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CONDUCTIVE-ATOMIC FORCE MICROSCOPY INVESTIGATION OF THE ELECTRICAL PROPERTIES OF LOW TEMPERATURE DEPOSED ZnO TRANSPARENT THIN FILMS

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ABSTRACT

The paper presents the investigation by conductive-atomic force microscopy (C-AFM) of the variation of the local conductivity and topography of the transparent ZnO thin films deposed onto soda lima glass substrates by spin-coating of pre-prepared ZnO nanoparticles. With conductivity measurements at the nanometer level, the chemical and crystalline structure of the thin films obtained at temperature below 200 °C was investigated by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction, respectively, as a function of the number of the deposed layers and conditions of their deposition, such as deposition rate and the temperature of post-deposition annealing. The increase of the thermal treatment temperature, from 120 to 180 °C, leads to increased values of all thin films, most notably for the thickest sample with three layers deposed at 500 rpm that shows the highest decrease of thickness, indicating the highest compaction. The samples with three layers post-treated at 180 °C show grain growth associated with increased roughness.

KEYWORDS: ZnO nanoparticles, transparent thin films, spin-coating, microstructure, conductive atomic force microscopy

1. Introduction

Due to the recent development of transparent and flexible electronics, there is a growing interest in depositing transparent thin-film metal-oxide semiconductors at low temperature that can provide flexibility, lighter weight, and potentially lead to cheaper manufacturing processing.

Zinc oxide, which is an II-VI group semiconductor with a broad energy band (3.37 eV), high thermal and mechanical stability even at room temperature, is a very attractive material for potential applications in electronics, optoelectronics and laser technology [1].

When using polymer flexible substrate, the device processing temperatures should not exceed 80 ºC, 150 ºC, 300 ºC for polyethylene terephthalate (PET), polyethylene naphtalate (PEN) and Polyimide (PI) substrates in order to avoid their degradation [2]. For this low temperatures processing, one potential route is represented by deposition of pre-prepared oxide nanoparticles dispersions.

There are more methods for the preparation of ZnO-based thin films, such as sol-gel, supercritical precipitation, colloidal synthesis, vapor-phase oxidation, thermal vapor transport and condensation, chemical vapor deposition, micro-emulsion, spray pyrolysis, combustion method and organometallic synthesis [3-7].

The efficient use of transparent thin films in flexible electronics applications requires advanced knowledge of their electrical properties at micro/ nano level. Conventionally, the study of electrical proprieties is done by four-point probe method that measures the average value of the electrical resistivity of the thin film at the macroscopic level. In contrast,

conductive-atomic force microscopy (C-AFM) technique allows obtaining a mapping of the local variations in the conductivity of the thin films surface at high spatial resolution of variations in height and current response simultaneously, giving information about the local electronic structure for a local morphology. This method allows to quantitatively investigate the electron transport at the nanometer-scale (nm-scale) [8].

In the present paper, we have used C-AFM to map the local conductivity variations of transparent ZnO thin films deposed onto soda lima glass substrates by spin coating, using an alcohol dispersion of ZnO nanoparticles pre-prepared from solution. The chemical and crystalline structure of the thin films obtained at temperature below 200 °C was investigated by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction, respectively, as a function of the number of the deposed layers and conditions of their deposition, i.e. deposition rate and the temperature of post-deposition annealing.

2. Experimental details

2.1. Materials and synthesis of ZnO nanoparticles

Zinc acetate dehydrate (purity >98%), potassium hydroxide and methanol (purity ≥99%) were purchased from Sigma Aldrich and were used without further purification.

For the synthesis of ZnO nanoparticles, two methanol solutions, A (KOH) and B (zinc acetate dehydrate), were prepared by getting dissolved in methanol under reflux at 60 °C. Over the solution A, solution B was added and the mixture was heated under reflux and magnetic stirring to precipitate ZnO NPs. High-speed centrifugation (9000 rpm) was used for the separation of ZnO NPs from the mother solution, and for each centrifugation step, a washing with ethanol was applied. The obtained powder was finally dried in air at 100 °C.

2.2. Thin film preparation

The prepared ZnO NPs were re-dispersed in methanol and deposed on soda lima glass substrates as thin films by spin-coating using Spin-Coater WS-650SZ-8NPP AS, Laurell. Single-layered (labeled with F1 to F4 in Table 1) and three-layered thin films samples (labeled with F5 to F8 in Table 1) were deposed at 500 and 1000 rpm and annealed at 120 and 180 °C.

