Sol-gel preparation of semiconductive oxides 1-D nanostructures on glass substrate

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Abstract. This paper presents the microstructure, optical and electrical properties of zinc oxide nanorodlike structures deposed on glass substrate by dip-coating method. The crystalline phases and morphology of 1-D nanostructured materials have been investigated using X-ray diffraction and scanning electron microscopy (SEM) techniques. The UV-VIS-NIR spectra and the electrical properties were also measured.

Keywords: zinc oxide, 1-D nanostructure, nanorod-like, sol-gel, UV-VIS-NIR spectra, electrical properties.

1. Introduction

The electrical and optical properties of nanostructured semiconductive oxide materials have attracted much researchers attention for their application in the fabrication of microelectronic and optoelectronic devices or sensors. ZnO is a low cost and non toxic excellent semiconductor material, which has attracted a continuously increasing attention in the last decade, due to a wide application range. A wide band gap semiconductor, ZnO-based nanostructures (thin films, nanotubes, nanowires, nanorods, etc) are considered as key components for a wide range of device applications in transparent electronics, one of the most advanced topics of our days. In these devices, the wide band gap semiconductors play the key role as passive or active component. Passive components are dielectric oxide in electronic devices or transparent electrical conductors in liquid crystal displays, solar cells, and optical sensors. As active materials (truly electronic semiconductor), the transparent oxide thin films are used in light emitting diodes (LEDs), lasers, UV sensors, transparent thin film transistors (TTFTs), etc [1-7].

The sol-gel method is one of the most efficient methods for the preparation of nanostructured metal oxides [1-4] and represents a simple and much low-cost processing alternative to the vacuum deposition techniques [5-7].

This paper presents the microstructure, optical and electrical properties of ZnO nanorodlike structures deposed on glass substrate by dip-coating method. The crystalline phases and the morphology of 1-D nanostructured materials have been investigated using X-ray diffraction and scanning electron microscopy (SEM) techniques. The UV-VIS-NIR spectra and the electrical properties were also measured.

2. Experimental

The sol used for the preparation of ZnO 1-D nanostructures was prepared by dissolution of zinc acetate dehydrate (99.5%) in ethanol. The nanoscale grains were deposed on soda-lime-glass substrates by dip-coating technique with withdrawal speed of 10 and 15 cm/min, at RT and RH conditions. After each layer deposition, the gel film was stabilized by pre-heating at 400^{o}C. The procedure was repeated 4 times and followed by post-heating in air at 500^{o}C.

The profile of the nanorodlike grains was observed using a Sloan Dektak 3D surface profilometer.

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The XRD patterns of the samples were recorded at room temperature using a Rigaku diffractometer (model RAD IIA), with CuKα radiation.

The morphology on the top surface of the deposed 1-D nanostructured grains on glass substrate was analyzed using a Hitachi S-1400 field emission microscope.

The optical transmittance was measured using a UV-VIS-NIR double beam spectrophotometer (UV-3100 PC, Shimadzu) in the wavelength range from 200 to 2500 nm.

The electrical properties were measured at room temperature in dark (special chamber) using PVD-deposed Al electrodes and a Keithley 6517 A electrometer.

3. Results and Discussions

The XRD patterns of ZnO nanostructured samples (Fig. 1) show, in the 2θ range 30-40degrees, the most important three peaks of hexagonal würtzite type ZnO structure. In contrast with the normal random orientation hexagonal structure of ZnO powder, characterized by (101) most intense peak, these patterns show a dominating (002) peak indicating a high preferential c-axis orientated type crystalline structure of the 1-D nanostructured grains.

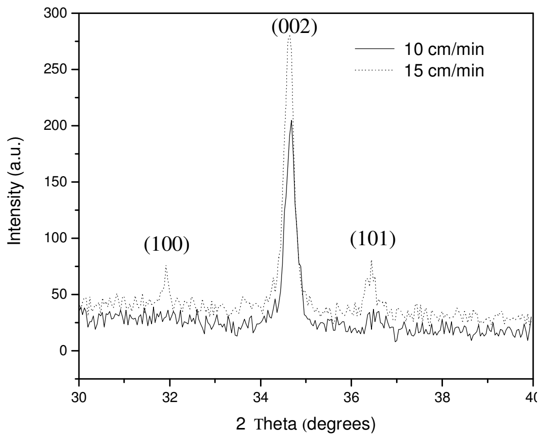

Fig 1. XRD patterns of ZnO nanostructures deposed at different withdrawal speed.

When the withdrawal speed deposition increases from 10 to 15 cm/min, the others peaks of würtzite type crystalline structure, (101) and (001), can be also observed in the XRD pattern, corresponding to grains with other than c-axis orientation structure. These results are confirmed by the morphological investigation, using scanning electron microscopy (SEM), presented in Figure 2.

