binding energy 60 meV and potential applications in chemical sensors, heterojunction solar cells, conductive transparent conductors and many others. Undoped ZnO films show n-type electrical conductivity and have poor stability in humid environment or corrosive medium and proprieties are altered by adsorption of O_2, CO_2 and water. ZnO have high transparency in the visible and near-ultraviolet spectral regions, wide conductivity range and conductivity changes under photoreduction/oxidation condition. Defects, that can be produced by doping of the sensing ZnO thin films with impurities such as Al, increase influence of nocive gases on the sensor conductivity. Therefore polycrystalline ZnO films have been doped with group III metal ions such as Al by several techniques for synthesis from aqueous solution, and in particular the successive chemical solution method [1,2].

The successive chemical solution method is known to be a simple, low temperature and inexpensive large-area deposition technique. SCS emerging as a possible alternative to the sol-gel or chemical vapor deposition (CVD) techniques in vacuum. In this work, we described nanostructured films of ZnO and Al-doped ZnO deposited using SCS method.

2. Experimental

2.1 Successive chemical solution growth of nanostructured films of Al- doped ZnO

The glass substrate were cleaned in HCl solution for 10 min, rinsed in deionized (DI) water, cleaned in H_2SO_4 solution for 10 min, rinsed in DI water, cleaned in HNO_3 solution for 10 min, rinsed in DI water and dried in a stream of hot air. The aqueous zinc complex solution comprises a mixture of zinc sulfate $(Zn(SO_4)\cdot 7H_2O)$, aluminum sulfate $(Al_2(SO_4)_3\cdot 18H_2O)$ and sodium hydroxide $(NaOH)$ mixed until complete dissolution. The concentration of the complex solution was diluted to obtain 0.05 – 0.15 M zinc concentration for deposition by adding respective quantities of deionized (DI) water [2]. The Al doping of ZnO nanostructured films was achieved by adding $Al_2(SO_4)_3\cdot 18H_2O$ in the aqueous solution. The SCS technique is based on the adsorption and reaction of the zinc complex ions from the aqueous solution, which were kept at room temperature. The immersion of the wet substrate in the anions solution kept at 95 – 98 ℃ during deposition. The 100 deposition cycles were performed. The duration of the each immersion procedure was above 5 s. The as-deposited ZnO nanostructured film were dried in air at 150 ℃ for 5 min. Finally, films were subjected to photothermal annealing at the temperatures 300 ℃ for 5 min.

2.2 Characterization

The samples of Al-doped ZnO films were analyzed by X-ray diffraction (XRD) using a Rigaky "DB/MAX" powder diffractometer with a nickel-filtered CuKα radiation source (λ = 1.54178 ?) and a

scanning rate of 0.05 $^{\circ}$ /s in the 2θ range from 10 to 90 $^{\circ}$. The compositional analysis of Al- doped ZnO nanostructured films was carried out using energy-dispersive X-ray spectroscopy (EDX), in combination with SEM. The different characterization techniques confirmed that the nanostructured films are crystalline.

Information on vibrational modes in pure and Al-doped ZnO nanostructured films was obtained from Raman backscattering experiments in a micro-Raman set Horiba Jobin Yvon LabRam IR spectrometer with a charge-coupled detector (CCD). This system has a spatial resolution of 2 μm . Raman spectra were excited with 1.96 eV photons form a Helium Neon lase ($\lambda \sim 633\ nm$) with less than 4 mW of power at the sample.

3. Results and discussions

3.1 Morphological Characterization

Duration of substrate immersion in chemical solutions and the number of successive dipping steps in aqueous solution bath are the important growth parameters to tune SCS nanostructured film's morphology and proprieties [1]. Figure 1 shows SEM images of undoped ZnO (a) and 0.3at%Al-doped ZnO (b) nanostructured films on glass substrate. Morphology of nanostructures was found to be influenced by doping with Al.

