

“Structural and optical properties of electrochemically deposited ZnO films in electrolyte containing  $\text{Al}_2(\text{SO}_4)_3$ ”, K. Lovchinov, M. Ganchev, A. Rachkova, H. Nichev, O. Angelov, V. Mikli, D. Dimova-Malinovska, (2012) J. Phys. in press

# Structural and optical properties of electrochemically deposited ZnO films in electrolyte containing $\text{Al}_2(\text{SO}_4)_3$

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**Abstract.** The present work concerns the electrochemical deposition of aluminium doped ZnO nanostructured thin films on  $\text{SnO}_2\text{:F}$  covered glass substrates. Doped with Al nanostructured ZnO (ZnO:Al) films are obtained by an electrochemical process using a three-electrode potentiostatic system with a saturated calomel electrode as reference electrode, in aqueous solution containing  $\text{ZnCl}_2$ , KCl and  $\text{Al}_2(\text{SO}_4)_3$ . The influence of the deposition parameters on the structural properties of the obtained ZnO:Al layers is investigated by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Energy Dispersive X-ray Analysis (EDAX) is applied for measurement of the Al content in the films. The SEM micrographs and AFM pictures show that the ZnO:Al films consist of nanograins with a shape of walls. The XRD spectra demonstrate (100), (002), (101), (110) and (103) the characteristic reflexes of the ZnO. Influence of the Al concentration on the IR reflectance spectra and haze ratio of ZnO:Al thin films are presented and discussed.

## 1. Introduction

Quasi-one-dimensional nanoscale ZnO like nanowires, nanorods, nanowiskers, nanowalls etc. got up increasing attention over the past few years for their potential application in solar cells [1] as an n-type electrode [2], near UV-leasers [3], field effect transistors [4], chemical sensors [5], etc. ZnO nanostructured layers can be prepared by different methods, like RF magnetron sputtering [6], sol-gel method [7], electrochemical deposition [8], etc. Electrodeposition presents a simple, inexpensive upscalable method for covering of large surface areas allowing the controlled and patterned growth of ZnO nanostructures [9].

In this contribution we report the deposition of ZnO nanostructured thin films on the  $\text{SnO}_2\text{:F}$  covered glass substrates at temperature 80°C from aqueous electrolyte containing  $\text{ZnCl}_2$ , KCl and  $\text{Al}_2(\text{SO}_4)_3$ . The concentration of doped Al, the surface morphology and the thickness of the ZnO layers are controlled by deposition potentials, temperature, plating time and  $\text{Al}_2(\text{SO}_4)_3$  concentration.

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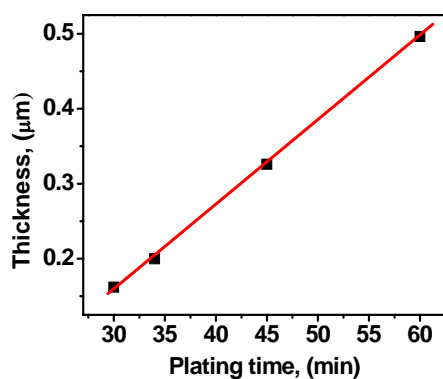
## 2. Experimental

Thin ZnO nanostructured films are deposited by an electrochemical process from slightly acid aqueous solution of  $\text{ZnCl}_2$  ( $5 \cdot 10^{-3}$  M) and KCl (0.5 M) with pH 4.0 at  $80^\circ\text{C}$  and  $-1000\text{mV}$  (vs SCE) using a three-electrode electrochemical cell [9]. Different quantity of stock solution of  $\text{Al}_2(\text{SO}_4)_3$  has been added to the electrolyte for varying of concentration of Al in the deposits.  $\text{SnO}_2:\text{F}$  coated glass substrates are used as working electrode. Spectrally pure graphite rod electrode is used as an anode. The electrolyte is agitated by magnetic stirrer. The deposition is carried out controlling the redox potential of the system. Duration of the ZnO deposition is between 30 and 120 min. The thicknesses of the prepared ZnO films are in the range of 1 and 2  $\mu\text{m}$ . Different concentrations of the doping compound  $\text{Al}_2(\text{SO}_4)_3$  in the electrolyte are explored:  $1 \cdot 10^{-5}$  M,  $2 \cdot 10^{-5}$  M,  $3 \cdot 10^{-5}$  M and  $4 \cdot 10^{-5}$  M  $\text{Al}_2(\text{SO}_4)_3$ . Samples without doping are deposited at the same conditions of the electrochemical process. Some of the samples are annealed at  $400^\circ\text{C}$  in forming gas for 1 hour.