2.3. Nanoparticles and thin films characterization

The thickness of the deposed thin film was measured with NanoCalc-XR type refractometer.

The crystalline structure of the investigated films was evaluated by X-ray diffraction on grazing incidence geometry using a PANalytical's X'Pert PRO MRD X-ray diffractometer in the 2θ scanning range of 20° - 70°, using a monochromatic CuK_{α} radiation source (wavelength 1.540598 Å). The average crystallite size (L) of ZnO thin films was calculated based on Debye-Scherrer's equation:

$$B(2\theta) = (K \cdot \lambda)/(L \cdot \cos\theta) \qquad (1)$$

where B is the full width at half of the maximum intensity (FWHM) of the peak, λ is the X-ray wavelength, θ is the diffraction angle and K is the Scherrer's constant whose value for spherical particles is 0.89 [10].

The active functional groups inside the films were identified by Fourier Transform Infrared (FT-IR) measurements, in the spectral region of 500–4500 cm^{-1}, using a Nicolet 6700 FTIR spectrometer.

Table 1. *Experimental deposition parameters and thickness of the investigated films*

Sample symbol	No. of layers	Deposition rate (rpm)	Annealing temperature (°C)	Film thickness (nm)
F1	1	500	120	271
F2			180	216
F3		1000	120	173
F4			180	126
F5	3	500	120	894
F6			180	558
F7		1000	120	713
F8			180	561

Simultaneous local current and topography measurements were made on the surface of ZnO thin films by conductive-atomic force microscopy (C-AFM) in ambient conditions, with Asylum Research MFP-3D Standalone atomic force microscope operating in contact mode with a 2.504 μm/s scanning speed; samples scanning was performed with a commercial Pt probe (Nanoworld ContPt) having a current sensitivity of 2 nA/V and 10 mV bias. The samples were contacted using a silver paint applied on the back side and margins of the samples. The image resolution is 256 x 256 and the roughness (RMS) was evaluated with Gwyddion software. Conductive channel measurements were overlaid on the AFM image by color mapping.

3. Results and discussions

3.1. Fourier Transform Infrared investigation

Figure 1 shows the FT-IR spectra of the deposed ZnO thin films with different thickness, consisting of one and three layers. All the spectra contain intense transmittance peaks at 550 cm^{-1} attributed to bending and stretching vibrations of Zn–O bond. The increase of their intensity is related to the increase of film thickness (Table 1). Two intense peaks at 1583 and 1414 cm^{-1} in the ZnO spectrum are assigned to the asymmetric and symmetric stretching modes of COO^- acetate groups, not totally removed by the washing procedure. Also a broad band is presented in the range of 3500-3000 cm^{-1} which can be assigned to the stretching modes of OH groups exposed on the particle surface and to the presence of residual water condensed on the surface of thin films.

