THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2007, ISSN 1453 – 083X

MULTIFUNCTIONAL ZnO-BASED THIN FILMS BY SOL-GEL METHOD

Viorica MUSAT[1], Elvira FORTUNATO[2]
[1]"Dunărea de Jos" University of Galaţi,
[2]NOVA University of Lisbon-CENIMAT, Portugal
emails: viorica.musat@ugal.ro and emf@fct.unl.pt

ABSTRACT

The paper presents the crystalline structure, morphology, optical transmittance, electrical properties and room temperature photoreduction-ozone oxidation properties of some Al-doped ZnO thin films prepared by sol-gel method. The investigated films are high transparent (85-95% within the visible and near IR wavelength region), high conductive (2.9 10^{-3} Ω cm) and have a reversible photoreduction-oxidation response.

KEYWORDS: ZnO thin films, sol-gel, transparent electrode, ozone sensing properties.

1. Introduction

In recent years, the low-cost and no-toxic nanostructured ZnO-based semiconductive thin films have attracted much researchers attention to replace other very expensive materials in different transparent electronics application [1-7], such as indium thin oxide (ITO) in solar cells and flat DCL devices [1-2, 6], GaN in broadband UV photodetectors with high tunable wavelength [3]. Important applications of UV detector are research-missile warning systems, high temperature flame detection, air quality monitoring, gas sensing [4], accurate measurement of radiation for the treatment of UV irradiated skin.

High excitonic binding energy (aprox. 60 meV) of ZnO provides efficient excitonic emission at room temperature, which offers prospects of laser with low thresholds even at low temperature. In addition, the efficient blue–green emission at room temperature, makes ZnO very important for the fabrication of practical devices like light emission diodes, laser diodes, and solar cells [5].

ZnO transparent thin films transistors (TTFTs) are a very recent development. Among the possible applications of TTFTs are as transparent select-transistor in each pixel of an active-matrix liquid-crystal display (AMLCD), or as transparent alternative to amorphous silicon or organic thin-film transistors (OTFTs) [7].

This paper presents some results on the field of preparation and optical, electrical and UV/gas sensing characterization of semiconductive Al-doped ZnO thin films. Sol-gel method has been used for film preparation. This is one of the most efficient chemical method for the deposition of thin films, and represent a simple and low-cost processing alterna-tive to the vacuum deposition techniques [1-3, 5-8].

2. Experimental

2.1. Films preparation

Al:ZnO thin films were deposed using sols prepared with $Zn(CH_3COO)_2 \cdot 2H_2O$ 99,5%, $AlCl_3 \cdot 6H_2O$ 98% as precursors and ethanol as solvent. The thin films were deposed on Corning 1737 glass substrate by dip-coating technique. After each layer deposition, the gel films were dried and then pre-heated in air at 350 ^oC. The stabilized films were post-heat treated 1 hour in air at 600 ^oC for crystallization.

2.2. Films Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded at room temperature using a Rigaku diffractometer (model RAD IIA), with CuKα radiation. The morphology on the surface and section of the films was analyzed using the atomic force microscopy (AFM). Tapping mode AFM experiments were performed in a Nanoscope IIIa Multimode AFM microscope (Digital Instruments, Veeco). Commercial etched silicon tips with typical resonance frequency of ca. 300 Hz (RTESP, Veeco) have been used as AFM probes.

The electrical resistivity of the films was measured in dark, using a KEITHLEY 617 Model Programmable Electrometer. The optical transmittance was measured using a UV-VIS-NIR double beam spectrophotometer (Shimadzu, UV-3100 PC) in the wavelength range 200 to 2500 nm. From the optical measurements, the optical energy gap, E_{gap}, was calculated assuming a direct transition between the edges of the valence and the conduction band, for which the variation in the absorption coefficient α with photon energy hν is given by the equation:

$$(\alpha h\nu)^2 = B(h\nu - E_{gap}) \quad (1)$$

where B is 1/d and d is the film thickness. By plotting $(\alpha h\nu)^2$ versus hν, and extrapolating the linear region of the resulting curves, the E_{gap} value was obtained.

