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# Correlation between the haze ratio and the surface roughness of electrochemically deposited nanostructured ZnO films

**K Lovchinov[1,3], O Angelov[1], H Nichev[1], V Mikli[2] and D Dimova-Malinovska[1]**

[1] Central Laboratory of Solar Energy and New Energy Sources,
Bulgarian Academy of Sciences, 72, Tsarigradzko Chaussee, 1784 Sofia, Bulgaria
[2] Centre for Materials Research, Tallinn University of Technology, Tallinn, Estonia

E-mail: lov4@abv.bg

**Abstract.** This work reports the synthesis of nanostructured ZnO by electrochemical deposition on glass substrates covered by a thin film of $SnO_2$ doped with F ($SnO_2$:F). Nanostructured ZnO films are deposited by an electrochemical process using a three-electrode potentiostatic system with saturated calomel electrodes as reference electrodes from an aqueous solution containing $ZnCl_2$, KCl, (pH 4.00) and an air flow or/and additional supplement of $H_2O_2$ or a ZnO powder suspension. The influence of the deposition conditions on the structural properties of the ZnO films prepared is studied by SEM, AFM and XRD. The SEM micrographs and the AFM images show that the ZnO films consist of nanograins with average size in the range of 52 – 83 nm depending on the deposition conditions. The XRD spectra demonstrate preferential (002) crystallographic orientation of the ZnO grains. The optical band gap values are in the range 3.26 – 3.46 eV. The spectra of total and diffused transmission are also measured. It is shown that the haze ratio depends on the surface roughness of the films.

## 1. Introduction

ZnO nanostructures have received increasing attention due to potential applications in solar cells, nanoscale electronics, optical and sensing devices, etc. [1-4]. In the fabrication of thin film solar cells of higher efficiency, ZnO films used as electrodes exhibit surface morphology suitable for light trapping and optical confinement.

This paper reports results from the study of the structural and optical properties of ZnO nanostructured films grown by electrochemical deposition on glass substrate coated by $SnO_2$:F.

## 2. Experimental

ZnO nanostructured films were deposited by an electrochemical process from an acid aqueous solution of $ZnCl_2$ ($5\times10^{-3}$ M) and KCl (0.1 M) with pH 4.0 at temperature of $60^0$C in flowing air and a suspension containing ZnO powder as a precursor. A three-electrode electrochemical cell was used with saturated calomel electrodes (SCE) as reference electrodes, as described earlier in [5]. It is assumed that the ZnO powder suspension can serve as a source of seeding particles. For comparison, a layer was also prepared without adding the ZnO suspension (table 1, sample 2). $SnO_2$:F coated glass

[3] To whom any correspondence should be addressed.

**Table 1.** Structural and optical characteristics of the deposited ZnO films: optical band gap, $E_g$; position of the (002) peak in the XRD spectra, 2θ; FWHM of the (002) peak, Δ2θ; stress, σ; average grains size, *D*; thickness, *d*; average roughness, *R*; and haze ratio at different wavelengths. For comparison, the corresponding data for the $SnO_2$:F films are given as well.

