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ZnO-BASED NANOSTRUCTURED MATERIALS BY CHEMICAL METHODS

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ABSTRACT

The ZnO-based nanostructured materials are considered as key materials for nanodevices fabrication. This paper presents the morphology, microstructure, optical and electrical properties of ZnO nanoparticles, ZnO nonorods with UV and ozone sensing response at room temperature and Al:ZnO TCO-type thin films, all prepared by sol-gel method.
Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-Ray Diffraction techniques were used for morphological and microstructural characterization of ZnO-based nanostructured materials. The nanoparticles size was studied by Light Scattering Measurements. The UV-VIS-NIR optical spectra were recorded and the electrical properties were investigated using Hall effect measurements. The variations of the electrical resistivity with gas atmosphere and UV radiation were measured for ZnO thin films, using a special set-up.

KEYWORDS: zinc oxide, nanoparticles, nanorods, thin films, chemical method.

1. INTRODUCTION

Zinc oxide is a well-known semiconductor material with a wide direct band gap (3.37 eV) and a large exciton binding energy of 60 meV at room temperature. It is used in many applications such as gas sensor devices, laser, optoelectronic devices and surface acoustic wave devices (SAW) [1]. ZnO nanostructured materials, like nanoparticles, nanowires, nanorods, nanobelts or thin films, have increased interest for short wavelength light emitters and transparent electronics [2].

Zinc oxide nanoparticles can be prepared by different chemical methods such as: hydrothermal [3], spray pyrolysis [4], precipitation or sol-gel [5, 6, 7, 8]. From these methods, the sol-gel method shows many advantages over the other techniques, such as simplicity and low equipment cost [9].

This paper presents the morphology, microstructure, optical and electrical properties of ZnO nanoparticles, nonorods and conductive thin films prepared by sol-gel method. The variation of the electrical resistivity with the gas atmosphere and UV radiation were measured for ZnO thin films, using a special set-up.

2. EXPERIMENTAL

ZnO-based nanostructures were prepared by sol-gel method. The solution used for the preparation of nanostructured materials, both nanoparticles, nonorods and thin films, was obtained using zinc acetate dehydrate (99.5%) and ethanol. The thin films and nanorods were deposed on soda-lime-glass substrates by dip-coating technique with different withdrawal speed in the range 1-20 cm/min, three layers, 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. ZnO nanoparticles were prepared by a modified sol-gel method proposed by Spanhel and Anderson [1, 5, 6], which offers a simple route to prepare quantum size ZnO particles.

The investigation of the particles shape, size and size distribution is based on *Light Scattering Methods* (DLS).

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

The morphology and surface roughness of ZnO seed-layer film was observed by the atomic force

microscopy (AFM) using a silicon nitride tip in contact mode.

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 a Keithley 6517 A electrometer and PVD-deposed Al electrodes.

The resistivity variation during the photoreduction of the film directly irradiated in vacuum by the UV light of a mercury pencil lamp with an average intensity of 4 mW/cm^2 at 254 nm for 20 min and then the exposed to an oxidative ozone atmosphere was measured, using a special set-up. An electric field of 50 V/cm was applied to the film sample and the electrical current was measured.

3. RESULTS AND DISCUSSION

3.1. ZnO Nanoparticles

The size distribution of the sol-gel prepared nanoparticles, dispersed in a solvent and measured by light scattering methods, are presented in Fig. 1. We investigated the effect of solvent on the degree of NPs dispersion, so on NPs size.

