Rev.Adv.Mater.Sci. 10 (2005) 331-334

ZnO NANOSTRUCTURED TRANSPARENT THIN FILMS BY PLD

S. Christoulakis[1,2], M. Suchea [1,2], M. Katharakis[3], N. Katsarakis[1,3], E. Koudoumas[3] and G. Kiriakidis[1,2]

[1]Institute of Electronic Structure and Laser, Foundation for Research & Technology Hellas, PO Box 1527 Vasilika Vouton, 71110 Heraklion, Crete, Greece
[2]Physics Department, University of Crete, 71110 Heraklion, Crete, Greece
[3]Center of Materials Technology and Laser, School of Applied Technology, Technological Educational Institute of Crete, Heraklion, Estavromenos, 71004 Heraklion, Crete, Greece

Received: May 25, 2005

Abstract. ZnO transparent thin films of different thickness were prepared with the Pulsed Laser Deposition (PLD) technique. The deposition of the films was carried out onto silicon and Corning glass substrates using a XeCl Excimer Laser (308 nm) as the light source and ZnO sintered ceramic targets in oxygen atmosphere. Structural investigations were carried out using Atomic Force Microscopy and X-ray Diffraction. As shown, the films grown have a polycrystalline wurtzite structure; the deposition parameters strongly affect the film surface topography (film roughness and shape/dimensions of grains) and the corresponding electrical/sensing properties. In addition, highly oriented nanostructures were identified, indicating the nucleation of nanorods with preferential orientation. The present work underlines that the film sensing properties can be controlled by modifying the deposition conditions.

1. INTRODUCTION

ZnO is a very interesting material for many different applications in both microelectronic and optoelectronic devices. It is a wide-band gap oxide semiconductor with a direct energy gap of about 3.37 eV. As a consequence, ZnO absorbs UV radiation due to band-to-band transitions [1], while it can be used as transparent electrode in solar cells and flat panel displays, grating in optoelectronic devices, and window in antireflection coatings and optical filters. Furthermore ZnO can be used as semiconducting gas sensor [2] due to conductivity changes it exhibits when exposed to oxidizing gases such as ozone. Many deposition techniques [2,3] have been applied for the production of ZnO films in order to improve their properties. Due to the interest related to the specific properties of transparent metal oxide thin films, our recent studies are focused in the correlation of surface and interface topography with deposition parameters and physical properties [4-6]. In this work, we examine the ozone sensing properties of ZnO films prepared using the Pulsed Laser Deposition (PLD) technique. The investigation concerns the influence of film thickness on the electrical/sensing properties of the films.

2. EXPERIMENT

The deposition of the ZnO films was carried out in a typical homemade PLD deposition chamber [1], using a XeCl Excimer Laser with 308 nm wavelength,

Corresponding author: M. Suchea, e-mail: mirasuchea@iesl.forth.gr

in oxygen atmosphere. The deposition temperature was 350 °C. Films with a thickness of 10, 40, 100, 150, 200, and 400 nm were deposited onto silicon and Corning 1737F glass substrates. The thickness was measured using an Alphastep profilometer. The surface morphology (grain size and surface roughness) was measured with a Nanoscope III atomic force microscope (Digital Co. Instruments, USA) using a normal silicon nitride tip (125 μm) in Tapping Mode scanning the surface with an oscillating tip to its resonant frequency (200-400 kHz). All measurements were made at room temperature (RT). In the present study the RMS roughness of the surface is defined as: RMS (nm)=$[\Sigma(z_i-z_{ave})^2/N]^{1/2}$ where z_i is the current value of z, z_{ave} is the mean value of z in the scan area, N is the number of points. Grain radius and features dimensions were evaluated using the Cross Section Analysis Menu facilities of NanoScope III Program. X-ray diffraction (XRD) using a Rigaku diffractometer with CuK_α X-rays was applied in order to determine the crystal structure of the deposited films. The optical transmittance was measured using a Varian Cary50 UV/Visible spectrophotometer with Varian data analysis tools. The conductivity measurements were carried out at room temperature in a homemade system at FORTH [7].