| Sample | *Eg*, (eV) | 2θ, (deg.) | FWHM (deg.) | σ, (GPa) | *D*, (nm) | *d*, (nm) | *R*, (nm) | Haze, (%) λ=400nm | Haze, (%) λ=550nm | Haze, (%) λ=1000nm |
|---|---|---|---|---|---|---|---|---|---|---|
| **1 –$SnO_2$:F** | 3.75 | 34.39 | 0.14 | -0.25 | 59 | 910 | 29 | 30 | 13 | 3 |
| **2 –w/t drops** | 3.39 | 34.39 | 0.15 | -0.24 | 56 | 550 | 315 | 82 | 65 | 23 |
| **3- 1 x drops** | 3.37 | 34.41 | 0.16 | -0.12 | 52 | 580 | 89 | 85 | 82 | 35 |
| **3'-1x drops** | 3.38 | 34.38 | 0.14 | -0.32 | 59 | 620 | 89 | 86 | 74 | 24 |
| **4- 2x drops** | 3.38 | 34.37 | 0.10 | -0.38 | 83 | 700 | 147 | 88 | 86 | 34 |
| **5-2x drops+$H_2O_2$** | 3.46 | 34.39 | 0.12 | -0.25 | 69 | 1570 | 82 | 90 | 73 | 29 |
| **6-3x drops** | 3.42 | 34.39 | 0.11 | -0.25 | 76 | 750 | 299 | 93 | 82 | 50 |
| **6'-3x drops** | 3.41 | 34.34 | 0.13 | -0.58 | 64 | 1000 | 225 | 91 | 82 | 50 |
| **7 -3x drops+ann.** | 3.26 | 34.48 | 0.13 | 0.36 | 64 | 1060 | 153 | 86 | 78 | 46 |
| **7'- 3x drops+ann.** | 3.27 | 34.50 | 0.13 | 0.47 | 64 | 850 | 78 | 91 | 77 | 31 |
| **8 -3x drops+$H_2O_2$** | 3.47 | 34.38 | 0.12 | -0.32 | 69 | 900 | 75 | 89 | 65 | 22 |
| **9- 3x drops+Ni** | 3.51 | 34.38 | 0.12 | -0.32 | 69 | 810 | 33 | 38 | 25 | 13 |

substrates were used as a working electrode (table 1, sample 1). In the case of sample 9, a thin Ni seeding layer (1 – 2 nm thick) was chemically deposited on the surface of the glass/$SnO_2$:F substrate before the electrochemical growth of ZnO. A spectrally pure graphite electrode was used as 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 −0.9 V vs. SCE, thus preventing metal Zn deposition. ZnO films of good quality were obtained at a redox potential within the range +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. The duration of the ZnO deposition was 60 min. The ZnO films prepared were 0.55 – 1.57 μm thick. Different regimes were explored: sample 2 – without drops (dr.), sample 3 – 1×dr., sample 4 – 2×dr., sample 5 – 2×dr. + $H_2O_2$, samples 6 and 6' – 3×dr., samples 7 and 7'– 3×dr. + annealing at 300 $^oC$, sample 8 – 3×dr. + $H_2O_2$ and sample 9 – 3×dr. + Ni seeding layer.

The film structure was studied by X-ray diffraction spectrometry (XRD) using a Brucker D8 Advance spectrometer with Cu $K_\alpha$ radiation: λ Cu $K_{\alpha1}$ =1.540560 Å and λ Cu $K_{\alpha2}$ = 1.544426 Å (intensity half of that of λ Cu $K_{\alpha1}$). The instrumental broadening in 2θ geometry was $0.04^0$. The surface morphology and the thickness of the deposited films were imaged by a Philips 515 scanning electron microscope (SEM). The average roughness was determined by AFM. The transmittance and the reflectance spectra, the diffuse transmittance and the diffuse reflectance were measured by a Shimadzu UV-3600 spectrophotometer in the range of 300 -2600 nm employing a 60 mm integrating sphere in the case of diffuse reflectance.

## 3. Results and discussion

XRD spectra of some of the deposited ZnO samples are shown in figure 1. For comparison, the XRD spectrum of the $SnO_2$:F film is displayed as well. The diffraction patterns demonstrate that the deposited ZnO films are polycrystalline with reflections corresponding to the (100), (002), (101), (102) and (103) planes of a wurtzite structure with the *c*-axis perpendicular to the substrate. The XRD peak of the (002) plane is the most intensive one. In the case of the as-deposited layers, its position is slightly shifted to the lower 2θ compared to the ZnO powder (2θ = $34.44^o$), which is evidence for the presence of stress, σ, in the layers, as confirmed by the calculated values of σ (table 1). The average size of the grains, *D*, is estimated using the FWHM of the (002) peak), Δ2θ. The value of the optical band, $E_g$, is calculated using the transmittance and reflectance spectra assuming a direct gap for ZnO [6]. The values of $E_g$ are typical for ZnO – 3.39 – 3.46 eV in the case of the as-deposited samples.