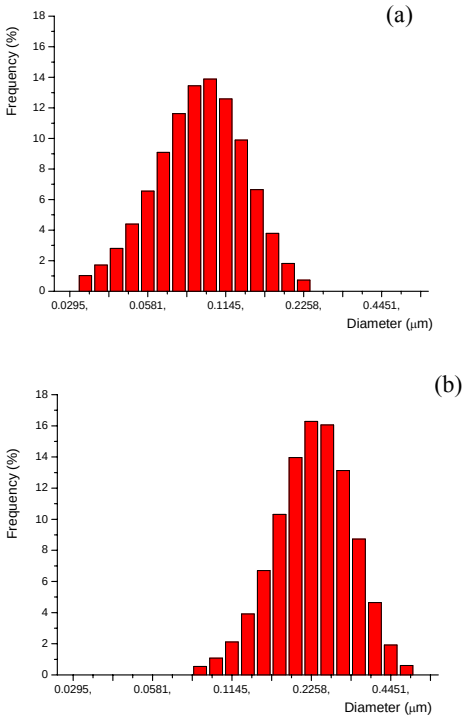

Fig. 1. Histograms of ZnO nanoparticles dispersed in n-butanol (a) and ethanol (b)

As observed in Fig 1, the size of NPs is affected by the solvent; higher hydrophobic catena of the alcohol used as solvent, higher distance between nanoparticles, higher degree of dispersion and smaller particle size (Fig. 1a).

The XRD patterns of ZnO nanoparticles (Fig. 2) show four peaks that can be indexed for wurtzite type hexagonal structure of ZnO. No peaks from other phase of ZnO or impurities are observed, suggesting that high-purity ZnO phase was obtained. The crystallite size, calculated using the Debye–Sherrer formula is 14,8 nm.

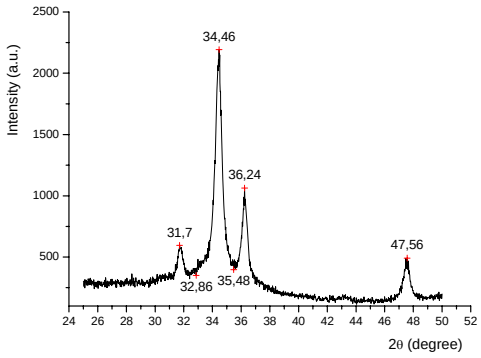

Fig. 2. X-ray diffraction pattern of sol-gel prepared ZnO nanoparticles

Fig. 3 shows the atomic force microscopy image of spin-coated ZnO nanoparticles on silicon substrates, using n-butanol-based dispersion. The as-deposed particles were annealed at 400°C for 1 hour. Small size diameter (~50 nm) and a relatively uniform shape of the particles dispersed on the substrate can be observed.

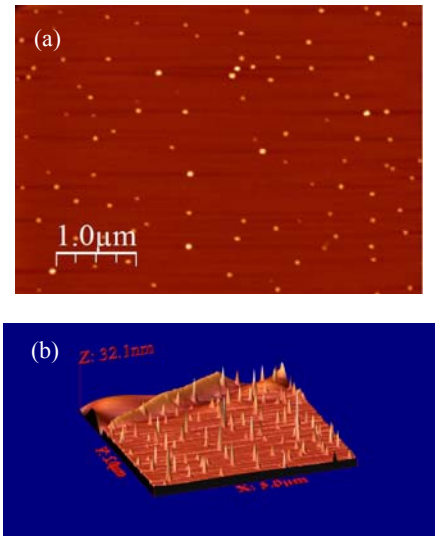

Fig. 3. AFM images of ZnO nanoparticles dispersed on silicon substrate, top image (a) and 3D image (b).

3.2. ZnO Nanorods

ZnO nanorod-like morphology, deposed on glass substrate by dipping at 20cm/min, can be observed in Fig. 4.

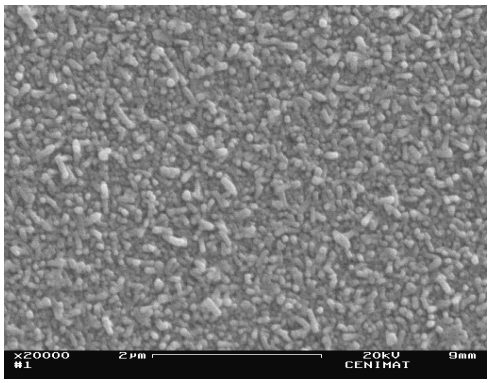

Fig. 4. SEM images on the top surface of sol-gel ZnO nanorod-like structures.