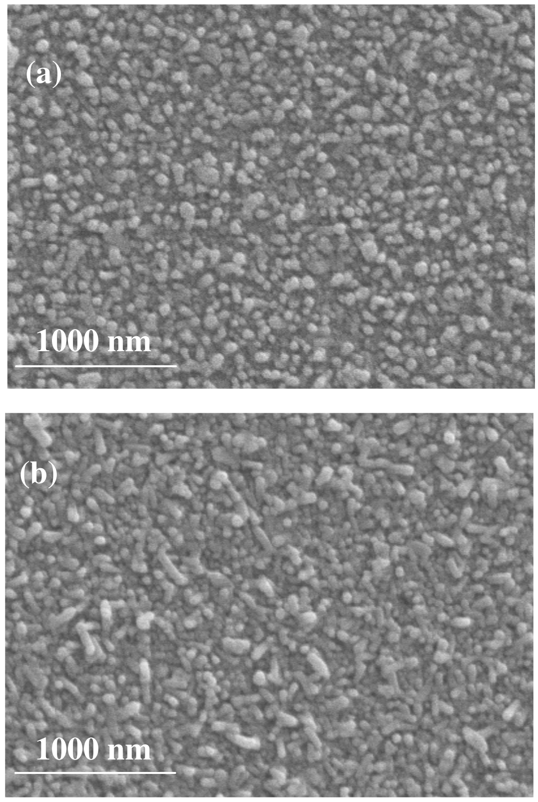

Fig. 2. SEM images on the top surface of ZnO nanorodlike structures deposed with different withdrawal speed: 10 cm/min (a), 15 cm/min (b).

The SEM images (Fig. 2) show the formation of nanorodlike grains morphology structure and confirm for the most of the grains an normal to the substrate orientation growth. The aspect ratios (length divided by width) of nanorods ranges from 3 and 10. Especially the length of the grain depends on the value of the withdrawal speed deposition. The length of rods increases when the withdrawal speed increases from 10 to 15 cm/min. An average value of about 230 nm was observed for the sample deposed at 15 cm/min (Fig. 3). In the same time, one can observe a lower normal to the substrate orientated growth of the nanorod, when the withdrawal speed increases (Fig. 2 b).

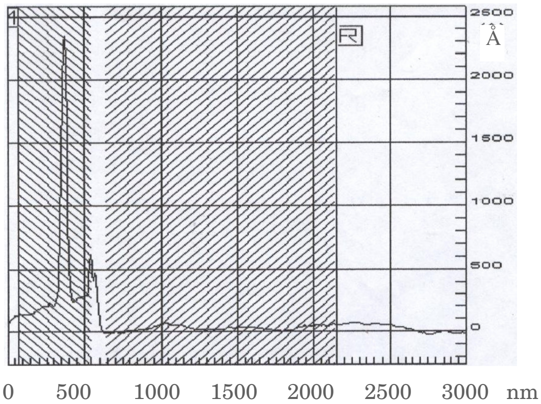

Fig. 3. The profile of one nanorodlike ZnO grain from the 1-D nanostructure deposed at 15 cm/min.

Figure 4. shows the room temperature optical absorbance spectra of the c-axes orientated ZnO 1-D nanostructures. A sharp adsorption edge at 364.7 cm^{-1} was observed from both samples deposed at 10 and 15 cm/min.

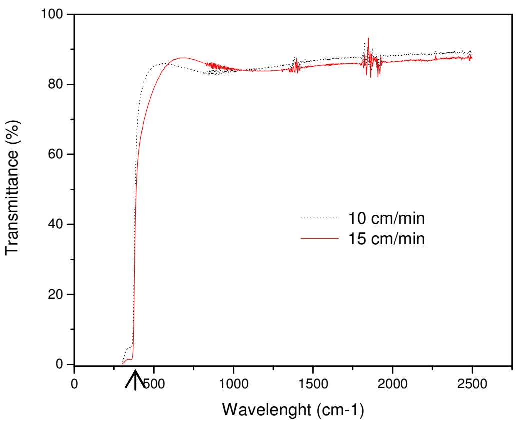

Fig. 4. Optical transmittance spectra of ZnO nanostructures deposed at withdrawal speed.

The absorption spectrum also reveals that the nanorod-like structures are highly transparent (82-87%) in the visible and near-IR regions.

The electrical measurements show resistivity values of $1.97.10^{-3}$ and $2, 47.10^{-3}$ Ωcm for samples deposed at 10 and 15 cm/min, respectively, after thermal treatment in reducing atmosphere.

4. Conclusions

ZnO nonorod-like nanostructures deposed on glass substrate with quasi well-aligned grains and a preferred c-axis wurtzite type structure were prepared by sol-gel dip-coating technique.

All the 1-D nanostructures are high transparent and conductive. Optical transmittance between 82-87% within the visible and near-IR wavelength region and resistivity values around $2\ 10^{-3}$ Ωcm have been obtained after special thermal treatment.

The experimental work will be continued in order to establish the optimum experimental conditions for vertically aligned growth of ZnO nanorods and nanowires structures.

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