Advances in Natural Science: Theory & Applications

Volume 1 No. 1 2012, 61-68
url: http://www.ansta.eu

ansta.eu

ELECTROCHEMICALLY DEPOSITED NANOSTRUCTURED ZnO FILMS FOR SOLAR CELLS APPLICATIONS

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Abstract: The structural and optical properties of nanostructured ZnO layers grown on SnO_2:F covered glass substrate by the method of electrochemical deposition are studied. The layers are deposited from aqueous solution containing $ZnCl_2$, KCl, pH 4.00 and additional supplement of ZnO powder suspension in the condition of flowing air. The influence of the deposition parameters on the structural properties of the obtained ZnO layers are studied by SEM, AFM and XRD. The SEM micrographs and AFM pictures show that the ZnO films consist of nanograins. XRD spectra demonstrate preferential (002) orientation of the nanograins with average size 64-69 nm. A correlation between the diffuse reflection, haze ratio spectra and the average surface roughness is observed.

1. Introduction

ZnO nanostructured films have received increasing attention due to the potential applications in solar cells, photonic devices, sensors, displays etc. [1-4]. In order to fabricate thin film solar cells with increased efficiency the ZnO films have to have such a future size on the surface that will define high light scattering and optical confinement.

Received: January 11, 2012

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This paper reports the results from the study of optical and structural properties of nanostructured ZnO films obtained by electrochemical deposition on glass substrate coated by a thin film of SnO_2 doped with F (SnO_2:F).

2. Experimental

ZnO nanostructured films were deposited by an electrochemical process from acid aqueous solution of $ZnCl_2$ (5.10^{-3} M) and KCl (0.1M) with pH 4.0 at temperature of 600^oC in flowing air and suspension containing ZnO powder as precursors using a three-electrode electrochemical cell and saturated calomel electrodes (SCE) as reference electrodes (samples A, B, C and D). It is supposed that ZnO powder suspension could serve as a source of seeding particles. For comparison a layer without adding of the ZnO suspension was prepared as well (sample O). SnO_2:F coated glass substrates were used as working electrode (samples O, A, B and C). In the case of sample D thin Ni seeding layer (1-2 nm thick) was chemically deposited on the surface of the glass/SnO_2:F substrate before ZnO electrochemical growth. Spectrally pure graphite electrode was used as an anode. The solution was stirred by air bubbling. The deposition was carried out by varying the redox potential of the system. Since the potential of Zn in the electrolyte is -1.05 V vs. SCE the deposition process of ZnO was carried out at -0.9V vs. SCE preventing a metal Zn deposition. The redox potential of the Pt electrodes is determined by the process:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

Good quality ZnO films were obtained at a redox potential within the range between +0.30 and +0.40 V vs. SCE. Oxygen saturation of the solution was maintained by air bubbling. Zinc peroxide (ZnO_2) was formed on the samples with bad adhesion to the substrate at a redox potential higher than +0.4 V. Duration of the ZnO deposition was 60 min. The prepared ZnO films were 0.8 - 1,5 μm thick. Different regimes were explored: sample O - without suspension, sample A - with 1x drops of suspension, sample B - with 2x drops, sample C - with 2x drops and annealing at 300^oC in air, sample D - with 2x drops and substrate glass/SnO_2/Ni. The film structure was studied by X-Ray Diffraction spectrometry (XRD) using a Brucker D8 Advance spectrometer with CuKα radiation: λ CuKα1 =1.540560 $\mathring{A}A$ and λ CuKα2 = 1.544426 $\mathring{A}A$ (intensity half of that of λ CuKα1). The instrumental broadening in 2θ geometry was 0.040. The surface morphology and the thickness of the deposited films were imaged under a Scanning Electron Microscope (SEM) Philips 515. The average roughness was determined by AFM. The transmittance and the reflectance spectra, the diffuse transmission and the diffuse reflectance were measured by a spectrophotometer Shimadzu UV-3600 in the range of 300 -2600 nm employing a 60 mm integrating sphere in the case of diffuse reflectance.

Table 1. The structural and optical characteristics of the deposited ZnO films: the thickness, the average roughness, the position of the (002) peak in the XRD spectra, 2θ, the FWHM of 2θ, $\Delta 2\theta$, the average grains size, D, the optical band gap, Eg, and

the values of the stress, σ. For comparison the corresponding data for the SnO_2:F films are given, too.