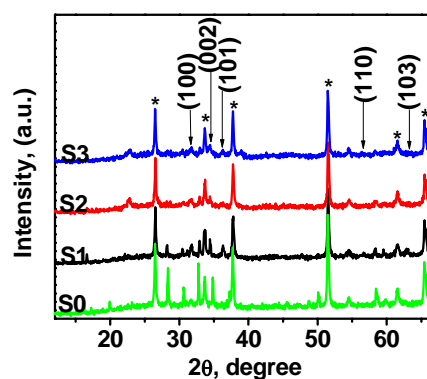
Quartz crystal resonators are used as microbalance to reveal the speed of electrodeposition of the ZnO nano-layer. The oscillators are HC-49 type package, 8 mm diameter polished quartz plates at AT-cut, 16 MHz base resonant frequency, with 600 nm thick gold electrodes with average surface area  $0.1256 \text{ cm}^2$ . The total oxygen content in solution is controlled in addition by DO&T meter Hanna Instruments 9146. The film structure is studied by X-Rays Diffraction spectrometry (XRD) using a Bruker D8 Advance spectrometer with  $\text{Cu K}\alpha$  radiation:  $\lambda_{\text{Cu K}\alpha 1} = 1.540560 \text{ \AA}$  and  $\lambda_{\text{Cu K}\alpha 2} = 1.544426 \text{ \AA}$  (intensity half of that of  $\lambda_{\text{Cu K}\alpha 1}$ ). The instrumental broadening in  $2\theta$  geometry is  $0.04^\circ$ . The Al content in the films is determined by Energy Dispersive X-ray Analysis (EDAX) using Link AN10000 system analyser. The surface morphology and the thickness of the deposited films are studied by a Scanning Electron Microscope (SEM) Philips 515. Surface topography of the layers is studied by AFM using the NT-MDT Solver 47 Pro system operated in a “semi-contact” (tapping) mode. Spectra of reflectance in IR region are measured by a spectrophotometer Shimadzu IR Prestige – 21 in the range of  $500 - 5000 \text{ cm}^{-1}$ . The total and diffused transmittance spectra are measured by a spectrophotometer Shimadzu UV-3600 in the range of  $320 - 2400 \text{ nm}$  employing a 60 mm integrating sphere.

## 3. Results and discussion.

For determination of the speed of film growth several experiments with deposition of ZnO on quartz resonator surface are performed. The ZnO is deposited at  $80^\circ\text{C}$  and potential of  $-1000 \text{ mV}$ , in aqueous electrolyte of  $0.5 \text{ mM ZnCl}_2$  and  $0.5 \text{ M KCl}$ .



**Figure 1.** Dependence of the film thickness of ZnO deposited on quartz resonators on plating time.



**Figure 2.** XRD spectra of the nanostructured thin films of ZnO, deposited with different concentrations of  $\text{Al}_2(\text{SO}_4)_3$  in the electrolyte. XRD peaks of  $\text{SnO}_2:\text{F}$  are marked by asterisks. The Al concentration in the samples S0, S1, S2

and S3 are given in Table 1.

Figure 1 shows the dependence of thin film ZnO thickness on deposition time. The thickness of the layers is calculated by change of resonant frequency caused of deposited ZnO film by the Sauerbrey equation (1) [10]. The points could be fit by a line described by the equation:

$$d = 11.23 t - 178.37, \quad (1)$$

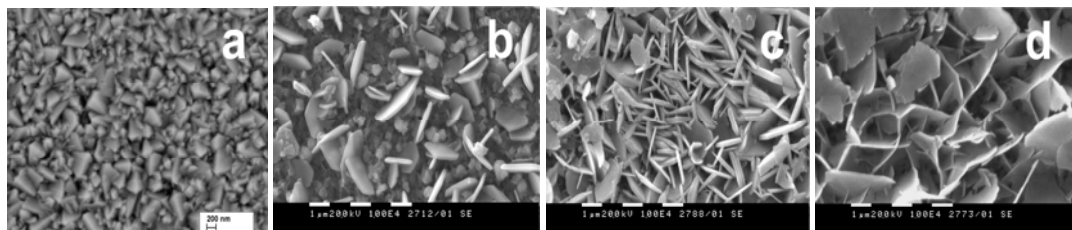
where  $d$  is the Sauerbrey thickness of the layer (in nm) and  $t$  is the plating time (in minutes). The slope of the line presents the value of the speed of the film growth equal to 11 nm/min. The negative part of the equation (1) indicates a delay of the start of the film growth (nucleation time). From the equation (1), it follows that the nucleation time (at  $d = 0$ ) is about 953 sec, which coincides quite right with the observation, that there is no deposited film till the 15 minutes plating time.