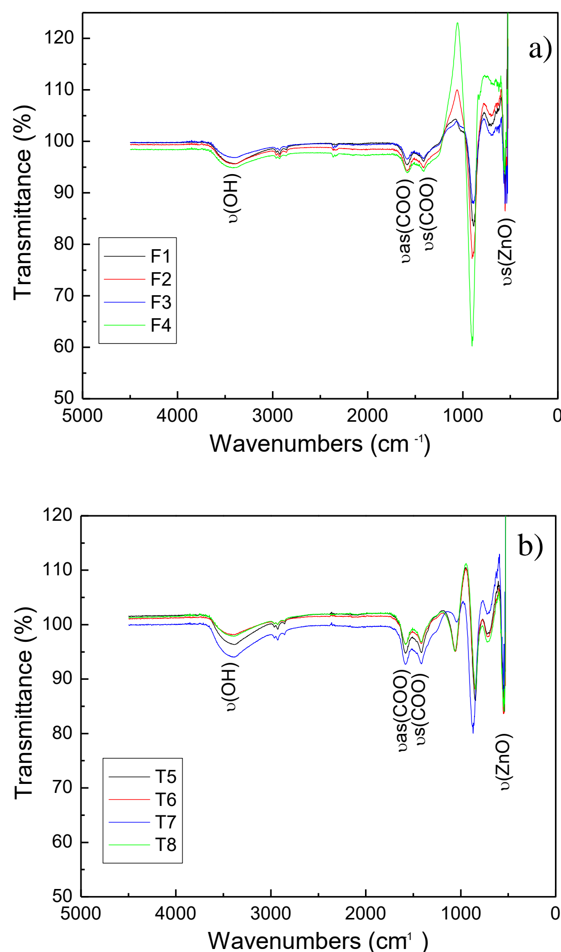

***Fig. 1.** The FTIR spectra of thin film samples with one (a) and three layers (b)*

3.2. Microstructural characterization

The XRD pattern of the deposed thin films presented in Figure 2 confirms the polycrystalline wurtzite-type zinc oxide phase. The three main diffraction peaks located at 2θ values of 31.7°, 36.2° and 56.6° are assigned to (100), (110) and (101) crystallographic planes, respectively. The average crystallite size (L) of the obtained thin films, calculated with Debye-Scherrer's for different diffraction peaks, shows different values, as follows: 10-13 nm estimated for (100) and (110) peaks, and 70-120 nm estimated for (101) peak, indicating an anisotropic crystal growth. The three-layered thin films show an increase of intensity of the diffraction peaks with respect to one layer thin films related to the increase of film thickness (Table 1) and crystallinity.

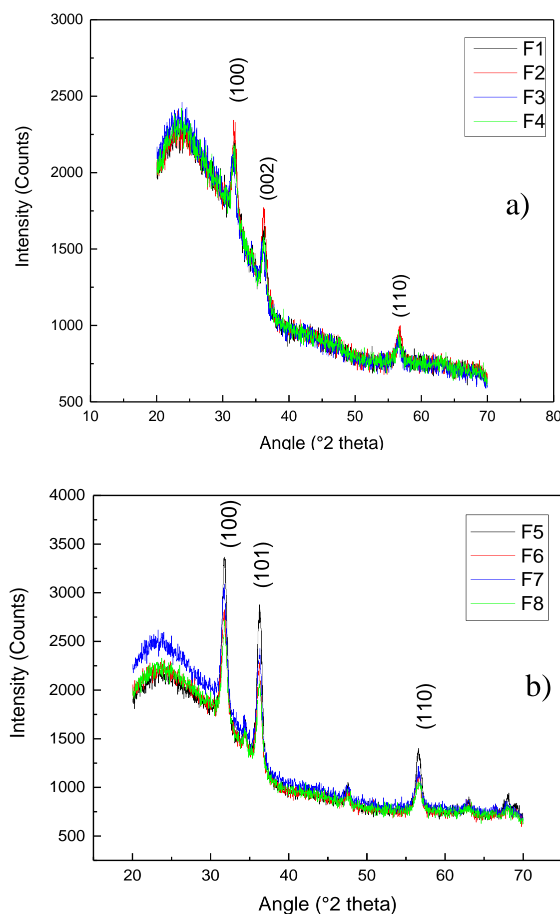

***Fig. 2.** X-Ray diffraction patterns of the one layer (a) and three-layer (b) thin films*

3.3. Conductive atomic force microscopy measurements

Figure 3 shows the superposition of current and topography C-AFM mapping of thin film samples, in 2D and 3D presentations. According to the C-AFM topography images, the thin films consist of relatively compact and homogeneous by size and shape roundish grains with diameters between 20 and 60 nm.

Generally, the C-AFM measurements revealed electrically resistive undoped ZnO thin films. In all samples, darker spots between the grains can be observed, indicating no-conductive pore spaces. Based on color tones, different gradients in current can be observed. The highest current gradient, from -11 to 122 pA, was obtained for the most compact sample (F8 in Fig.3).

