Nanoporous Zinc Oxide Films Prepared by Magnetron Sputtering

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***Abstract* – In this paper we demonstrate an inexpensive approach for the fabrication of nanoporous zinc oxide films by using magnetron sputtering. Study of the structural properties proves the crystallographic perfection of porous nanostructures and the possibility of its controlling by adjusting the technological parameters in the growth process. The XRD pattern of nanoporous ZnO films exhibits high intensity of the peaks relative to the background signal which is indicative of the ZnO hexagonal phase and a good crystallinity of the samples grown by magnetron sputtering.**

***Index Terms* – ZnO, nanoporous, films, magnetron sputtering.**

I. INTRODUCTION

Over the last decade, nanostructured materials have received much greater attention because of their new properties promising for various applications [1-6]. Control of size and morphology of materials is of interest to researchers dealing with the design of functional devices; especially taking into account that optical and electronic properties of nanometer sized materials depends upon the dimensions and shape [1,7].

Exploration of zinc oxide has proven its piezoelectric properties, which led to its application in electronics, in particular in thin layers for devices with surface acoustic waves [8]. Currently the research of zinc oxide as a semiconductor material exhibits a new period of intense development. Over the last years, remarkable results have been published in the most prestigious international journals. Increased interest in ZnO as an optical material has been unleashed on *p*-type conductivity with ferromagnetic properties, and manufacture of field effect transistors in thin layers. A major driving force for research of zinc oxide as a semiconductor material is its prospective use as a wide-band semiconductor for light emitting devices and solar cells [4-6]. Note that the exciton binding energy of 60 meV is bigger than the effective thermal energy at 300 K (26 meV).

These characteristics make ZnO promising in a variety of fields, along with electronics and optoelectronics. Further development of efficient systems for drug delivery for health care needs new sensible and selective biosensors [9-10]. ZnO nanoparticles have been used in many applications in our daily life, such as drug carriers and cosmetics [11]. However, although inhalation of ultrafine ZnO particles at relatively high dose (500 mg/m^3) for 2 hours did not induce acute systemic effects in humans, inhalation of ZnO fumes in an occupational setting can cause metal fume fever (fatigue, chills, fever, myalgias, cough, dyspnea, leukocytosis, metallic taste, and salivation) [12]. Generally, nanostructures with high surface to volume ratio exhibit high sensitivity to adsorbed molecules and therefore are suitable for implementation in sensors. There are many types of biosensors for use in physiological environments. Of these, those based on potentiometric measurement technique (there, where current flow is not necessary during the measurement) using zinc oxide, are interesting and necessary, because current flow could damage biological systems and environments. Zinc oxide is biocompatible, biosafe and, moreover, it is a semiconductor with photonic properties potentially usable for biophotonics. It is important to note that, along with UV, it emits in the visible region [13-15]. In addition, ZnO has an excellent electrochemical activity and good properties of electron transport. Nanowire arrays or nanoporous films found application dye-solar cells as well [13-15]. Most importantly, in the nanostructured form zinc oxide can be grown on any substrates, either crystalline or amorphous, and at various temperatures, including the possibility to grow it at relatively low temperatures, even at the temperature as low as 300 K. In this work, we will present the magnetron sputtering of zinc oxide nanoporous films. Its structural, morphological and vibrational properties are shown and discussed in details.

II. EXPERIMENTAL PART AND DISCUSSIONS

Basic parameters of the magnetron sputtering method are the voltage and discharge current power, specific power on the cathode, the gas pressure in the working chamber and magnetic induction. The main advantages of this method consist in high speed of layers deposition and reproducibility accuracy of the composition of the deposited layers. The condensation rate of the magnetron sputtering depends on the power of the discharge current and gas pressure in the working chamber. Thus, using this method we succeeded to grow ZnO layers in the atmosphere of argon by applying a constant current (DC) and radio-frequency (RF) AC. A disc of 99.99 % pure zinc served as target.

Pure porous-Zn was deposited over SnO_2 thin films of size 1.5 cm^2 on glass substrates by direct current (DC) magnetron sputtering. Preliminary, the substrates were cleaned for 2-3 hours in the mixed solution of chromium (7g$K_2Cr_2O_7$-10ml

H_2O-100ml H_2SO_4) at room temperature. The argon (Ar) working gas pressure was regulated in such a way to maintain a constant vacuum pressure of 5×10^{-3} Torr. The DC current used was 0.12-0.15 A, and the deposition time was 9-22 min. The substrate was kept at a constant temperature around 210°C. Several sets of samples have been prepared in this way. Afterwards, these nanolayers grown on tin oxide/glass substrate were introduced into a reactor and annealed at a temperature of 481°C for 45 minutes in an oxygen atmosphere; gas flow was approximately -100 ml/min.