Adding $H_2O_2$ results in an increase of $E_g$, (samples 5 and 8). After annealing (samples 7 and 7'), the value of $E_g$ decreases to 3.26 – 3.27 eV compared to the values of the as-deposited samples. This is probably related to the removal of $Zn(OH)_2$ that could be present in the as-deposited layer in electrodeposition of ZnO from aqueous solution. The diffuse reflectance spectra, $R_{diff}$, are shown in figure 1 c. The values of the diffuse reflectance, $R_{diff}$, of the ZnO layers grown are higher than that of the $SnO_2$:F coated glass substrate. It is seen that the $R_{diff}$ values increase when the quantity of the ZnO suspension added to the electrolyte is raised and when a Ni intermediate film is used. After annealing, the values of $R_{diff}$ decrease slightly in the whole range of the spectrum.

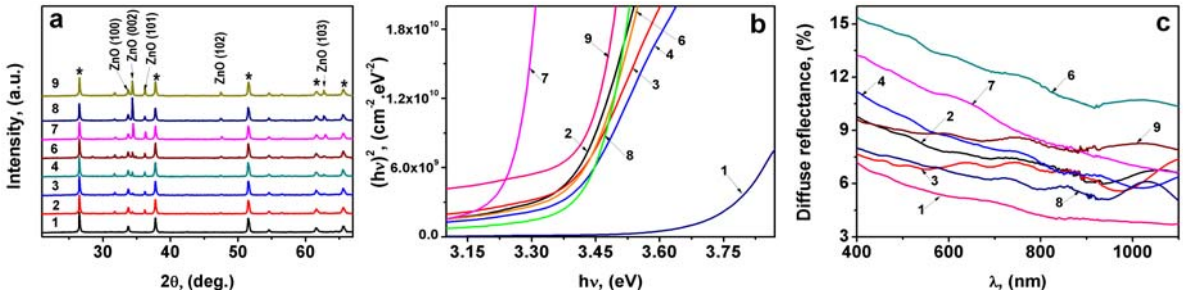


**Figure 1.** XRD spectra (a), $(\alpha E)^2$ versus energy, E, (b) and diffuse reflectance spectra of the ZnO layers deposited at different conditions (c). The corresponding curves (1) of $SnO_2$:F are given, too. The XRD peaks of $SnO_2$:F are marked by *.

Figures 2 and 3 display examples of the SEM and the AFM images of the $SnO_2$:F substrate and of some of the samples. The ZnO layer grown without adding a ZnO suspension (sample 2) consists of grains with size of about 56 nm (very inhomogeneous grains size, *D*) and has an average surface roughness of ~82 nm (figure 2b). It is seen that the grain size in the layers increases as different quantities of the suspension are added, which is in agreement with the data obtained by XRD (table 1). Annealing of the film at 350°C for 1 hour results in changes in the morphology – the individual grains grow into conglomerates (figure 2d) and the surface roughness of this sample decreases.

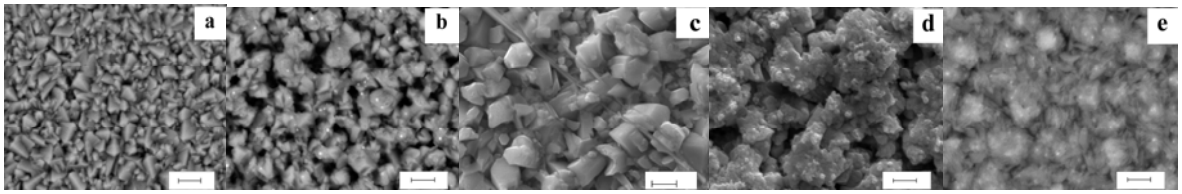


**Figure 2.** SEM plane views of $SnO_2$:F film (a) and ZnO layers – samples: 2- (b), 6 - (c), 7 - (d) and 9 - (e). The marker corresponds to 500 nm.

