Study of nanostructured ZnO thin films prepared by sol-gel spin-coating technique

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INTRODUCTION

ZnO is a semiconductor material, with a direct wide band gap of 3.37 eV and a large excitonic binding energie (60 meV). It is an important functional oxide, exhibiting near-UV emission and visible light transparency which makes it a suitable material in photonic applications. It is a piezo-electric, which is a key advantage in electro-mechanical coupled sensors and transducers. In this project ZnO and ZnO:Al thin films were obtained by spin-coating on amorphous SiO2 substrata, being structurally characterized by Glancing Incidence X-ray Diffraction (GIXRD), X-ray Reflectivity (XRR), Grazing-Incidence Small-Angle X-ray Scattering (GISAXS), Atomic-Force Microcopy (AFM) and Field-Effect Scanning Electron Microscopy (FESEM).

EXPERIMENT

Nanocrystalline pure and Al doped zinc oxide films have been obtained by sol-gel process using two different ZnO precursors solution (S and X), as it was described in a previous work [1]. In the case of the doped films, aluminium nitrate nanohydrate was added to solution X (solution Xd) in the atomic ratio of Al/Zn = 5 %. The precursor solutions were deposited by spin-coating technique at 3000 rpm for 10 s on amorphous SiO_2 substrates and dried at 200 ^oC for 10 min. The procedure was so repeated to get n-layers films. Then, the pre-baked films were annealed at 450 ^oC for 3 hs for crystallization. Sample microstructure was studied first by X-ray diffraction (XRD) using a PW 3710 Philips diffractometer with Cu-K_α radiation, operated with glancing angle geometry. The general aspect of the films was characterized by Atomic Force Microscopy (AFM) and by Field Effect Scanning Electron Microscopy (FESEM).

GISAXS and XRR experiments have been performed to study the films structure. Synchrotron XRR and GISAXS experiments were carried out using the D10A-XRD2 beamline of the LNLS.

RESULTS AND DISCUSSION

Densities

The apparent densities of the film were determined from the XRR patterns (Fig. 1), in a direct way, measuring the critical angle. The obtained values were:

Pure ZnO $4.7 < \delta\ (g/cm^3) < 5.5$ and ZnO:Al 5 % $2.8 < \delta\ (g/cm^3) < 3.4$

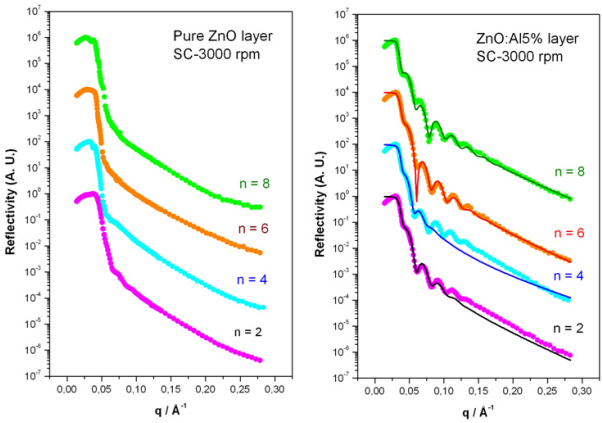

FIG. 1: XRR patterns of pure ZnO and ZnO-Al 5% films. Symbols: experimental data, Lines: best fitting

Thickness

For Al-doped ZnO films the thickness were obtained firstly from the XRR patterns by fitting with the Parratt32 sotware using a two layers model[2]. The total thickness values obtained are presented in Fig. 2.

Besides, both the profile thickness films of pure and doped ZnO films were measured by FESEM and are showed also in Fig. 2. It can be seen that for Al-doped films both measures show no significative variation vs. the number of deposits.

On the other hand, the (101) peak areas (A) of the GIXRD pattern (not present here) vs. the number of deposits (n) corroborate in a qualitative manner the results of Fig. 2, showing a very little variation of A vs. n for doped and a linear dependence for pure ZnO samples, with slope very near to the showed in Fig. 2.