Table 1

Sample	Thick-ness, nm	Average rough-ness	2θ, deg	$\Delta 2\theta$, FWHM, deg	c_{hkl}, nm	D,nm	Eg, eV	σ, GPa
Glass/	SnO_2:	805	31	33.74	0.09	-	- 3.75	- F
O ZnO	638	82	34.39	0.15	0.5211	56	3.39	-0.22
A ZnO	956	89	34.39	0.12	0.5210	69	4.19	-0.18
B ZnO	1000	299	34.39	0.11	0.5217	76	3.42	-0.49
C ZnO	1064	153	34.48	0.13	0.5196	64	3.26	0.36
D ZnO	809	33	34.38	0.12	0.5211	69	3.41	-0.22

3. Results and Discussions

Fig. 1a displays the XRD spectra of the deposited ZnO layers. For comparison the XRD spectrum of SnO_2:F film is shown as well. The diffraction patterns demonstrate that the deposited ZnO films are polycrystalline with reflection corresponding to the (100), (002), (101), (102) and (103) planes of the wurtzite structure with c-axis perpendicular to the substrate.

The graphical dependencies of the calculated values of density of the samples under study are plotted in Figire 3.1

The most intensive is the peak of (002) plane. In the case of the as-deposited layers its position is lightly shifted to the lower 2θ compare to the ZnO powder (2θ =34.44$_o$) which is evidence for the presence of the tensile stress in the layers confirmed by the calculated values of the c axis and σ (Table 1). Using the data for the Full Width at the Half Maximum (FWHM) of the (002) peak, $\Delta 2\theta$, the value of the stress, σ, and the average size of the grains, D, are calculated. The values of the stress are negative for the as-deposited layers. In the case of the sample C, obtained at the same conditions as sample B, however annealed at 3500C, the (002) peak position shifts to the lower $\Delta 2\theta$, the c is lower than in the bulk ZnO (cbulk= 0.5206 nm) and the value of the stress is a positive one ? the compressive stress is present in the layer after annealing. The spectral dependence of the coefficient of absorption, ?, of the ZnO layers is displayed in Fig. 1b. The value of α is calculated using transmittance and reflectance spectra with correction for the SnO_2:F transmittance assuming a direct gap of ZnO [5, 6]. The optical band gap, Eg, is determined and the values are typical for ZnO - 3.39-3.46 eV in the case of the as-deposited samples [5, 6]. After annealing (sample C) the value of Eg decreases to 3.26 eV compared to the values of the as-deposited samples. This is probably related to the removal of the $Zn(OH)_2$ presented in the as-deposited layer that could exists in electrodeposited ZnO from aqueous solution [7]. Fig. 2 and

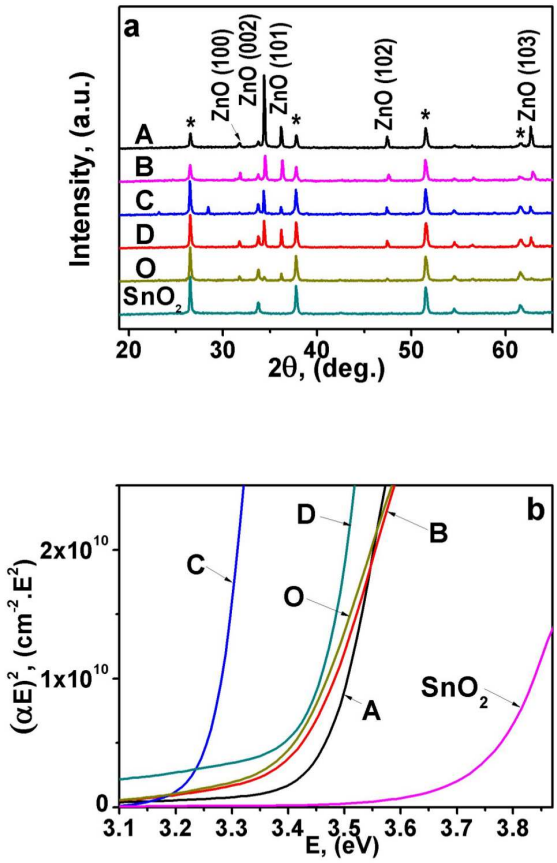

Figure 3.1: XRD spectra (a) and $(?E)^2$ versus energy, E,(b) of the ZnO layers deposited at different conditions. The corresponding curves of SnO_2:F are given, too. The XRD peaks

3 demonstrate SEM and AFM pictures of the electrochemically deposited ZnO layers. The ZnO layer grown without adding of ZnO suspension (sample O) consists of grains with size of 56 nm and has an average surface roughness 82 nm (Fig. 2b, Fig. 3a).

