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Preparation of ZnO nanowires by electrochemical deposition

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Abstract

This work reports the results from the synthesis of nanostructured ZnO thin films via electrochemical deposition on glass substrates coated with F doped SnO_2. The influence of the deposition parameters on the properties of the obtained ZnO films was studied. The Raman spectra of the ZnO films contain the typical for ZnO vibrational bands. The scanning electron microscope micrographs demonstrate that the films consist of ZnO nanowires. Growing of ZnO in the conditions with addition of H_2O_2 in lower concentration and without flowing air results in larger grain formation. The ZnO layers demonstrate high diffuse reflection.

Keywords: morphology of films; nanowires; scanning electron microscopy; Raman spectra; diffuse reflection.

1. Introduction

Crystalline nanostructures such as ZnO nanowires deposited on a substrate have received increasing attention due to potential applications in solar cells, nanoscale electronics, optical and sensing devices, etc [1,2]. Different physical and chemical methods have been applied for the synthesis of nanowires [3]. Since, however, the preparation conditions determine to a great extent the properties of the nanowires, their fabrication with predetermined size and perfect morphology is still a challenging task.

In this work preliminary results on the preparation of ZnO nanostructred films by electrodeposition on glass substrate coated with SnO_2 doped with F (SnO_2:F) are reported. The influence of some technological parameters such as improving of the conditions for oxidation on the structural properties of the obtained ZnO films was studied by scanning electron microscope imaging, Raman spectroscopy, total transmission and diffuse reflection measurements.

2. Experimental

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ZnO nanostructured films were deposited by the electrochemical process from acid aqueous solution of $ZnCl_2$ (5 mM) and KCl (0.1 M) with pH = 4.0 at a temperature of 60^0C in flowing air and/or addition of H_2O_2 as precursors using a three-electrode electrochemical cell and saturated calomel electrodes (SCE) as reference electrodes. SnO_2 doped with F coated glass substrates were used as working electrode. A spectrally pure graphite electrode was used as anode. The solution was stirred either by air bubbling or by a magnetic stirrer. 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. Good quality ZnO films were obtained at a redoxy potential within the range between +0.30 and +0.40 V vs. SCE. Oxygen saturation of the solution was maintained either by air bubling or adding of hydrogen peroxide. The duration of the ZnO deposition ranged between 30 and 60 min. The thickness of the films was 1.5 – 2.5 μm. Different regimes (see Table 1) were explored – with (samples A and B) and without flowing air (samples C and D) during the electrochemical deposition. Samples B, C and D are synthesized with addition of H_2O_2 of two different quantities.

Table 1. The deposition conditions of different samples.

Samples	A	B	C	D
Conditions	Flowing air	Flowing air and lower H_2O_2 concentration	Lower H_2O_2 concentration; Magnetic stirrer	Higher H_2O_2 concentration; Magnetic stirrer

The surface morphology and the thickness of the deposited films were imaged under a Scanning Electron Microscope (SEM) Philips 515. The structure of the deposited ZnO films was studied by Raman spectroscopy. The Raman spectra were recorded with a Horiba Jobin Yvon LabRAM HR800 spectrometer. The total transmission and diffuse reflection measurements were performed with a Shimadzu UV-3600 spectrometer employing a 60 mm integrating sphere.

3. Results and discussion

Figure 1 shows the SEM micrograph of the SnO_2:F film deposited on glass substrate. It is clearly seen a typical surface tetrapodlike morphology of the SnO_2:F film with relatively uniform grain size. The scanning electron micrographs of the surface and growth morphologies of the ZnO films on SnO_2:F/glass substrate under the conditions of flowing air only are displayed in figure 2 a and b, respectively. The micrographs demonstrate that the ZnO films consist of nanowires grown perpendicularly to the substrate. The ZnO has column structure with wire diameter within the 200 - 500 nm range. The scanning electron micrographs of the sample B deposited under the conditions with added H_2O_2 with lower concentration and using flowing air is displayed in figure 3. It is clearly seen that the surface morphology changes in comparison with the sample deposited without H_2O_2 in the electrochemical solution. The size of the wires increases - they are in the 500 - 1000 nm range and grow in different directions, not only perpendicularly to the substrate, as it is in the case of sample A (figure 2). Figure 4 displays the SEM picture of the sample C deposited with lower H_2O_2 however without flowing air. In this case the shape of the grains is similar to that of sample B, but the grain size increases and is in the range of 1-1.2 μm. The surface morphology of the ZnO

