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Preparation of wire structured ZnO films by electrochemical deposition

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Abstract. This article reports the synthesis of wire structured ZnO by electrochemical deposition on a glass substrate covered by thin film of ITO or SnO₂ doped with F (SnO₂:F) and on a carbon tissue. The influence of the structure of the transparent conductive films on the structural properties of the ZnO films obtained was studied by SEM and Raman spectroscopy. The results show that the films have a columnar structure with grain size of about 200-500 nm. The films deposited on the SnO₂:F coated glass substrate have better structural properties. Pillar structure is observed on the surface of the fiber of the carbon tissue.

1. Introduction
Crystalline pillar structures such as ZnO wires 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 ZnO thin films with wire structure [3]. Since, however, the preparation conditions determine to a great extent their properties, their fabrication with predetermined size and perfect morphology is still a challenging task.

In this work preliminary results about the preparation of ZnO films with pillar structure by electrodeposition on different substrates: ITO or SnO₂ doped with F (SnO₂:F) coated glass and carbon tissue are reported. The influence of the type of the substrates on the surface morphology and the structural properties of the deposited ZnO films are investigated.

2. Experimental
ZnO films were deposited by an electrochemical process using a three-electrodes potentiostatic system with saturated calomel electrodes as reference electrodes. InSn1-xO₂ (ITO), SnO₂ doped with F (SnO₂:F) coated glass substrates and carbon tissue (for bio-medical applications) were used as substrates and working electrodes. The ZnO films were deposited from an aqueous solution containing ZnCl₂ 5×10⁻³ M, KCl 0.1 M, with pH = 4.00 and using an air flow. The electrochemical deposition took a place at 60⁰C. The deposition process was carried out potentiostatically at a potential of −0.9 V vs. the saturated calomel electrode.

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The surface morphology and the thickness of the deposited films were determined using scanning electron microscopy (SEM) and the structure of the deposited ZnO films was studied by Raman spectroscopy. The Raman spectra were recorded by a Horiba Jobin Yvon LabRAM HR800 spectrometer using a 1800 l/mm grating and a HeNe laser for excitation. The samples were placed under the 100X achromatic objective of a BX41 microscope and measured in back scattering configuration.

3. Results and discussion
Figures 1 a and b show SEM micrographs of the surface morphology of the ITO deposited on a glass substrate (a) and of the ZnO wire structured film deposited on an ITO coated glass substrate. The cross sectional images of the ZnO films grown on the ITO surface taken at 0° and 30° are demonstrated in figures 2 a and b, respectively. The ITO film is about 1 μm thick. It exhibits columnar grains with a diameter of less than 200 nm grown with their c-axis perpendicular to the substrate surface. The interface between the ITO and the grown ZnO film is rough. The ZnO film has a columnar structure with well-defined grains with size between 200 and 500 nm. The surface of ZnO films exhibits high porosity.

![Figure 1. SEM images of the surface of the ITO layer on a glass substrate (a) and of a ZnO wire structured film on an ITO coated glass substrate (b).](image1)

![Figure 2. SEM cross-section taken at 0° (a) and at 30° (b) of a ZnO layer on ITO coated glass substrate.](image2)

Figure 3 a and b demonstrate the surface morphology of the SnO₂:F and the electrodeposited ZnO film on the SnO₂:F coated glass substrate, respectively. The SnO₂:F film surface shows tetrapodlike morphology with a relatively uniform grain size (figure 3 a). Cross-section SEM micrographs of a ZnO film deposited on a SnO₂:F /glass substrate taken at 0° and at 30° are displayed in figures 4 a and b, respectively. The interface between SnO₂:F and the ZnO film grown on it is very homogeneous and relatively smooth compared with that in the case of using an ITO coated glass substrate. The ZnO film is porous, has a columnar structure with grain diameter of about 200-500 nm as in the case of the film grown on ITO coated glass (figure 1 b and figure 2 b), but is denser.
Figure 3. SEM images of the surface of SnO$_2$:F (a) and of ZnO wire structured film on a SnO$_2$:F coated glass substrate.

Figure 4. SEM cross-section taken at 0° (a) and at 30° (b) of a ZnO layer on SnO$_2$:F coated glass substrate.

The structure of the ZnO film deposited was studied by Raman spectroscopy. Raman spectra of the ZnO films deposited on ITO and SnO$_2$:F coated glass substrate are shown in figures 5 and 6, respectively. For comparison, the Raman spectra of the ITO and SnO$_2$:F films on glass substrate are given as well. The strongest SnO$_2$ band at 634 cm$^{-1}$ ($A_{1g}$) [18] is clearly visible in all spectra. Typical bands for ZnO at 437 cm$^{-1}$ ($E_2$), 407 cm$^{-1}$ ($E_1$), 574 cm$^{-1}$ ($A_1$) are observed [19]. The Raman bands in the spectrum of the ZnO film deposited on SnO$_2$:F coated glass substrate are better expressed and their Full Width at Half Maximum (FWHM) is smaller which is an indication for better structural quality of

Figure 5. Raman spectra of a ZnO film deposited on an ITO coated glass substrate (a). For comparison the Raman spectrum of an ITO film deposited on a glass substrate is given too (b).

Figure 6. Raman spectra of a ZnO film deposited on a SnO$_2$:F coated glass substrate (a). For comparison, the Raman spectrum of a SnO$_2$:F film deposited on a glass substrate is given too (b).
the film. This conclusion is confirmed by the observations from SEM micrographs. It is reasonable to assume that the tetrapode structure and the flatter surface of the SnO$_2$:F films create conditions for growth of ZnO with better structural quality.

ZnO pillars were deposited on the surface of a carbon tissue used for bio-medical applications. The SEM images of the deposited ZnO pillars are demonstrated in figure 7. The pillars have a size of about 200-500 nm and growth perpendicular to the surface of the tissue fibers.

Figure 7. SEM of ZnO pillars on a carbon tissue surface. Note the different magnification of the two pictures.

4. Conclusion
We studied the structural properties of wire structured ZnO films deposited by electrochemical process using a three-electrodes potentiostatic system with saturated calomel electrodes as reference electrodes on two types of glass substrates coated with ITO and SnO$_2$:F, respectively. The possibility to deposit ZnO with pillar structure using carbon fibered tissue as a substrate is demonstrated as well. The structure was investigated by SEM and Raman spectroscopy. It was shown that the structure of the substrates influences the structure of the electrodeposited ZnO films. The films have a columnar structure with grain size of about 200-500 nm. Denser ZnO films with better structural quality were deposited using the SnO$_2$:F coated glass as a substrate. The specific tetrapod structure and more homogeneous surface morphology of the SnO$_2$:F films created more favorable conditions for ZnO films growth.

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References