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ELECTROCHEMICALLY DEPOSITED NANOSTRUCTURES ZnO FILMS

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Abstract: Crystalline nanostructures such as nanowires have received increasing attention due to potential applications in solar cells, nanoscale electronic, optical and sensing devices, etc. This work reports the growth of nanostructured ZnO by the method of electrochemical deposition on glass substrates covered with a thin film of SnO_2 doped with F (SnO_2:F). ZnO nanostructured films are deposited by an electrochemical process using a three-electrode potentiostatic system with a saturated calomel electrode as reference electrode, from aqueous solution containing $ZnCl_2$, KCl and $Al_2(SO_4)_3$ in addition of flowing air for oxygen suply. The influence of the deposition parameters on the structural properties of the obtained ZnO films is studied by SEM and optical Spectroscopy. The SEM micrographs show that the ZnO films consist of hexagonal sliced nano-particles with average thickness 100-150 nm and planar size in the range of 1 – 2 μm in dependence on the deposition conditions. The diffuse reflection and haze ratio spectra in the visible region of light are presented as well.

Keywords: electrodeposition, nanostructures, ZnO:Al, annealing, optical characterizations

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1. Introduction

As a front electrode, the tin oxide doped with fluorine has been the most favored transparent conducting oxide for hydrogenated amorphous silicon solar cells. Compared with SnO_2:F, the textured aluminum doped zinc oxide thin film has the equivalent electrical properties, but also it has a lot of advantages, such as high stability of the electrical properties against hydrogen plasma, effective light trapping features, which are favorable to improve the performance of a-Si:H solar cell [1]. Many manufacturers use Al doped ZnO layers to produce different devices such as solar cells, nanoscale electronics, optical and sensing devices, etc. [2-5].

In this work results from the study of structural and optical properties of ZnO nanostructured films (undoped and doped with Al) grown by electrochemical deposition on glass substrates coated by SnO_2:F are reported.

2. Experimental

ZnO nanostructured films were deposited by an electrochemical process from slightly acid aqueous solution of $ZnCl_2$ (5. 10^{-3} M) and KCl (0.1 M) with pH 4.0 at two different temperature regimes (first – 60 min. at 60^0C and second – 15 min. at 60^0C followed by 105 min. at 80^0C) in flowing air for oxygen supply, using a three-electrode electrochemical cell and saturated calomel electrodes (SCE) as a reference electrode as described elsewhere [5]. In order to manipulate electro-physical properties of electrodeposited thin films stock solutions of $Al_2(SO_4)_3$ has been added to the electrolyte for gradual exchange of concentration of the doped (Al) in the deposits. SnO_2:F coated glass substrates were used as working electrode. Spectrally pure graphite rod electrodes were used as anode. The electrolyte was agitated by air bubbling or/and magnetic stirrer.

The deposition was carried out controlling the redox potential of the system. The equilibrium potential of Zn in the electrolyte ($E_{Zn2+/Zn}$) is -1.050 V vs. SCE. To prevent metal Zn deposition, the electrode potential should be more positive or not exceed this value. Usual deposition potential was kept between - 0.850 and – 1.000 V (vs. SCE). The deposition process of ZnO passes through chemical precipitation of Zn^{2+} on the electrode with OH^- groups which are formed from reduction of dissolved oxygen in the water. The indicator for activity of the dissolved oxygen is redox potential of the electrolyte. Oxygen saturation of the solution was maintained by air bubbling. Good quality ZnO films were obtained at a redox potential within the range between +0.300 and +0.400 V (vs. SCE). At a redox potentials higher than +0.4 V (vs. SCE) Zinc peroxide (ZnO_2) was formed on the samples with bad adhesion to the substrate. Duration of the ZnO deposition was 60 and 120 min. The thickness of the prepared ZnO films were between 0.50 and 2 μm. Different concentrations of the doping compound were explored: 2.10^{-4} M, 4.10^{-4} M, 6.10^{-4} M and 8.10^{-4} M $Al_2(SO_4)_3$.