2.3. Sensing Test

The photoreduction - gas (ozone) reoxidation sensing behavior of thin films were investigated by electrical measurements at room temperature, which were carried out in a special chamber presented elsewhere [9]. The conductivity of the films decreases when are exposed in an ozone atmosphere. and increases by photoreduction, when the films were 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. First the films was exposed at UV light irradiation and after that, the chamber was backfilled with oxygen at a pressure of 600 Torr and an UV lamp was used to produce ozone (the films are shielded from the lamp). The films were maintained in this ozone atmosphere, when the re-oxidation of cobalt oxide crystallites results in a decrease of the film conductivity. An electric field of 50 V/cm was applied to the film sample and the electrical current was measured.

3. Results and Discussions

This paper presents some results obtained in the field of the preparation of transparent electrodes based on Al-doped ZnO thin films. The crystalline structure, morphology, optical, electrical and UV photodetection - ozone sensing behavior of these films are discussed.

The surface SEM micrographs (Fig. 1a) show a compact structure with quasi-regular grains, in both size and shape, with average grain size of about 60 nm. The cross-section SEM micrograph (Fig. 1b) show a very compact structure and a smooth surface.

Figure 2 show the XRD pattern of the film post-heated at 600^{o}C for the 2θ range where the three most important peaks of ZnO hexagonal (wurtzite type) structure are found. In contrast with the pattern of ZnO hexagonal structure with normal random orientation, this pattern shows a c-axis orientated structure where only the (002) peak is well developed. This preferential orientation of the grain growth, perpendicular to the surface substrate, favors the electrical conductivity of the film.

Tabel 1 presents the electrical properties of Al:ZnO thin film post-heated at 600^{o}C, obtained from Hall effect measurements. The high values of n-type carriers concentration and Hall mobility lead to high conductivity ($2.9 \cdot 10^{-3}$ Ω·cm) of the thin film.

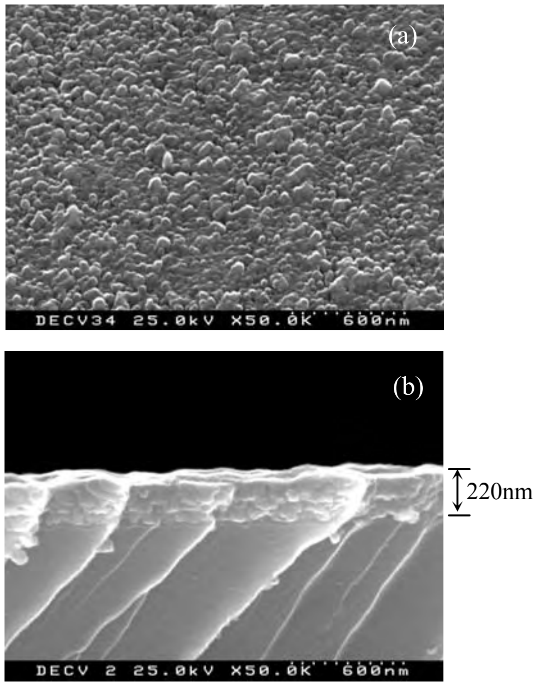

Fig. 1. *SEM micrographs of the surface (a) and cross-section (b) of the Al-doped ZnO thin film.*

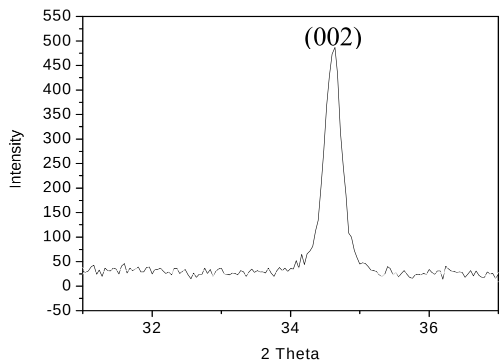

Fig. 2. *XRD patterns of Al:ZnO thin film*

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2007, ISSN 1453 – 083X

Tabel 1. *Electrical properties of Al:ZnO thin film*

Film Type	Electrical properties		
	Resistivity ρ (Ω·cm)	Carriers concentration N (cm^{-3})	Hall mobility μH (cm^2/Vs)
Al: ZnO	$2.9 \cdot 10^{-3}$	$3.80 \cdot 10^{19}$	29.3

Figures 3 and 4 show the optical transmittance spectra and the calculation of the optical energy gap (E_{gap}), respectively. The optical transmittance spectra show a very good transmittance, between 85 and 95%, within the visible and near IR wavelength region.