It is seen from Fig. 2 c and d that the grain size in the layers increases with adding of different quantity of the suspension which is in agreement with the obtained from the XRD data (Table 1). Annealing of the film at 350^{o}C for 1 hour results in changes in the morphology - agglomerates of the allowed grains are grown (Fig. 2e). The surface roughness of this sample decreases. The ZnO layer grown on the SnO_2:F coated by a thin Ni seeding film has a totally different shape of the grains - they look like the

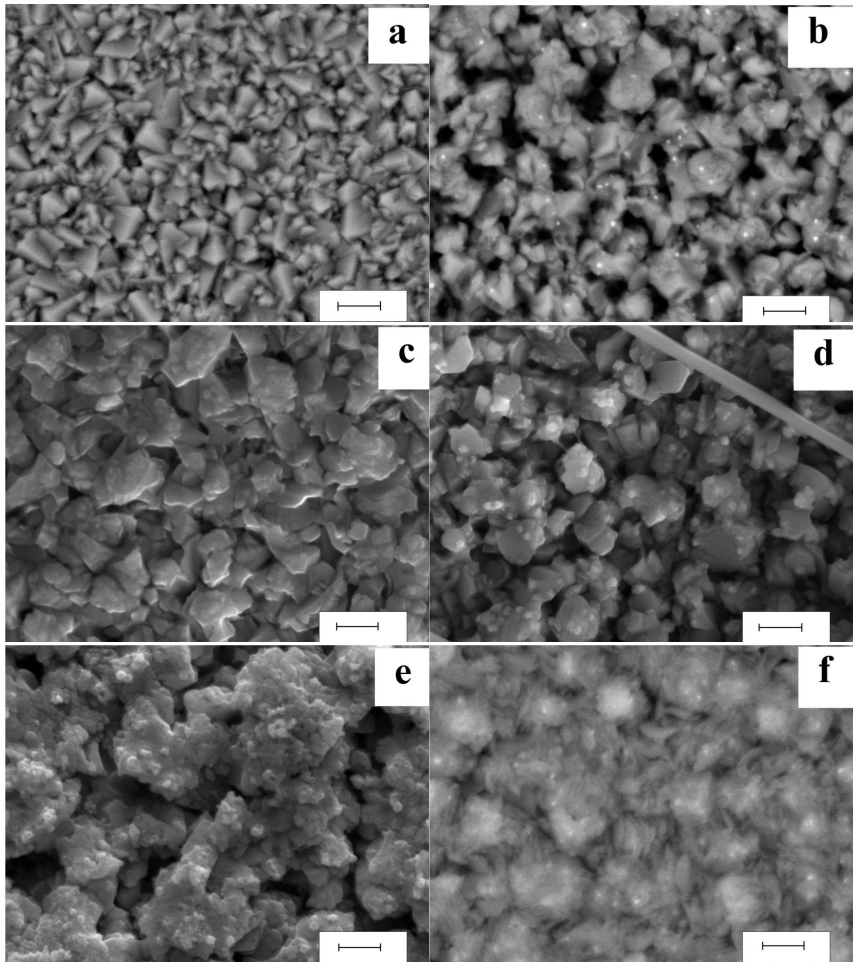

Figure 3.2: SEM plane views of SnO_2:F film (a) and ZnO layers: samples O (b), A (c), B (d), C (e) and D (f).The marker corresponds to 500 nm.

spheres, and the average roughness decreases significant (Fig. 2f and Fig. 3d), however it is still higher than that of SnO_2:F film. The spectra of diffuse reflectance, Rdiff, are shown in Fig. 4a. The corresponding spectrum for SnO_2:F is presented as well. The values of the diffuse reflectance, Rdiff, of the grown ZnO layers are higher than those of SnO_2:F coated glass substrate. It is seen that with increasing of the quantity of the added ZnO suspension in the electrolyte and by using of the Ni intermediate film the Rdiff values increase. After annealing the values of Rdiff decrease slightly in the whole range of the spectrum. The spectral dependence of the haze ratio of the ZnO samples in the range of 400 - 1000 nm is presented in Fig. 4b. The values of the haze ratio of the electrodeposited ZnO layers are much higher than those of the SnO_2:F coating. It has