The oxygen content in solution was determined by Dissolved Oxygen and Temperature Meter Hanna Instruments 9146. The surface morphology and the thickness of the deposited films were imaged under a Scanning Electron Microscope (SEM) Philips 515. The transmittance and the reflectance spectra, the diffuse transmittance and the diffuse reflectance were measured by a spectrophotometer Shimadzu UV-3600 in the range of 300 - 1800 nm employing a 60 mm integrating sphere in the case of diffuse reflectance.

3. Results and discussion

Time dependence of oxygen content and of redox potential is displayed in Figure 1. Figure 1a showed this dependence without aeration in solution and Figure 1b with aeration in to the same solution. In solution without aeration (Figure 1a) oxygen content increases with the time and after 15 min. oxygen level is stabilized, while redox potential decreases slowly. The oxygen content increases up to the 15-th minute and then slowly decreases in the case with aeration (Figure 1b). Redox potential in this case stays stable. Presented features looks like with a fair approach of accuracy and will be subject of further particularization.

Figure 2 demonstrate the SEM pictures of the electrochemically deposited ZnO layers. The ZnO layer (Figure 2a) is grown at 60^0C without addition of Al. When the film is deposited at higher temperature 80^0C (Figure 2b), the size of micro-crystals increases more than 10 times. Single crystallites are grown in foliate form with average planar size 2-3 μm and thickness about 100 nm. When $Al_2(SO_4)_3$ is added into the solution (Figure 2c) the edges of the crystallites become more rough probably due to additionally incorporated alumina (hydro)-oxides.

Spectra of diffuse reflection and haze ratio are shown in Figure 3. The corresponding spectrum for SnO_2:F is presented as well. The values of the diffuse reflectance of the as-grown ZnO layers are higher than those of SnO_2:F coated glass substrate. The layers doped with Al have higher value of diffuse reflection, than undoped ones (Figure 3a). This could be related to the presence of surface feathers with foliate form that act as scattered centre for the light. The layers deposited in presence of $Al_2(SO_4)_3$ in the

solution have higher diffuse reflection in the whole of the spectra region under investigation. Annealing results in increasing of diffuse reflection and haze ratio.

This could be explained with the increased roughness by growing of feathers with foliate shape as SEM images demonstrate (Figure 3b and 3c).

Transmittance spectra of samples ZnO with different concentration of $Al_2(SO_4)_3$ in solutions are shown in Figure 4. Layers with higher concentration of $Al_2(SO_4)_3$ demonstrate lower transmittance (in exception of sample 0.2ml $Al_2(SO_4)_3$, which is thinner than the others) (Figure 4a). The samples become more transparent after annealing at 400^0C for 1 hour in forming gas (figure 4b). Probably this is due to the decreasing of the average roughness of the films, as well, to the decreasing of number centres of the light scattering after annealing.

Mirror reflectance spectra of samples ZnO with added $Al_2(SO_4)_3$ in solution are shown in Figure 5. In the IR region ($\lambda > 1600$ nm) a slight decreasing of the reflectance is observed for the samples deposited in the electrolyte with added $Al_2(SO_4)_3$. After annealing the trend for decreasing of reflectance remains stable in IR region. Decreasing of the value of reflectance in the IR can be explained by increased absorption by free electrons as a result of Al doping, when the ZnO films are grown in electrolyte with $Al_2(SO_4)_3$.

4. Conclusion

ZnO films with rough structure and foliate shape are grown by electrochemical method. Spectra of reflectance demonstrate that doped layers, ZnO:Al, have lower value of the reflectivity in the range 1600-1800 nm compared to undoped samples. This decreasing tendency of the reflectivity in the IR region is evidence for increased absorption due to the absorption by free electrons. The doped with Al electro-deposited ZnO samples have higher value of the diffused reflection and haze ratio in comparison with the undoped ones. The deposited ZnO layers could be applied as light trapping structures in thin film solar cells.