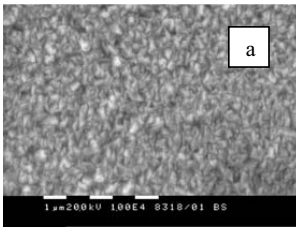
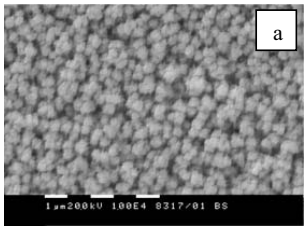


Figure 1. SEM image of the surface of the SnO_2:F film deposited on glass substrate.



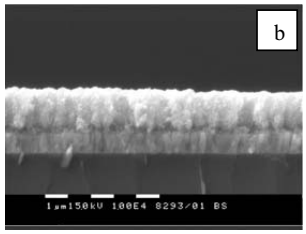


Figure 2. SEM image of the surface (a) and cross section (b) of the ZnO nanostructured film deposited on SnO_2:F coated glass substrate in the conditions with flowing air only (sample A) .

synthesized in the conditions with higher H_2O_2 concentration and without flowing air is shown in figure 5. The morphology changes dramatically. The higher H_2O_2 concentration affects both the shape and dimensions, displaying sharp, nonoriented nanowires with typical mean diameters of about 0.5-1 μm.

The results of the study of the morphology of electrochemically prepared ZnO layers show that the synthesis in these conditions results in deposition of ZnO layers with large grains and the orientation of the wires different from only perpendicular to the substrate. The presence of H_2O_2 in the electrolyte and using flowing air create conditions for better oxidation of the Zn ions. Growing of ZnO in the conditions with addition of H_2O_2 in the lower concentration and without flowing air results in larger grain formation. Possibly the conditions of higher oxidation during the electrochemical deposition of ZnO slow down the growth rate of the nanowires.

The structure of the ZnO films was studied by Raman spectroscopy. Raman spectra of the deposited ZnO films are shown in Figure 6. For comparison the Raman spectrum of the SnO_2:F film on glass substrate is given as well. The strongest SnO_2 band at 634 cm^{-1} (A_{1g}) [4] is clearly visible in the spectra. Typical bands for ZnO at 437 cm^{-1} (E_2), 407 cm^{-1} (E_1), 574 cm^{-1} (A_1) are observed [5]. The best pronounced spectrum is that of sample D prepared in the conditions with higher H_2O_2 concentration and without flowing air. X-ray diffraction measurements are in progress to identify the crystalline orientation of the deposited ZnO films.

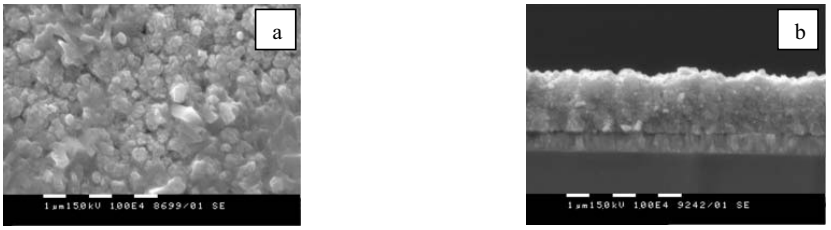


Figure 3. SEM image of the surface (a) and cross section (b) of the ZnO nanostructured film deposited in the conditions with lower H_2O_2 concentration with flowing air (sample B).