**Table 1.** Data of the ZnO films: the  $(\text{Al}_2\text{SO}_4)_3$  concentration in the electrolyte, the Al concentration in the ZnO films,  $C_{\text{Al}}$ , (at.%), the thickness, ( $\mu\text{m}$ ), and the average roughness, (nm). For comparison the thickness and the average roughness of the  $\text{SnO}_2:\text{F}$  layer is given, as well.

Sample	$\text{Al}_2(\text{SO}_4)_3$ , (M)	$C_{\text{Al}}$ , (at.%)	Thickness, ( $\mu\text{m}$ )	Average roughness, (nm)
$\text{SnO}_2$	-	-	0.9	30
S0	0	0.0	2.8	340
S1	$2 \cdot 10^{-5}$	1.40	2.2	300
S2	$3 \cdot 10^{-5}$	3.20	2.4	320
S3	$4 \cdot 10^{-5}$	5.70	1.4	460

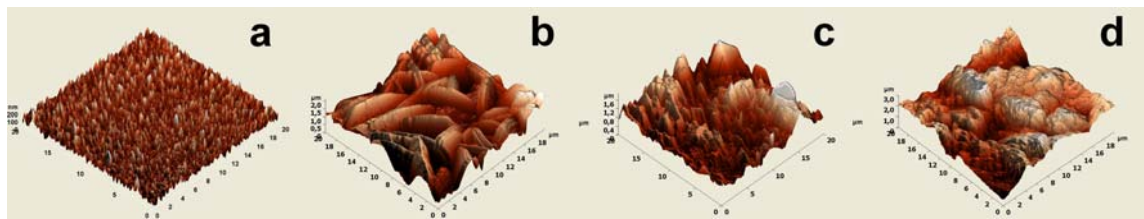
The value of the  $\text{Al}_2(\text{SO}_4)_3$  concentration in the electrolyte used, the Al concentration in the deposited films,  $C_{\text{Al}}$ , the thickness and the average roughness of the ZnO films obtained from the AFM images are given in Table 1. The corresponding data for the  $\text{SnO}_2:\text{F}$  and undoped ZnO film are given as well. The Al concentration obtained from EDAX analysis changes from 1.40 at.% till 5.70 at.% with increasing of the  $\text{Al}_2(\text{SO}_4)_3$  concentration in the electrolyte.

Figure 2 presents the typical X-Ray Diffraction patterns of thin ZnO films, electrodeposited for 90 minutes without and with different concentration of  $\text{Al}_2(\text{SO}_4)_3$  in the electrolyte (see Table 1). XRD diffraction pattern reveals the existence of ZnO with hexagonal wurtzite structure. The reflexes from the  $\text{SnO}_2:\text{F}$  are marked by asterisks. The reflexes from (100), (002), (101), (110) and (103) planes of ZnO are observed [11-13]. The intensity of the XRD peaks of ZnO decreases with increasing of  $\text{Al}_2(\text{SO}_4)_3$  concentration in the electrolyte which demonstrates deterioration of the crystalline structure with Al concentration.



**Figure 3.** SEM pictures of the surface of  $\text{SnO}_2:\text{F}$  film (a), nanostructured thin films of ZnO - undoped (b) and doped with Al with different concentrations of  $\text{Al}_2(\text{SO}_4)_3$  in electrolyte: (c) –  $2 \cdot 10^{-5}$  M (sample 1) and (d) –  $4 \cdot 10^{-5}$  M (sample 3). The markers correspond to 200 nm (a) and 1  $\mu\text{m}$  (b, c and d).