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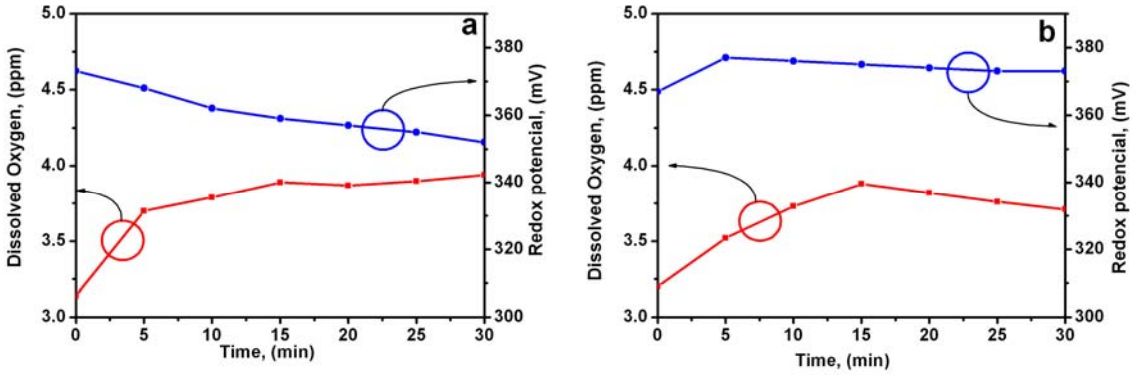