The phase structure of the deposited films was studied using Rigaku X-ray diffractometer (XRD) (CuK_α radiation (λ=1.54178 Å)) and optimized operating conditions of 30 mA and 40 kV at a scanning rate of 0.04°/s in the 2θ range of 24-90°. The XRD pattern of doped nanoporous ZnO films is shown in Figure 1. All tin oxide substrate peaks are marked and are assigned to SnO_2 according to PDF 00-041-1445 card.

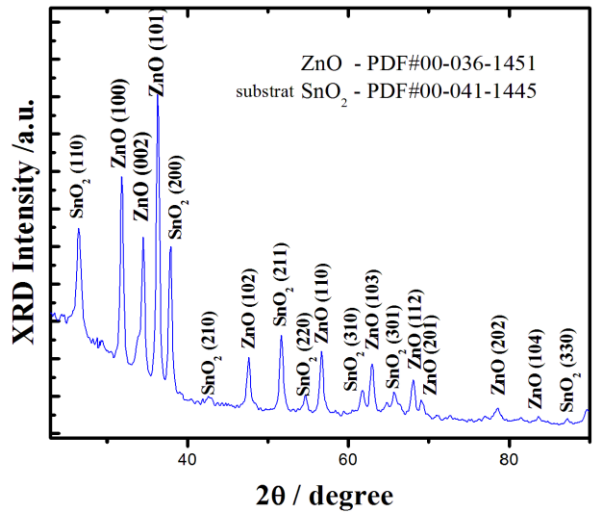


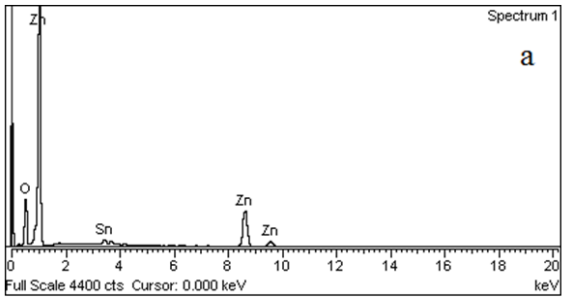
Fig. 1. XRD pattern of nanoporous ZnO grown by magnetron at 5°C on tin oxide/glass substrate. Substrate peaks are marked as SnO_2.

The diffraction peaks in the pattern can be indexed to hexagonal wurtzite structured ZnO [space group: $P6_3mc$(186); a=0.3249 nm, c=0.5206nm] and diffraction results are in agreement with JCPDS 036-1451 card for ZnO [16]. The intensity of the peaks relative to the background signal demonstrates high purity of the ZnO hexagonal phase of the products and a very good crystallinity of the samples [17-19] grown by magnetron sputtering. The characteristic peaks of impurities was not observed, which is indicative of a single phase hexagonal ZnO. The nanocrystallites are oriented along the (101) indicated by the highest intensity peak [16].

The morphology and chemical composition of the nanostructured films of ZnO were studied using a TESCAN Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA Energy Dispersive X-ray (EDX) system. The EDX analysis of the produced structures demonstrates a relative stoichiometric ZnO composition (within a precision of 1 at.%). The composition was characterized by Energy Dispersion X-ray Spectrometer (EDX).

In the Figure 2a the results of EDX analysis of the nanostrucured films are represented. As one can see from the table, the chemical compozition shows 41.44 % of zinc and 57.27 % of oxygen.

A section of ZnO structure morphology is represented in Figure 2. It is clearly seen that the zinc oxide layer is porous and is quite homogenous over the whole surface of the samples.



Element	Weight%	Atomic%	
O K	24.25	57.27	
Zn K	71.70	41.44	
Sn L	4.05	1.29	
Totals	100.00		