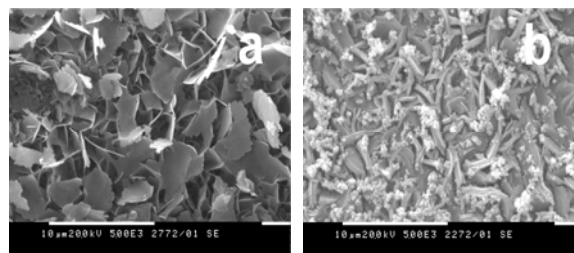
Figure 3 shows SEM micrographs of undoped and doped with Al ZnO nanostructured thin films, deposited at constant charge density. For comparison the SEM of SnO<sub>2</sub>:F film is given as well (figure 3a). Figure 3b displays the surface morphology of electrodeposited undoped ZnO layer. The picture exhibits the view of the film surface which consists of planar hexagonal ZnO walls with different length in the range of 1- 4 μm and 100-200 nm thick, stacked with the narrow side to the substrate surface. SEM image of ZnO film deposited with 2.10<sup>-5</sup> M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is shown in figure 3c. The Al doped ZnO film has a similar morphology, as undoped one – the ZnO:Al nanoparticles represent hexagonal walls, almost vertically oriented to the substrate surface with smaller length (1-2 μm) than the particles in the undoped samples. With increasing of the Al concentration in the films up to 5.7 at.% the number of the nanowalls per unite area decreases.



**Figure 4.** AFM pictures of the SnO<sub>2</sub> substrate (a) and nanostructured of ZnO thin films doped with Al: sample S0 (a), sam-ple S1 (c), and sample S2 (d)

The surface roughness of the deposited ZnO layers is determinate by AFM. An example of AFM pictures of un-doped and doped with Al ZnO film (samples S0, S1 and S3) are presented in figure 4. The average surface roughness increases with increasing of Al content in the grown ZnO:Al layers from 300 nm till 460 nm when Al increase from 1.40 at.% till 5.70 at.%. It has to be noted that the thickness of the doped ZnO films is lower than in undoped ones (Table 1), thus the roughness depends on the conditions of growing in the presence of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the electrolyte and not on the thickness of the layers.

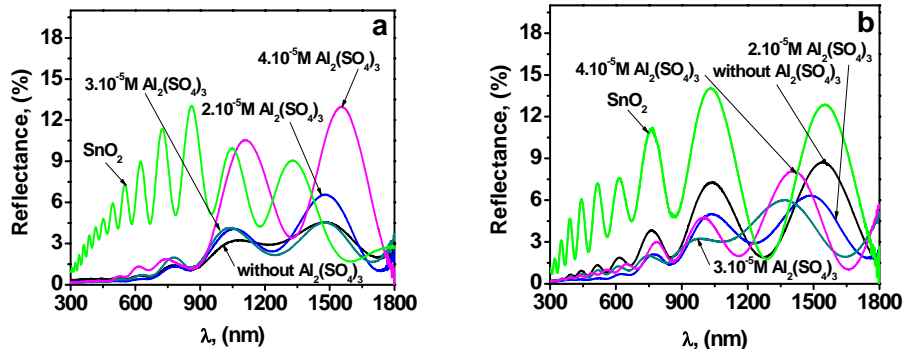
The influence of the thermal annealing in forming gas for 1 hour on the surface morphology of deposited ZnO:Al is demonstrated in SEM images in figure 5. As can be seen that the annealing results in agglomeration of the nanowalls and increasing of their surface density with certain decrease in their size; additionally the small sized grains appear on their surface (figure 5b). The optical properties of the films are studied by spectra of reflectance and haze ratio in the visible and IR region [13].



**Figure 5.** SEM pictures of as deposited ZnO:Al with 4.10<sup>-5</sup>M Al: as deposited - (a) and after annealing at 400°C in forming gas for 1 hour (b). The markers correspond to 10 μm.

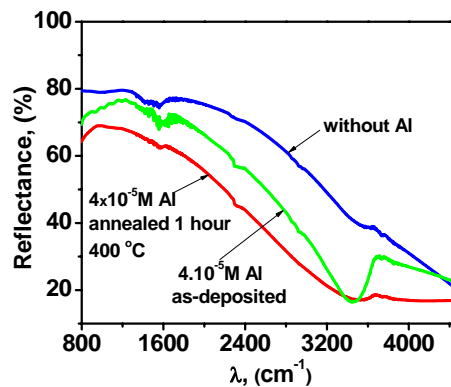
Figure 6 shows the spectra of reflectance in the visible and near IR region of undoped ZnO and doped ZnO:Al nanostructured films deposited in electrolyte with a different Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> concentration before (figure 6a) and after annealing (figure 6b). The corresponding spectrum of SnO<sub>2</sub> substrate is given as well. It is seen that the electrochemically deposited ZnO films have lower value of the

reflectance in the visible part of the spectra which make them suitable for application as a transparent antireflective coating in the solar cells.