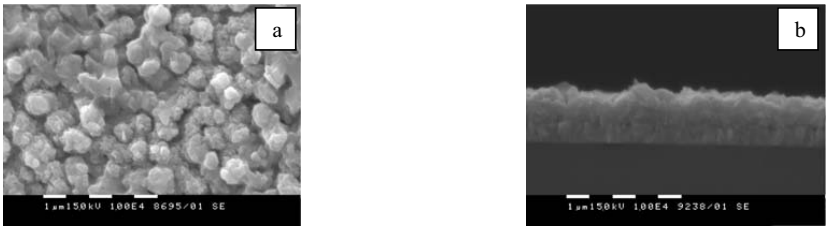


Figure 4. SEM image of the surface (a) and the cross section (b) of the ZnO nanostructured film deposited in the conditions with lower H_2O_2 concentration without flowing air (sample C).

Figure 5. SEM image of the surface (a) and the cross section (b) of the ZnO film deposited in the conditions with higher H_2O_2 concentration and without flowing air (sample D).

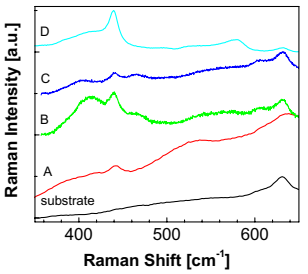


Figure 6. Raman spectra of the SnO_2:F substrate and the ZnO samples as indicated in the figure.

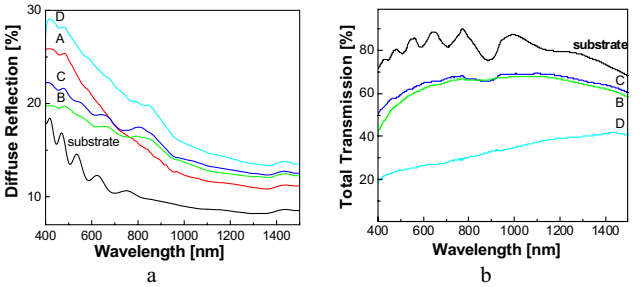


Figure 7. Diffuse reflection (a) and total transmission (b) spectra of the SnO_2:F substrate and the ZnO samples as indicated in the figure.

In figure 7 the diffuse reflection (a) and total transmission (b) spectra of the substrate and the ZnO samples are shown. The deposition of the ZnO nanorods predictably increases the diffuse reflection of the samples nearly twice in comparison with the SnO_2:F coated glass substrate. Samples B and C, which are similar in structure, have comparable diffuse reflection spectra and sample C, the one with larger grains, exhibits slightly higher values of the diffuse reflection. The highest diffuse reflection is demonstrated by sample D, which has the roughest surface. The values of the measured diffuse reflection are comparable to those measured for nanostructured ZnO [6]. The total transmission is not so high. This is not significant if the films are used in a back contact of solar cells.

The sheet resistance of the structure SnO_2/ZnO is high (about 50-100 Ω/□). The deposition of the Al and B doped ZnO films as well as the deposition of ZnO on metal coated glass substrates are in progress.

4. Conclusion

In this work the surface morphology and Raman spectra of electrochemically deposited ZnO films were studied. It was observed that the ZnO films with larger grain size were obtained in the conditions providing a lower oxidation of Zn ions - lower H_2O_2 concentration and without flowing air during the electrochemical deposition. The ZnO layers demonstrated higher diffuse reflection in the near IR and visible range of the spectrum compared to the SnO_2 doped with F coated glass substrate. ZnO layers with such surface morphology and after appropriated doping could be applied as a back contact for increased light trapping in thin film solar cells.

Acknowledgements

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References

[1] Schropp, R. E. I., H. Li, R. H. Franken, J. K. Rath, C. H. M. Van der Werf, J. W. A.Schüttauf, R. L. Stolk (2008) Thin Solid Films 516, 6818-6823.
[2] Sun, Z.-P.,. L. Liu, L. Zhang, D.-Z. Jia (2006) *Nanotechnology* 17, 2266-2272.
[3] Pauzauskie,P.J., P.Yang (2006), Nanowire photonics, *Materials Today* 9, 36-40.
[4] Abello, L., B. Bochu, A. Gaskov, S. Koudryavtseva, G. Lucazeau, M. Roumyantseva, (1998) J. Solid State Chem. 135, 78-85.
[5] Damen, T. C., S. P. S. Porto, B. Tell (1966) *Phys. Rev.* 142, 570-574.
[6] Keis, K., A. Roos (2002) *Optical Materials* 20, 35–42.