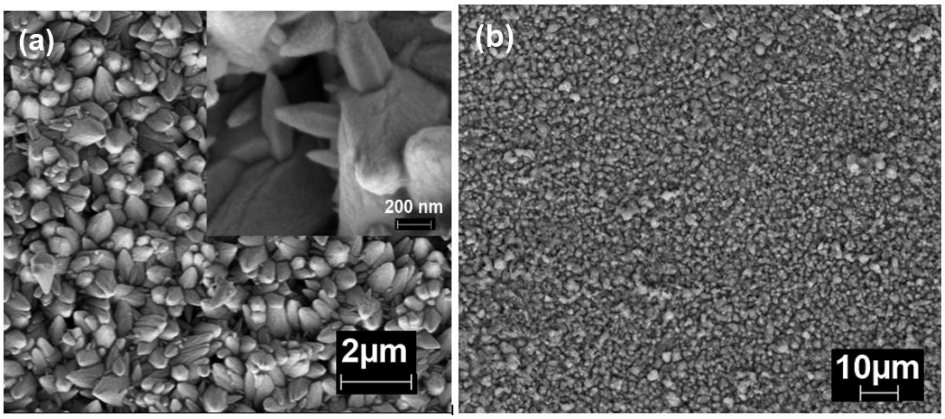

Fig. 1 SEM images of: (a) undoped as-grown nanostructured ZnO film after photothermal annealing 300°C , 5 min; (b) as-grown 0.3at%Al-doped ZnO after photothermal annealing 300°C , 5 min.

3.2 Chemical characterization

Figure 2 shows the EDX spectrum of undoped and 0.3at%Al-doped ZnO nanostructured films. It can be distinguished Zn, O peaks from the ZnO nanostructured film, and Zn, O, Al peaks from 0.3at%Al-doped ZnO nanostructured film, also it can be seen peaks of S and Cl. The O:Zn ratio was found to be 48.6:51.4 atomic ratio in pure ZnO thin film. Al content in as-grown zinc oxide thin films was found about 0.3at%.

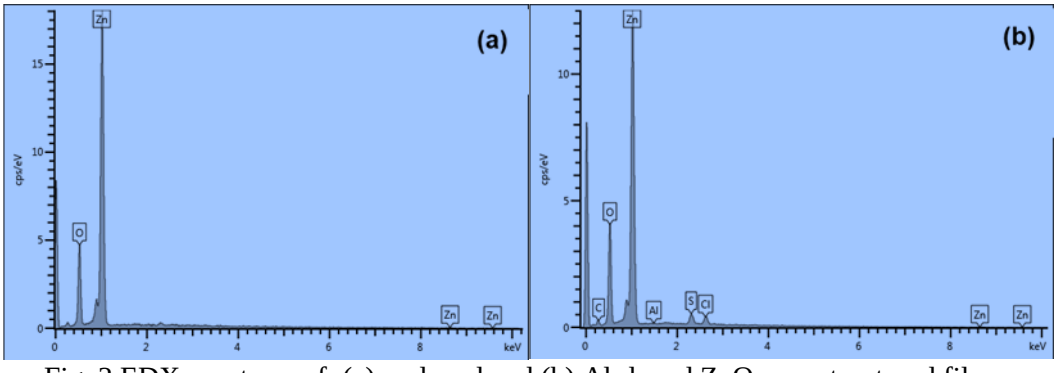

Fig. 2 EDX spectrum of: (a) undoped and (b) Al-doped ZnO nanostructured films.

3.3 Structural analysis

Figure 3(a) and (b) shows the XRD patterns of pure and 0.3at%Al-doped ZnO films recorded in range of 10-90 $^{\circ}$ with scanning step of 0.05 $^{\circ}/s$. The diffraction peaks in the pattern can be indexed to hexagonal Wurtzite structured ZnO [space group: $P6_3mc(186)$: $a = 0.3249\ nm$, $c = 0.5206\ nm$]. The data are in

agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036-1451).

In Figure 3 (a) the strongest detected *(hkl)* peaks are at 2θ values which correspond to the following lattice planes: (100), (002), (101), (102), (110) and (103), respectively. In Figure 3 (b) for 0.3at%Al-doped ZnO nanostructured film was observed that diffraction peak for (100) direction was increased in comparison to (002) peak from pure ZnO sample.