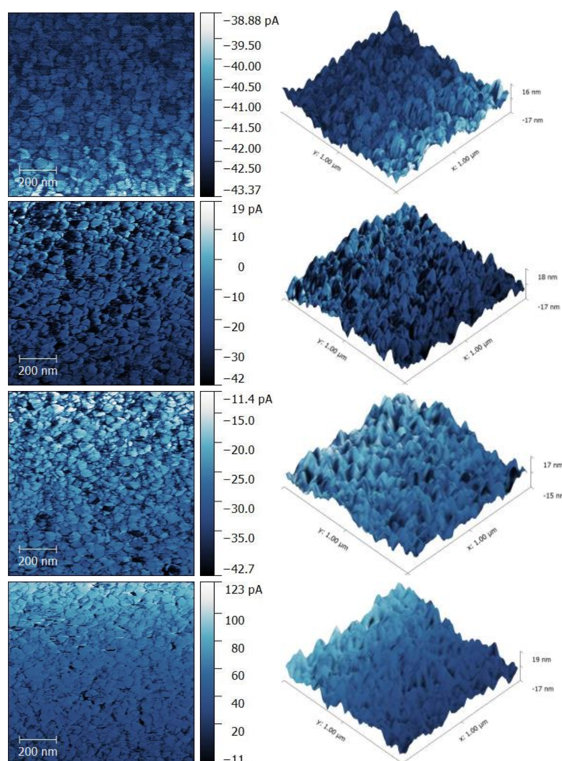

***Fig. 3.** C-AFM mapping of three-layer thin film samples, in 2D and 3D presentations*

The influence of the post-deposition temperature on the films thickness, Rms roughness and the highest grain conductivity are quantified in Figure 4. The increase of thermal treatment temperature from 120 °C to 180 °C induced changes in thicknesses, roughness, porosity and conductivity for all the investigated films. Considering the thickness of thin films (Fig 4a), one can observe a shrinkage of all samples, about 20% for samples deposed at 1000 rpm with one (sample F4) and three layers (sample F8). Higher shrinkage of about 27% (sample F2) and 37% (sample F6) can be observed for samples with one and three layers, respectively, deposed at 500 rpm (Fig. 4a).

The increase of the annealing temperature has induced an opposite effect to the surface roughness, depending on the number of layers and deposition rate (Fig 4b). For the films with one layer, the Rms values decrease by 12% and 20% for 1000 and 500 rpm, respectively, while for the samples with three layers the Rms values increased by 9.1 and 8.4% when the deposition rate was 1000 and 500 rpm, respectively (Fig. 4b).

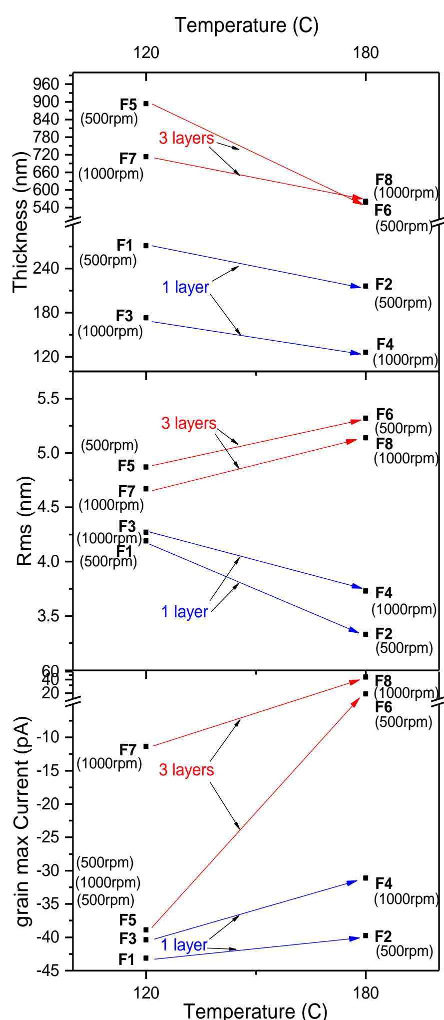

***Fig. 4.** Variation of the thin films thickness (a), Rms roughness (b) and maximum peak grain conductivity (c) versus the temperature of the post deposition treatment*

The increase of thermal treatment from 120 °C to 180 °C led to higher conductivity values for all

samples, most notably for the thin film sample with three layers deposed at 500 rpm (Fig. 4c). One can notice an increase of the overall surface current response with the increase of thickness for all samples. The thermal treatment has lowered the value response of grain maximum peak for one-layer samples, which is in accordance with the decreased values of roughness. The best conductivity is achieved by sample F8 as a result of better compaction, lower grain boundary scattering, higher conductivity [11].

4. Conclusions

ZnO thin films were obtained by spin-coating using pre-prepared oxide nanoparticles, at deposition rate of 500 and 1000 rpm and subsequent thermal treatment at 120 and 180 °C.

The increase of thermal treatment from 120 °C to 180 °C led to increased values of conductivity for all thin films, most notably for the thickest sample with three layers deposed at 500 rpm which showed the highest decrease of thickness, indicating the highest compaction. The samples with three layers post-treated at 180 °C showed a simultaneous grain growth, associated with an increase of sample roughness.

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