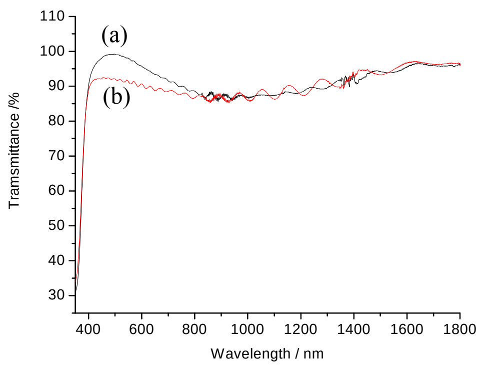

Fig. 3. *Optical transmittance spectra of Al:ZnO thin films before (a) and after thermal annealing.*

The optical transmittance data presented in Fig. 3 curve (b) have been used for the calculation of direct optical energy gap (E_g), Fig. 4, according to the equation (1). The E_{gap} value of 3.48 eV has been obtained.

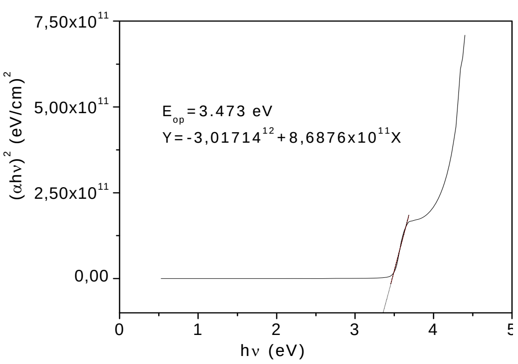

Fig. 4. *The plot $(\alpha h\nu)^2$ vs. hν and the calculation of the optical energy gap (E_{gap}).*

The photoreduction-oxidation cycles (Fig. 5) show a reversible change of two orders of magnitude in film resistivity during successive exposure to UV light and subsequent oxidative atmosphere of ozone.

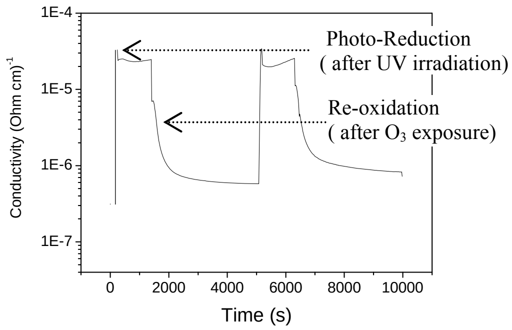

Fig. 5. *Typical photoreduction - reoxidation cycles (room temperature)*

4. Conclusions

Transparent conductive Al-doped ZnO thin film Corning 1737 glass substrate were prepared by sol-gel non-alkoxide route and the dip-coater technique for film deposition.

The Al-doped (2 wt.%) ZnO thin film with (002) direction oriented wurtzite type structure are high transparent (optical transmittance 80-95% within the visible and near IR wavelength region) and high conductive (resistivity of 2.9 10^{-3} Ω cm).

All the investigated films reveal reversible room temperature change in electrical resistance during UV irradiation followed by re-oxidation in ozone atmosphere.

References

[1] S. Bandyopadhyay, G.K. Paul and S.K. Sen, Solar Energy Materials & Solar Cells 71 (2002) 103.
[2] S. Fujihara, C. Sasaki and T. Kimura, Appl. Surf. Sci. 180 (2001) 341.
[3] Z.Q Xu, D. Deng, J.Xie, Y.Li, X.T. Zu, Appl. Surf. Sci., Appl. Phys. Lett. 90, 241918 (2007)
[4 W. Shen, Y.Zhao, C. Zhang, Thin Solid Films 483 (2005) 382-387.
[5] S. Chakrabarti, D. Das, D. Ganduli, S. Chaudhuri, Thin Solid Films 441 (2003) 228-237.
[6] E. Fortunato, P. Nunes, A. Marques, D. Costa, H. Aguas, I. Ferreira, M.E.V. da Costa, M.H. Godinho, P.L. Almeida, J. P. Borges and R. Martins, Surface & Coatings Technologies 151-152 (2002) 247.
[7]. B.J. So, Noris, J. Anderson, J.F. Wager, D.A. Keszler, J.Phys.D: Apply Phys. 36 (2003) L105-L107.
[8] M. Crisan, M. Zaharescu, D. Crisan, R. Ion and M. Manolache, J. Sol-Gel Science and Tech. 13 (1998) 775.
[9] A. Pimentel, E. Fortunato, A. Gonçalves, A. Marques, H. Águas, L. PereiraA, I. Ferreira, R. Martins, Thin Solid Films, 487 (2005) 212.