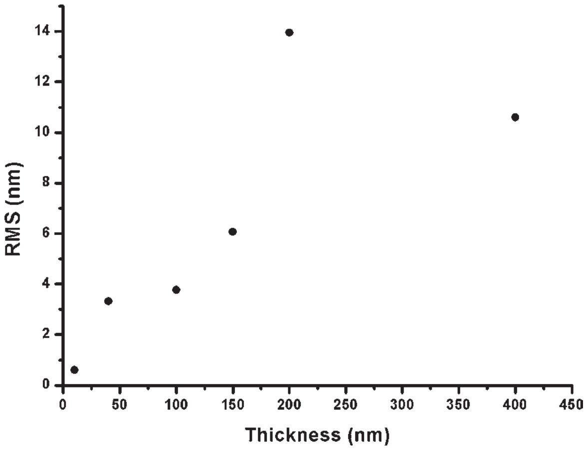

Fig. 1. RMS dependence on film thickness.

3. RESULTS AND DISCUSSION

AFM surface characterization of ZnO thin films with varying thickness revealed different surface topography. The roughness of these films increases from about 0.60 nm to 13.95 nm as shown in Fig. 1. These variations are correlated with the film crystal formation. In the case of thinner films, the growth time is shorter and the surface behavior reveals a more homogeneous distribution of small grains (30-40 nm). At longer deposition periods, we observe that small grains aggregation leads to the formation of larger grains with a subsequent increase in the measured lateral grain size leading to an overall rougher surface. The maximum RMS value was found for the 200 nm thick film, which exhibited the presence of 'nanospaghetti' like features on its surface (see Fig. 2b). Feature dimensions on the ZnO thin films prepared by PLD vary from 10 nm to 700 nm and can be well controlled through deposition parameters. As shown in Fig. 2, film thickness has a strong influence on the surface morphology.

XRD measurements revealed that ZnO films deposited by PLD show a preferred growth orientation along the c-axis, i.e. (002) plane, which is perpendicular to the substrate (see Fig. 2d). In the case of the 400 nm thick film the (004) plane reflection was also observed. The broadened diffraction peaks (FWHM) with decreasing thickness can be correlated with the decrease of crystallite size, which was also observed by AFM analysis for thicker films showing a grain-subgrain structure.

The as-deposited ZnO thin films were found to be highly transparent in the visible wavelength region with an average transmittance of 90% and showed an absorption edge in the UV depending slightly on film thickness. Optical band gap calculation gives us an E_{gap}~3.21 eV, smaller than the intrinsic gap value. Such a band reduction has been discussed in the past and is attributed to defect states near the band edges.

The mechanism responsible for the conductivity changes in ZnO films is the formation and annihilation of oxygen vacancies. UV irradiation of the sample with energies above the bonding energy between Zn and O leads to the transformation of oxygen atoms from a bound state to the gaseous state. The photoreduction treatment results is an increase of the conductivity of about three orders of magnitude while conductivity values changed up to two orders by subsequent ozone oxidation for the ZnO films with 40, 100, and 150 nm thickness as it can be seen in Fig. 3. In the case of the 200 nm thick film the conductivity changes were very small even if it has the highest RMS value, a fact which can be attributed to the presence of the nanorods on the surface and thus to an improved surface crystallinity and stoichiometry leading to less oxygen vacancies. The film sensitivity correlation with surface parameters can be explained using the conduction model of metal oxide gas sensors approximation given by Barsan *et al.* [7]. The base of gas detection is the interaction of the gaseous species