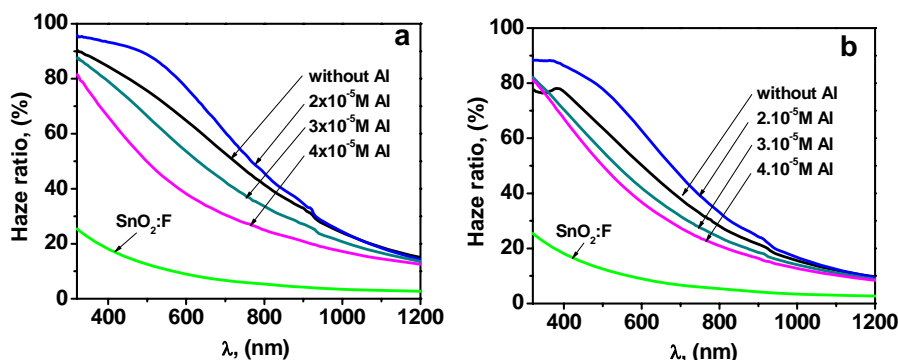
**Figure 6.** Spectra of reflectance of ZnO:Al films, deposited at different electrolyte concentrations of  $\text{Al}_2(\text{SO}_4)_3$  before (a) and after (b) annealing

In Figure 7 the reflectance spectra in the infrared region of undoped ZnO and doped ZnO:Al nanostructured films deposited in electrolyte with  $4.10^{-5}$  M  $\text{Al}_2(\text{SO}_4)_3$ , as deposited and annealed at  $400^\circ\text{C}$  for 1 hour are demonstrated.



**Figure 7.** Infrared reflectance spectra of undoped and Al-doped ZnO films before and after annealing.

The value of the reflectance decreases for Al-doped ZnO and this is more pronounced for the annealed sample. This behaviour could be explained by plasmon absorption by free electrons in the Al doped ZnO films. Spectra of haze ratio (H) of the undoped and doped with Al ZnO films, as deposited and after annealing in forming gas at  $400^\circ\text{C}$ , are shown in figure 8(a) and (b), respectively. The value of haze ratio of the sample with  $C_{\text{Al}} = 1.4$  at.% is higher than H of undoped ZnO film. The undoped ZnO and doped one with 1.4 at.% Al have values of the haze ratio in the visible region in the range of 60-90% which is much higher than that of  $\text{SnO}_2:\text{F}$  layer. With increasing of the Al concentration the haze ratio decreases in the all spectral region under investigation, however it is still higher than H of  $\text{SnO}_2:\text{F}$ . The annealing of the sample results in slight decrease of the haze (figure 8 b). Probably different combinations of the size of the nanostructures and roughness of the layers are a reason for differences in the haze ratio.



**Figure 8.** Spectra of haze ratio of ZnO samples prepared by electrochemical deposition undoped and doped with different concentration of Al: (a) – as deposited; (b) – annealed. The corresponding spectrum of SnO<sub>2</sub>:F is presented as well.

#### 4. Conclusion.

Detailed study of the structural and optical properties of nanostructured ZnO:Al layers deposited by electrochemical methods is performed. The speed of electrodeposition in the technological conditions used is calculated to be about 11 nm/min and follows linear dependence. It is observed that nucleation time does not depend on the process conditions. The concentration of the Al in the deposited ZnO layers increases with the concentration of the Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the electrolyte. The obtained films consist of nanosized particles with a shape of walls. It is observed that the size of the nanowalls increases with increasing of the Al concentration. The deposited films demonstrate low reflectance in the visible which makes them suitable of application as antireflective coating. The doped with Al ZnO layers have lower values of the reflectance in the IR spectrum than undoped ones due to the plasmon absorption by the free electrons. The electrodeposited ZnO layers on SnO<sub>2</sub>:F coated glass substrate have higher value of the haze ratio than the SnO<sub>2</sub>:F. AFM investigation shows an increase in the roughness with increase of Al concentration in the layers which is confirmed by the SEM study. The observed behaviour of the haze ratio, probably, is a consequence of alteration of nanowalls size and average roughness with increasing the doping concentration.

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