Roughness

Films roughness was studied by AFM images. It can be observed that doped films show a structure with grains of smaller mean diameters than pure ZnO films. The respective profiles measure over different lines show oscillations ranging from 20 to 30 nm for the pure ZnO and 3 to 7 nm and for doped films.

The roughness values (σ) obtained by fitting XRR patterns for doped samples were: $2.0 < \sigma\ /\ nm < 5.5$; these values agree with those determined by AFM.

It would be concluded that the low roughness of doped samples is responsible for the pattern oscillations as well as the absence of them indicates high roughness for pure samples.

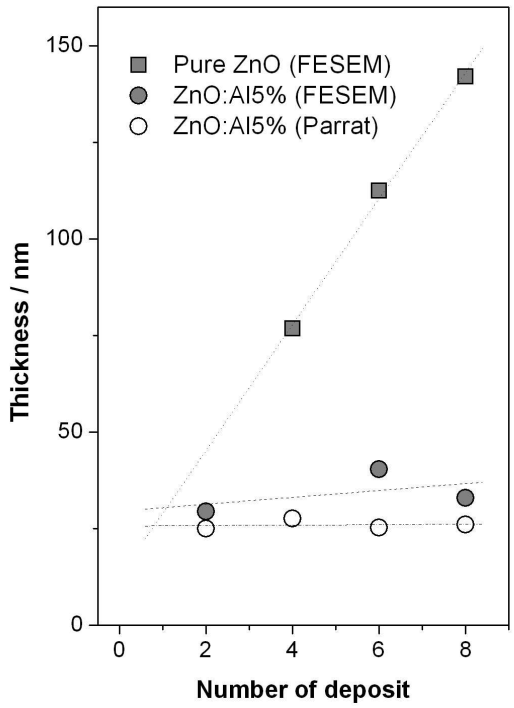

FIG. 2: Thickness of pure and doped ZnO films obtained by FESEM and XRR.

Pore Characterization

Nanopores structure were studied by GISAXS with an incidence angle of 0.4 degrees, being the exposition time 90 s. GISAXS intensities produced by diffusion in nanopores dispersed in the studied films were registered on an image plate. IsGisaxs 2.6 software was used to analyse GISAXS spectra, using the Born distorted wave approximation (DWBA) with a model of layer hole of spheroidals nanopores dispersed in the ZnO matrix [3]. Preliminary results have shown mean nanoporous radius (R) between 2.3 y 2.5 nm for pure ZnO samples and 2 to 3 nm for doped ZnO samples. The relation H/R was 1.6 to 1.9. Fig. 3 shows, the Gisaxs intensity diagram and experimental curves (symbols) and best fit using the IsGisaxs program (lines) for sample ZS4S3A.

Parameters obtained: Mean radius (R) = 2.53 nm Height / Radius = 1.60

CONCLUSION

Densities of pure ZnO samples were higher than Al doped samples. GIXRD and FESEM show that thickness of pure ZnO films grown linearly with the number of deposits while for doped samples this variation was not significative. This last conclusion was best determined by fitting XRR patterns. Pure ZnO samples exhibit higher roughness than doped samples. inhibiting the presence of oscillations in XRR patterns.

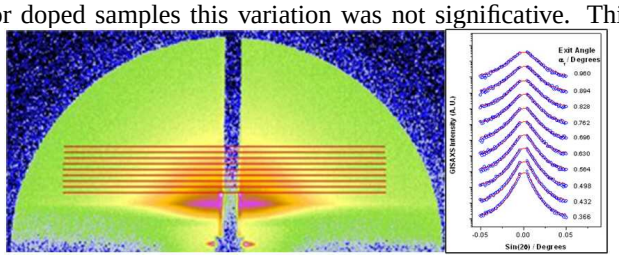

FIG. 3: Gisaxs image (left) and experimental curves and best fitting (right)

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