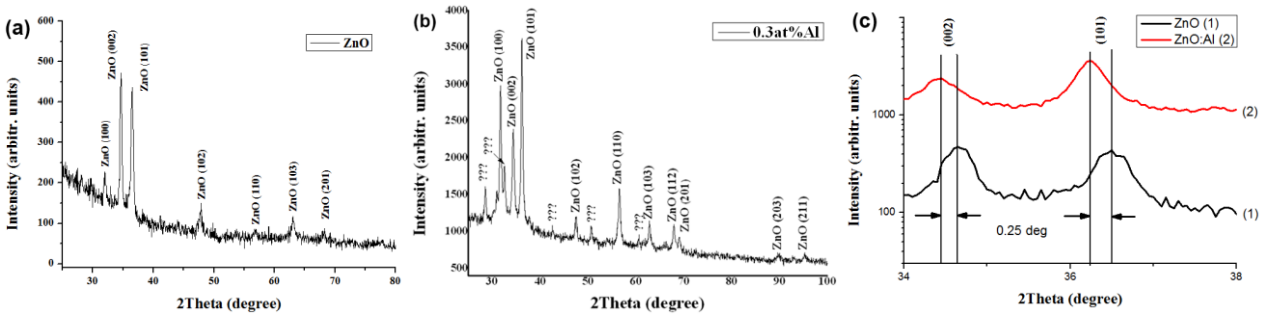

Figure 3. XRD patterns of the ZnO nanostructured films: (a) undoped as-grown film; (b) as grown 0.3at%Al-doped ZnO; (c) comparison of (002) and (101) peaks before and after annealing with Al.

To study the effect of doping of the ZnO nanostructured films, the intensity of the (002) and (101) diffraction peaks of Al-doped and pure ZnO films was monitored (Figure 3c). In Figure 3(c) we observed a small shift (0.25°) of 2θ angle value of the XRD diffraction peaks. The intensity of the diffraction peaks (002) is decreased for 0.3at% Al-doped films, and their full width at half-maximum (fwhm) increased (Table 1). Such changes in crystallinity might be the result of changes in the atomic environment due to Al-doping of ZnO thin films. The ionic radii of Al and Zn are $r(Al^{3+})$) 0.067 nm and $r(Zn^{2+})$) 0.074 nm, respectively. A lattice deformation was caused due to differences in ionic radii.

Table 1. Parameters obtained for the (002) and (101) diffraction peaks

sample	description	(hkl) planes	2θ (deg)	[fwhm] (deg)
#1	ZnO	(002) (101)	34.65 36.5	0.392 0.443
#2	0.3at%Al	(002) (101)	34.4 36.25	0.515 0.386

The lattice constants *a* and *c* of wurtzite structure ZnO were calculated. For the (100) orientation at , the lattice constant *a* was calculated by [3]:

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \tag{1}$$

and for the (002) orientation at , the lattice constant c was calculated by [3]:

$$c = \frac{\lambda}{\sin\theta} \tag{2}$$

The lattice constants a and *c* were determined a $= 3.585$ Å , $c = 5.736$ Å for pure ZnO, and $a = 3.606$ Å , $c = 5.768$ Å for Al-doped ZnO.

3.4 Micro Raman Scattering

In order to investigate the influence of Al-doping of ZnO films on the Raman scattering, room temperature micro-Raman spectra of samples were explored. ZnO with a wurtzite structure belongs to the C_{6v}^4 ($P6_3mc$) space group, and there are 12 degrees of freedom since there are 4 atoms per primitive cell.

Therefore, there are 9 optical phonon modes (LO) and six transverse-optical (TO) branches, one longitudinal-acoustic (LA), and two transvers-acoustic (TA) [4].