The aspect ratios (length divided by width) of the nanorods ranges from 3 and 10. Especially the length of the grain depends on the value of the withdrawal speed deposition. An average value of about 230 nm was observed for the samples deposed at 20 cm/min (Fig. 4).

The XRD pattern of the noanorods like sample (Fig. 5) show a dominating (002) peak indicating a high preferential c-axis orientated wurtzite type crystalline structure of the 1-D nanostructured grains. Higher withdrawal speed, higher nanorod length and a slight lower preferential c-axis orientation of the nanorod, also confirmed by the SEM data.

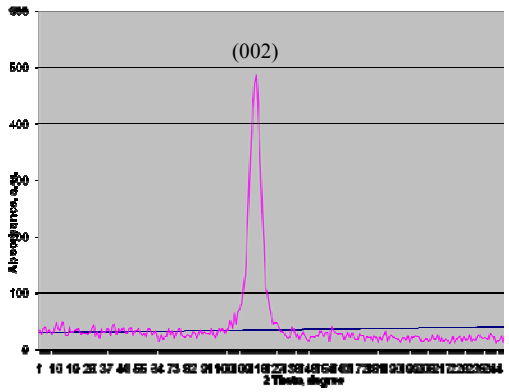

Fig. 5. XRD pattern of ZnO 1-D nanorod-like structure deposed at 15 cm/min.

The absorption spectra (Fig. 6) revealed that the nanorod-like vertical array 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 20 cm/min, respectively.

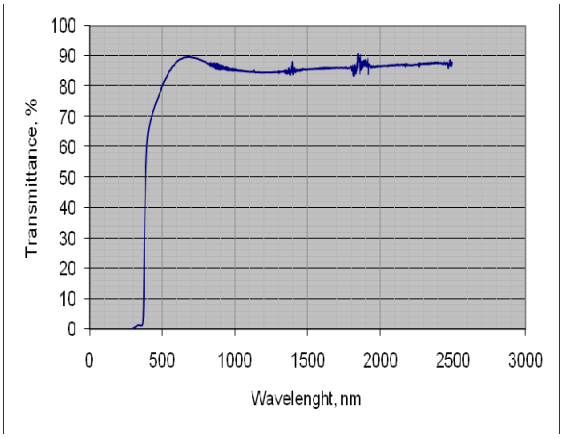

Fig. 6. Optical transmittance spectra of ZnO 1-D nanorod-like structure deposed at 15 cm/min.

Fig. 7 presents the UV photoreduction-ozone reoxidation cycles of the nanorod-like structured film. A reversible resistivity variation response to over three orders of magnitude was observed during UV irradiation followed by re-oxidation in ozone atmosphere.

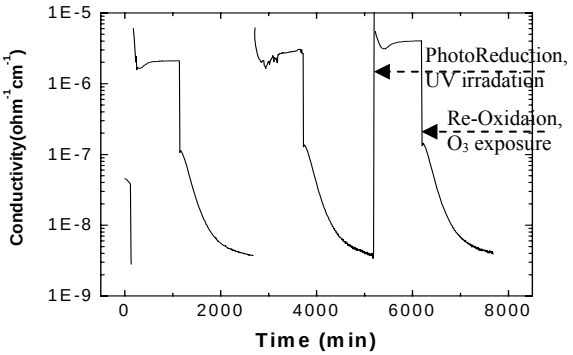

Fig. 7. Photoreduction - ozone reoxidation cycles of ZnO 1-D nanorod like structure deposed at 15cm/min.