Figure 1

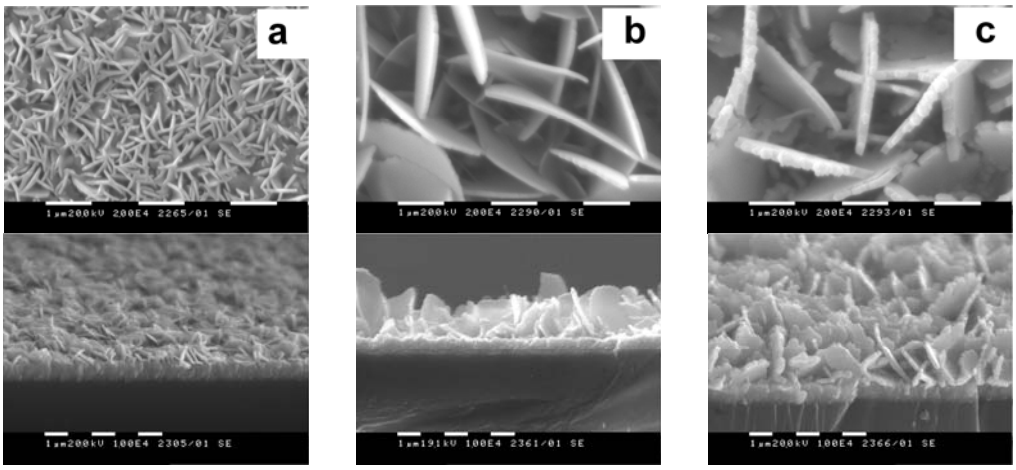

Figure 2

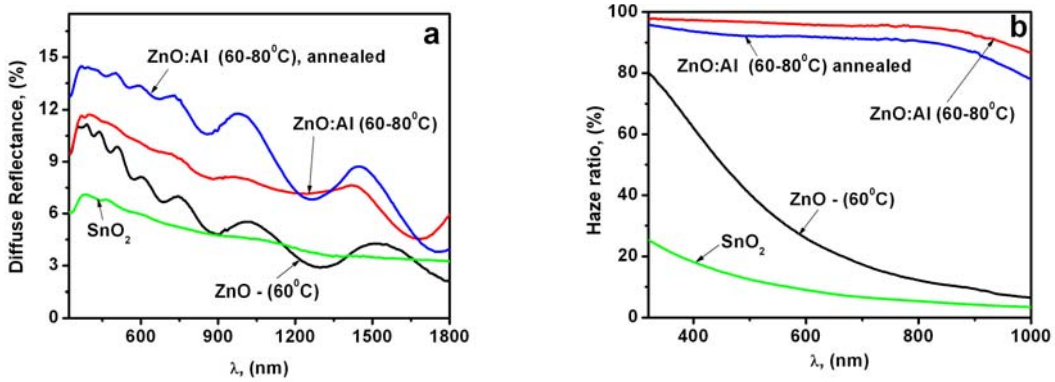

Figure 3

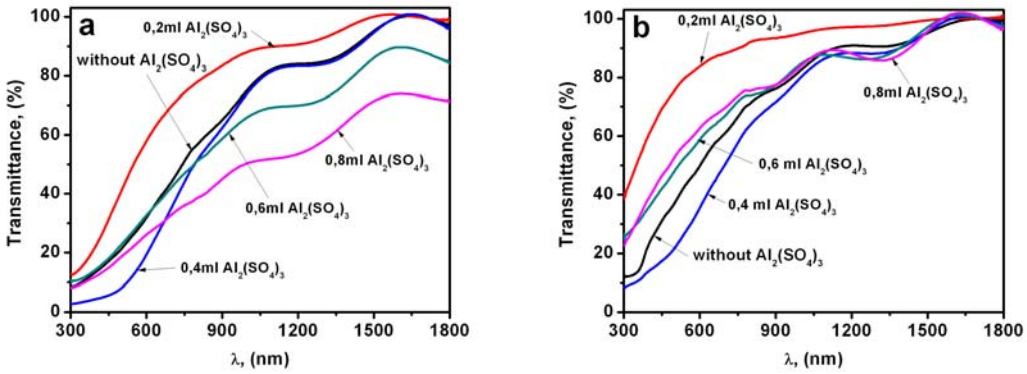

Figure 4

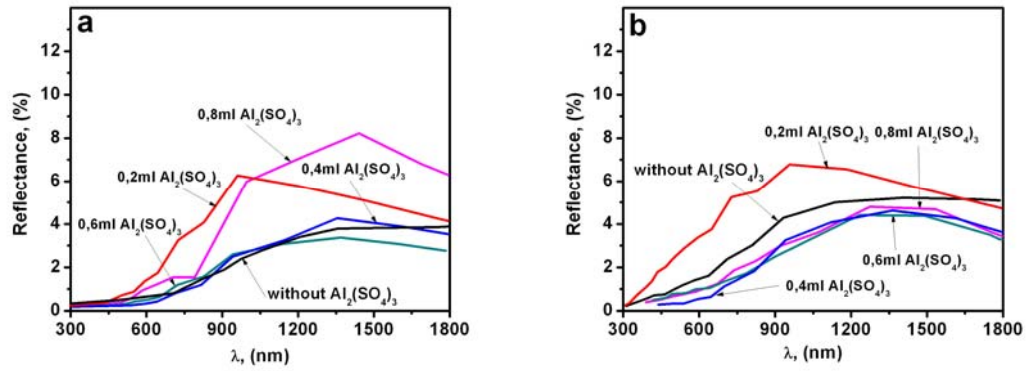

Figure 5

Figure captions

Figure 1. Dependence of the oxygen content in the electrolyte and redox potential on the time in the case, without aeration (a) and with aeration (b) of the solution.

Figure 2. The SEM of samples obtained by electrochemical deposition at 60^0C (a), samples obtained by electrochemical deposition at 60^0C + 80^0C (b) and obtained by electrochemical deposition at 60^0C + 80^0C with adding of $Al_2(SO_4)_3$ in the electrolyte and annealed (c). First row represents a surface view and the second row a cross-section view.

Figure 3. Spectra of diffused reflection (a) and haze ratio (b) of ZnO samples prepared by electrochemical deposition without and with Al ions in the electrolyte The corresponding spectra of SnO_2:F are given as well.

Figure 4. Spectra of transmittance of samples ZnO prepared by electrochemical deposition without and with added $Al_2(SO_4)_3$ in the electrolyte before (a) and after annealing (b).

Figure 5. Spectra of reflectance of samples ZnO prepared by electrochemical deposition without and with added $Al_2(SO_4)_3$ in the electrolyte before (a) and after annealing (b).