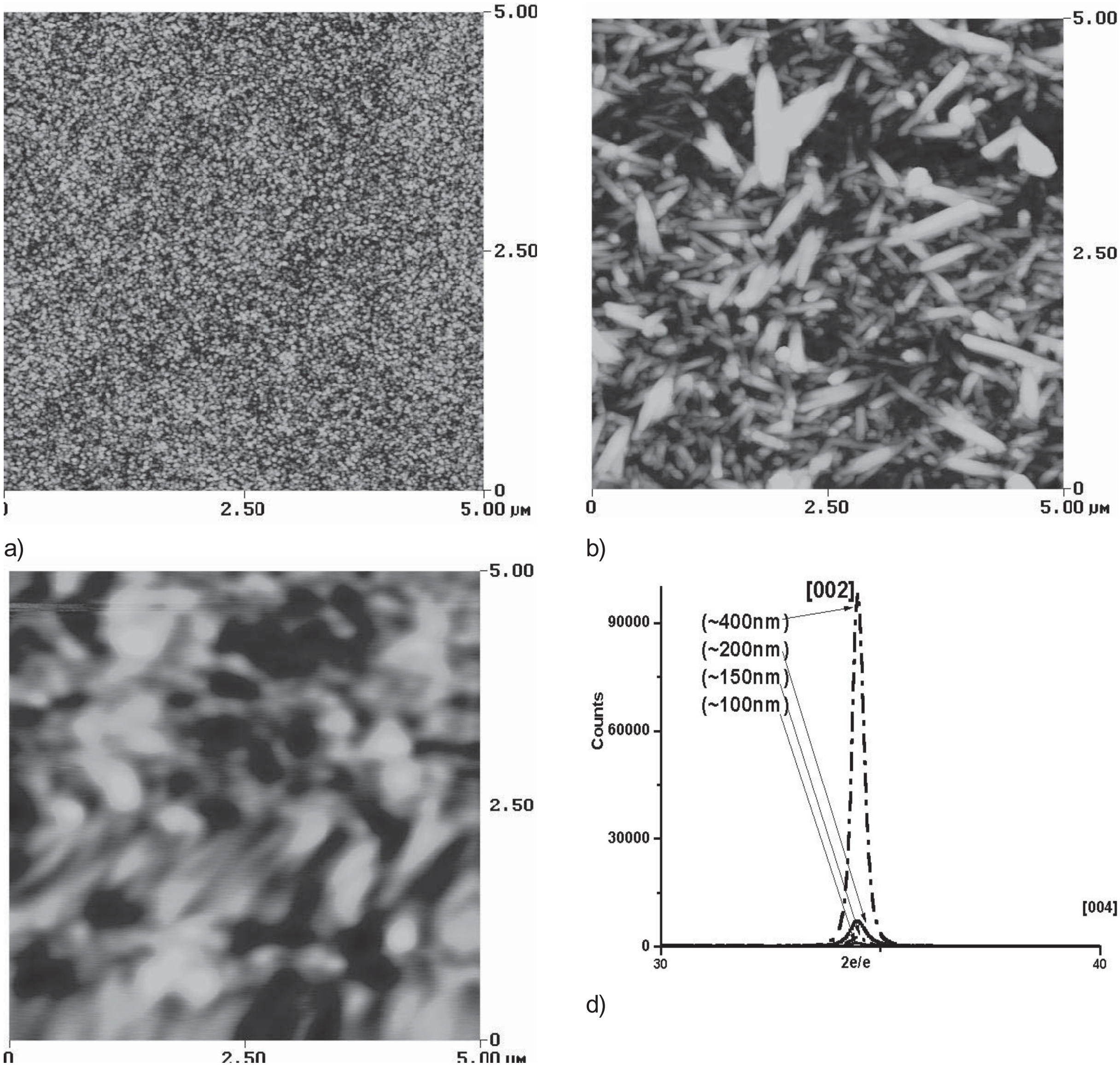

Fig. 2. AFM images (scan size 5×5 μm) of ZnO film surfaces with a thickness of a) 100 nm b) 200 nm c) 400 nm d) XRD patterns of PLD deposited ZnO films with different thickness.

with the surface of the semiconducting sensitive metal oxide layer. As a consequence of this surface interaction charge transfer takes place between the absorbed species and the semiconducting sensitive material. According to this model, for small grains and narrow necks, when the mean free path of free charge carriers becomes comparable with the dimensions of the grains, grain boundaries dominate the transport mechanism and thus the surface influence on mobility become dominate over bulk phenomena. In the presence of the ionic species on the surface, after UV photoreduction, the electronic concentration in the surface states increases. The surface states concentration is correlated with the roughness and grain size via surface-to-volume ratio. Therefore, the gas sensitivity is directly correlated with the film roughness proving the importance of surface-to-volume ratio for high sensing applications. Therefore, the effect of thickness on the film sensitivity is related to structural surface properties and, as a result the sensitivity decreases as the thickness increases.