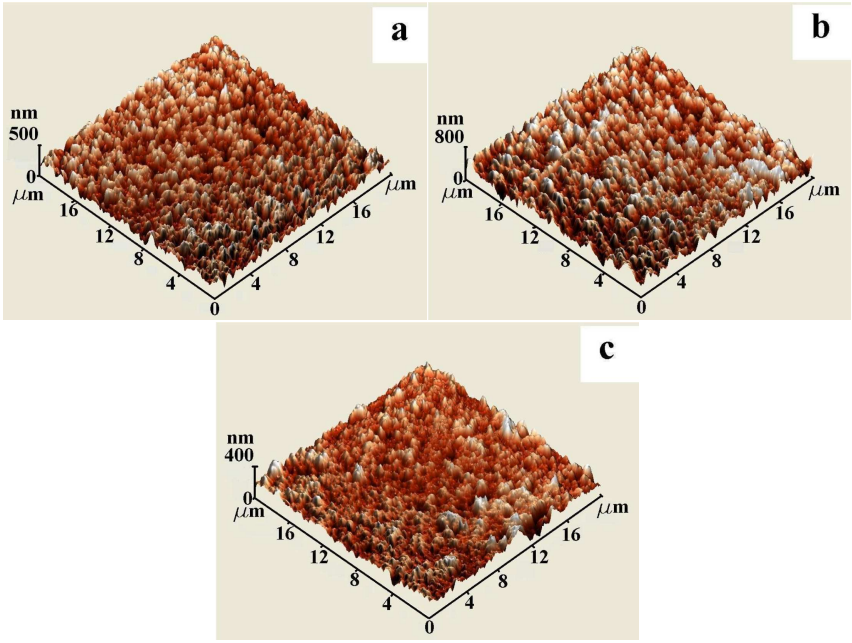

Figure 3.3: AFM images of the ZnO layers: samples: O (a), B (b) and D (c).

to be noted that those layers with higher values of the average roughness determined by AFM (Table 1) demonstrate higher diffusion reflectance and haze ratio.

4. Conclusions

The influence of the ZnO water suspension added to the electrolyte - aqueous solution containing $ZnCl_2$, KCl, pH 4.00, on the structure, the grain size, the diffuse reflectance and the haze ratio of the electrochemically deposited ZnO films is studied. The correlation between the grain size, average roughness and the optical properties is observed. The higher values of the diffuse reflectance and haze ratio in the spectral range 400 - 1100 nm demonstrate studied in this work ZnO layers with larger average grain size (76 nm) and higher average surface roughness (299 nm). ZnO layers with similar properties could be applied as light trapping structures in thin film solar cells.

Acknowledgements

This work was funded by 7FP - project NanoPV FP7-NMP3-SL-2011-246331, and a Bulgarian National Scientific Fund - project DO02-207. The authors thank to Dr. M. Sendova-Vassileva for the optical measurements.

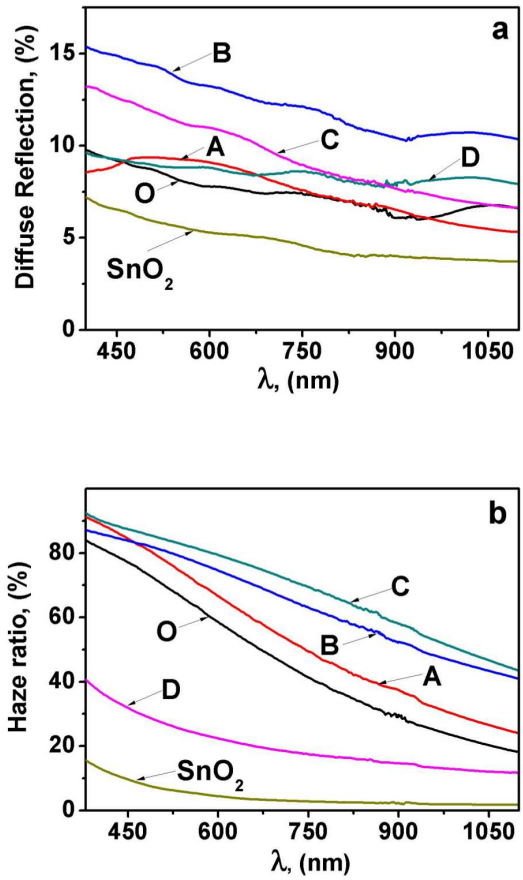

Figure 3.4: Diffuse reflectance (a) and haze ratio (b) spectra of SnO_2:F film and the five ZnO samples (O, A, B, C and D)

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