Ticker films (more than 500 nm) showed a two order of magnitude smaller response, suggesting that an ultra-thin surface layer is mainly contributing to the photoconductivity in polycrystalline ZnO films, and not the bulk conductivity.

3.3. Al:ZnO thin films

Transparent and conductive ZnO:Al thin films on Soda-lime-glass and Corning 1737 substrates were prepared by sol-gel non-alkoxide route using zinc acetate and aluminium chloride as raw materials and spin-coating or dip-coating techniques for film deposition. These films doped with 2 wt.% Al present a compact structure with quasi-regular grains, in both shape and size and an average grain size value of about 60 nm (Fig. 8).

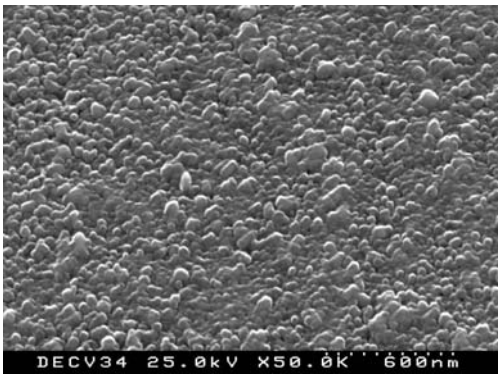

Fig. 8. SEM images on the top surface of sol-gel Al:ZnO thin film.

All the prepared films were optically transparent and exhibited high preferred along (002) direction crystal orientation, with the c-axis perpendicular to the substrate surface (Fig. 9).

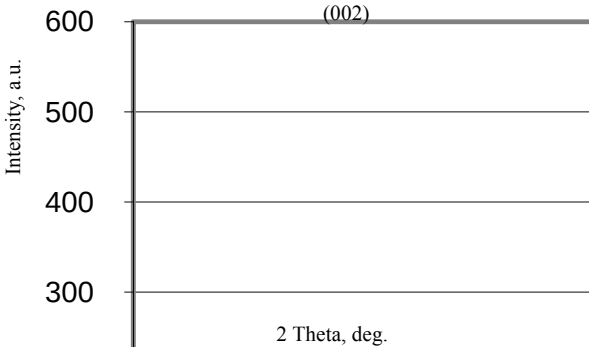

Fig. 9. XRD pattern of of sol-gel Al:ZnO thin film.

The optical transmittance spectra of the film shows a very good transmittance, between 85 and 95%, within the visible wavelength region. The resistivity of 3.2 10^{-3} Ωcm was obtained for the about 250 nm thick film, after annealing under a reduced atmosphere of forming gas.

4. CONCLUSIONS

This study showed that the wet chemical method called sol-gel, is a highly versatile method for obtaining oxide nanostructured multifunctional materials for advanced applications: sensors, transparent electronics, light emitters, etc.

In this paper, ZnO-based nanoparticles, nonorods and thin films, with wurtzite type crystalline structure, have been prepared and investigated.

ZnO monocrystalline nanoparticles with controlled shape and size have been obtained as colloidal dispersion or deposed on silicon substrate. The solvent significantly affects the particle size distribution. Values in the ranges 50-200 nm and 100-400 nm were measured in n-butanol-based dispersion and ethanol-based dispersion, respectively.

ZnO thin films of 1-D nanorod-like morphology (aspect ratio 3 to 10 nm) and polycrystalline structure show a reversible resistivity variation to over three orders of magnitude (between 10^9 and 10^6 Ωcm) during UV reduction followed by gas re-oxidation. The ultra-thin surface layer is mainly contributing to the photoconductivity in polycrystalline ZnO structures and not the bulk conductivity. These nanostructures have a high potential application as UV detectors and/or gas (ozone) sensors.

High transparent (~90%) and conductive (10^{-3} - 10^{-4} Ωcm) polycrystalline Al:ZnO thin films ~ 250 nm thick have been prepared. These properties recommend its as transparent electrode in transparent electronic devices.

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