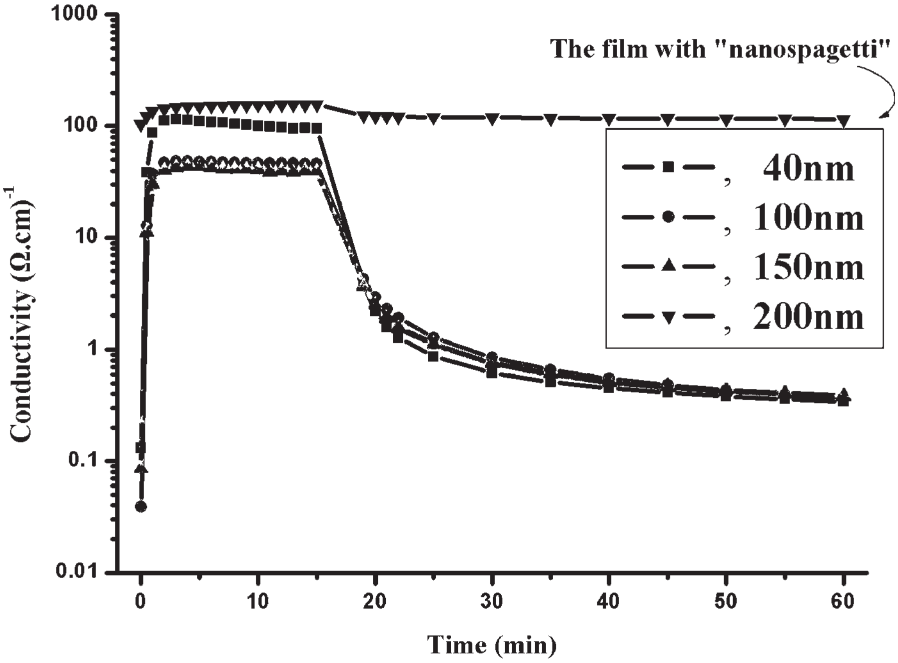

Fig. 3. Conductivity changes under UV exposure in ozone atmosphere for films with different thicknesses.

4. CONCLUSIONS

The surface morphology of ZnO thin films with different thickness prepared by PLD was investigated by AFM and XRD. The preparation conditions determine the characteristic parameters of the surface (i.e. RMS) and the crystallinity of the films with strong influence in electrical/sensing properties. Therefore, the ZnO films grown are suitable for ozone detection and their sensitivity can be improved by controlling the deposition parameters.

ACKNOWLEDGEMENTS

This work was partially supported by ASSEMIC MRTN-CT-2003-504826 and 3rd Gen LAC No NNE5-2001-00961 European founded projects.

REFERENCES

[1] D. P. Norton, Y. W. Heo, M. P. Ivill, K. Ip, S. J. Pearton, M. F. Chisholm and T. Steiner // *Materials Today* **7** (2004) 34.

[2] T. K. Subramanyam, B. S. A. Naidu and S. Uthanna // *Cryst. Res. Trechnol*. **35** (2000) 1193.

[3] E. Vasco, C. Zaldo and L. Vázquez // *J. Phys.: Condens. Matter* **13** (2001) L663.

[4] M. Suchea and G. Kiriakidis, In: *IEEE CAS 2004 Proc. Int. Conf*. (Sinaia, Romania, 4-6 October 2004) p. 345.

[5] G. Kiriakidis, N. Katsarakis, M. Katharakis, M. Suchea, K. Galatsis, W. Wlodarski and D. Kotzias, In: *IEEE CAS 2004 Proc. Int. Conf.* (Sinaia, Romania, 4-6 October 2004) p. 325.

[6] M. Suchea, M. Katharakis, S. Christoulakis, N. Katsarakis and G. Kiriakidis // *IOP J. Physics: Conference Series MMN2004 International Conference*, (Athens, 14-17 nov.2004), in press.

[7] N. Barsan and U. Weimar // *Journal of Electroceramics* **7** (2001) 143.