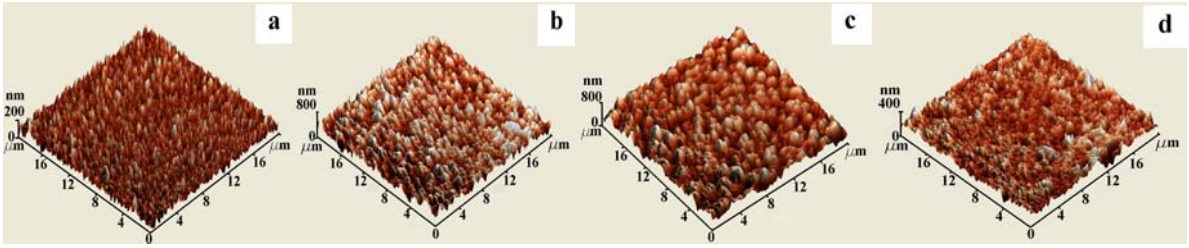


**Figure 3.** AFM images of a $SnO_2$:F film (a) and ZnO layers - samples: 6 - (b), 7 - (c) and 9 - (d).

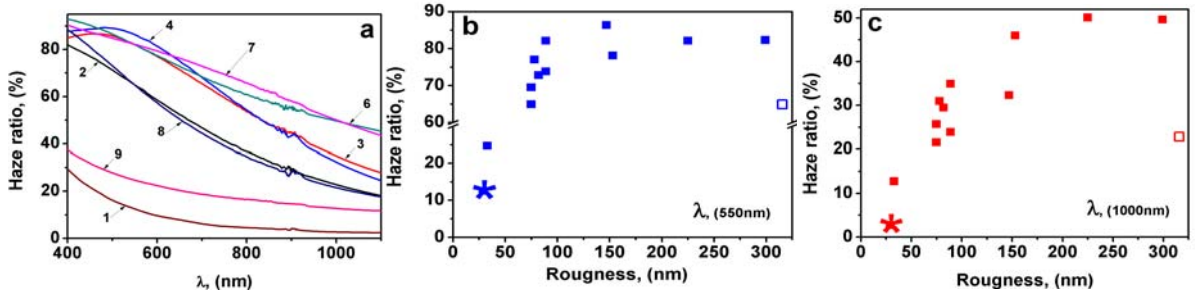


**Figure 4.** Spectral dependence of the haze ratio (a) and dependence of the haze ratio on the surface roughness at wavelengths 550 nm (b) and 1000 nm (c). The signs * and □ correspond to $SnO_2$:F (samples ) and to the sample obtained without adding drops of ZnO suspention (sample 2), respectively.

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 spheres and the average roughness decreases significantly (figure 2e and figure 3d), however it is still higher than that of $SnO_2$:F film.

The spectral dependence of the haze ratio of the ZnO samples in the range of 400 - 1000 nm is presented in figure 4a. The values of the haze ratio of the electrodeposited ZnO layers are much higher than those of the $SnO_2$:F coating. Higher values of the haze ratio are observed for the samples deposited with higher quantities of the ZnO suspension added. It must be noted that the layers with higher values of the average roughness, as determined by AFM (table 1), demonstrate higher diffuse reflectance and haze ratio. Figure 4 b and c show the variation of the haze ratio with the roughness of the deposited films at two wavelengths – 550 and 1000 nm. It is very clearly seen that the value of the haze ratio increases with the increase of the surface roughness with maximal values of about 93%, 86% and 50% at 400 nm, 550 nm and 1000 nm, respectively.

## Conclusions

The influence is studied of ZnO water suspension added to the electrolyte – an aqueous solution containing $ZnCl_2$, KCl, (pH 4.00), on the structure, the grain size, the diffuse reflection and the haze ratio of the electrochemically deposited ZnO films. The higher values of the diffuse reflectance and haze ratio in the spectral range of 400 - 1100 nm are evidence of ZnO layers with larger average grain size and higher average surface roughness. ZnO layers with similar properties could be used as light trapping structures in thin film solar cells.

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