Figure 4 shown Micro-Raman spectra of 0.3at%Al-doped ZnO nanostructured films. These measurements where performed at room temperature over the frequency range from 10 to 800 cm^{-1}. Dominant peaks at 99 and 437 cm^{-1} are attributed to the low- and high-E_2 mode (E_2^L and E_2^H) of nonpolar optical phonons, peaks at 330 cm^{-1} is attributed to second order Raman processes involving acoustic phonons [5], and at 381 cm^{-1} is attributed to A_1 (TO) mode. Figure 4b show the Raman mapping of the samples for a defined area. When the range from 430 to 440 cm^{-1} which is centered at 435 cm^{-1} is scanned, the dark and bright parts represent the minimum and maximum intensities of this peak, respectively.

Gas sensing studies were performed in order to find selectivity to H_2 gas of Al-doping of ZnO films.

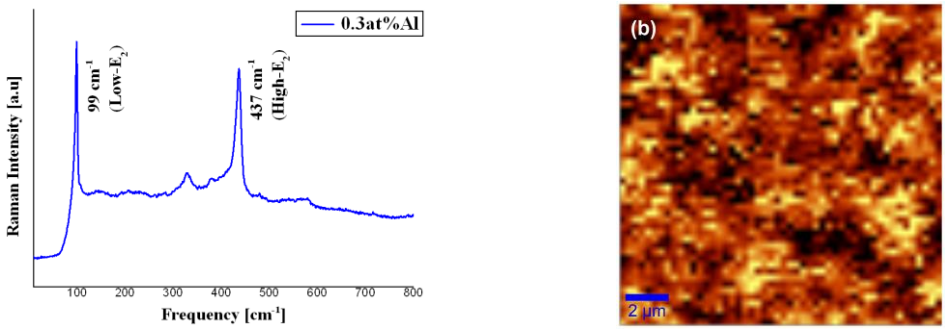

Fig. 4 (a) Micro-Raman scattering spectra of the Al-doped ZnO nanostructured film, excitation wavelength is 532 nm; (b) Micro-Raman mapping of of the sample (E_2high mode).

4. Conclusions

In summary, ZnO and Al-doped ZnO nanostructured film were grown on glass substrate using a SCS method. According to XRD results, the as-grown ZnO and Al-doped film has a (002)-preferred orientation. It suggests that the film is aligned with the *c*-axis oriented perpendicularly to the glass substrate. Also were observed a small shift (0.25°) of 2θ angle value of the XRD diffraction peaks. The lattice constants a and c were determined a $= 3.585\,\text{Å}$, $c = 5.736\,\text{Å}$ for pure ZnO, and $a = 3.606\,\text{Å}$, $c = 5.768\,\text{Å}$ for 0.3at%Al-doped ZnO. From Micro-Raman spectra was observed dominant peaks at 99 and 437 cm^{-1} that are attributed to the low- and high-E_2 mode (E_2^L and E_2^H) of nonpolar optical phonons.

Acknowledgements

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References:

1. O. Lupan, L. Chow, S. Shishiyanu, E. Monaico, T. Shishiyanu, V. Şontea, B. Roldan Cuenya , A. Naitabdy, S. Park, A. Schulte *Nanostructured zinc oxide films synthetized by succesive chemical solution deposition for gas sensor application s* Materials Research Bulletin 44 (2009) 63 - 69.
2. O. Lupan, S. Shishiyanu, V. Ursaki, H. Khallaf, L. Chow, T. Shishiyanu, V. Şontea, E. Monaico, S. Railean *Synthesis of nanostructured Al-doped zinc oxyde films on Si for solar cells applications* Solar Energy Materials & Solar Cells 93 (2009) 1417 - 1422
3. O. Lupan, L. Chow, L. K. Ono, B. R. Cuenya, G. Chai, H. Khallaf, S. Park, A. Schulte *Synthesis and Characterization of Ag- or Sb-Doped ZnO Nanorods by a Facile Hydrothermal Route* J. Phys. chem. C 2010, 114, 12401-12408
4. Arguello, C. A.; Rousseau, D. L.; Porto, S. P. S. *Phys. Rev.* 1969,
5. M. Rajalakshmi, A.K. Arora, B.S. Bendre, S. Mahamuni, J. Appl. Phys. 87 (2000) 2445.