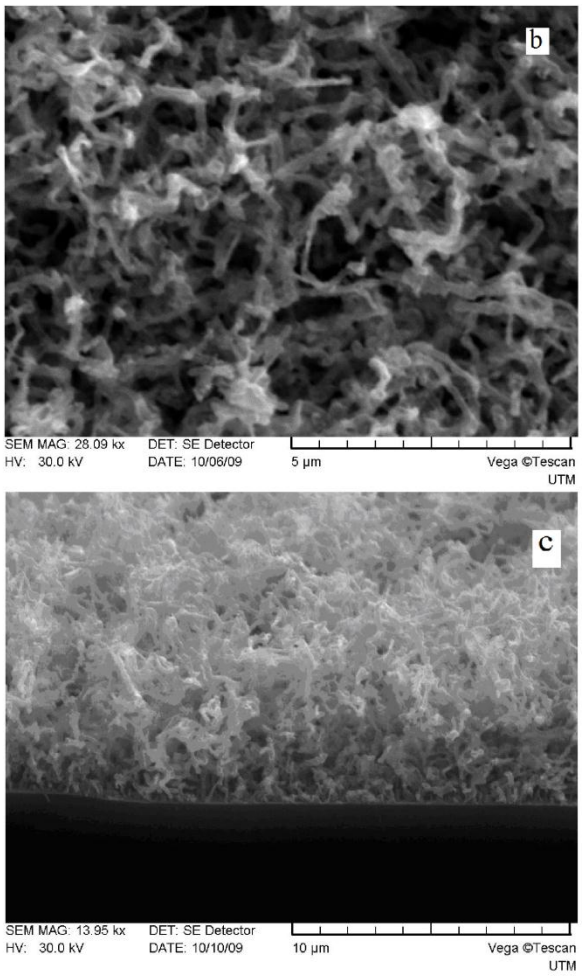


Fig. 2. a) EDX images of nanoporous ZnO; b,c) SEM images of nanoporous zinc oxide films grown by magnetron sputtering on tin oxide/glass substrate: top and cross-sectional views, respectively. Scale bars are 5 µm and 10 µm, respectively.

The room temperature Raman scattering was studied with

a Confocal Laser Raman System in the backscattering geometry under the excitation by a laser. Raman investigations (see Fig. 3) provide information about the material quality, the phase and purity, allowing one to understand vibrational properties and phonon interaction with the free carriers [15,17]. The group for ZnO is C_{6v}, and 12 degrees of freedom exist since there are four atoms per primitive cell. There are nine optical phonon modes and three acoustic phonon modes. Phonon modes E_2 (low and high frequency), A_1 [(TO)-transverse optical and (LO)-longitudinal optical] and E_1 (TO and LO) are expected, all being Raman and infrared active [17,20]. According to group theory, the optical modes at the Γ point of the Brillouin zone can be expressed by [20]:

$$\Gamma_{opt} = 1A_1 + 2B_1 + 1E_1 + 2E_2$$

A_1(z), E_1(x), E_1(y) and E_2 are Raman active modes, except the silent mode B_1. Figure 3 shows the Raman spectrum measured in backscattering geometry in the nanoporous ZnO grown by magnetron sputtering on TO substrate. The E_2 optical mode corresponds to dominant peaks at 100 cm^{-1} and 438 cm^{-1}, which are commonly detected in the wurtzite structure of ZnO [20]. The Raman spectrum of the ZnO films demonstrates a high quality of the wurtzite crystal structure in the produced material.

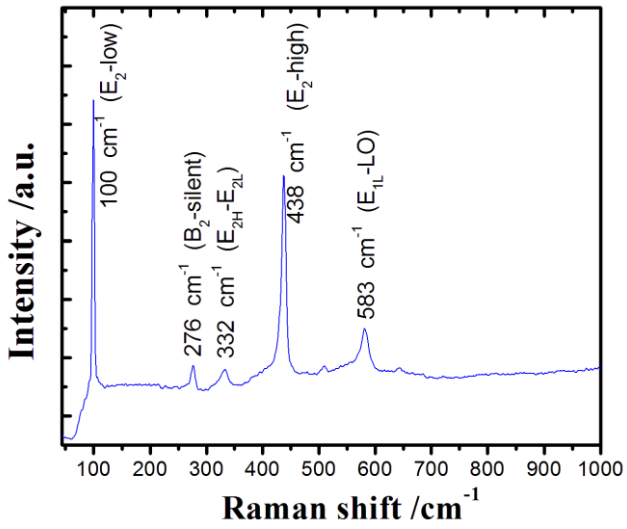


Fig. 3. Raman spectrum for nanoporous zinc oxide films grown on tin oxide/glass substrate.

III. CONCLUSION

Novel nanoporous ZnO films were synthesized by magnetron sputtering. The obtained results of the ZnO structure morphology and the XRD data prove the possibility to control the properties in a controlled fashion. Wurtzite crystal structure corresponds to a single hexagonal phase of ZnO, where the nanocrystallites are oriented along the (101) axis. This study allows one to conclude that these layers are useful for DSSC solar cells and light emitting devices.

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