

ZnO transparent thin films for gas sensor applications

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Abstract

Zinc oxide (ZnO) transparent thin films were deposited onto silicon and Corning glass substrates by dc magnetron sputtering using metallic and ceramic targets. Surface investigations carried out by Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) have shown a strong influence of deposition technique parameters on film surface topography. Film roughness (RMS), grain shape and dimensions are correlated with the deposition technique parameters as well as with the target material. XRD measurements have proven that the dc sputtered films are polycrystalline with the (002) as preferential crystallographic orientation. AFM analysis of thin films sputtered from a ceramic target has shown a completely different surface behavior compared with that of the films grown from a metallic target. This work demonstrates that the target material and the growth conditions determine the film surface characteristics. The gas sensing characteristics of these films are strongly influenced by surface morphology. Thus correlating the optical and electrical film properties with surface parameters (i.e. RMS and Grain Radius) can lead to an enhancement of the material's potential for gas sensing applications.

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1. Introduction

Zinc oxide is one of the earliest discovered metal oxide gas sensing materials. It is an n-type semiconductor of wurtzite structure with a direct energy wide-bandgap of about 3.37 eV at room temperature [1]. As a consequence, it absorbs UV radiation due to band-to-band transitions [2] at $\lambda < 368$ nm, while it can be used as transparent electrode in solar cells and flat panel displays as well as for the fabrication of gratings in optoelectronic devices, as a window material in antireflection coatings and in optical filters. Furthermore, ZnO is used as a semiconducting gas sensor [3,4] due to its conductivity changes when exposed to oxidizing gases such as ozone. Until now ZnO-based elements have attracted much attention as gas sensors because of their chemical sensitivity to volatile and other radical gases, their high

chemical stability, suitability to doping, non-toxicity, and low cost. Furthermore, the physical properties of ZnO films are generally dependent on deposition parameters [5,6] and post-deposition conditions such as post-annealing [7].

The sensitivity of nanostructured ZnO gas elements is relatively high and is related to the grain-size effect [8]. Many deposition techniques [1,3,4] have been applied for the production of ZnO films in order to improve the properties of the films. Sputtering is preferred among these techniques due to its relative high deposition rates, good film properties and process stability [1]. Due to the interest related to the specific properties of these transparent metal oxide thin films, recent studies are focused on the correlation of surface and interface topology with deposition parameters and physical properties. Thus efforts for understanding the correlation of microstructure with the electrical properties of ZnO thin films are essential. In this work, we investigate how the target material and the plasma gas flow ratio (O_2 to Ar) affect the morphology of dc sputtered ZnO thin films as well as the correlation of film's conductivity and optical band gap with the surface characteristics.

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2. Experimental details

The deposition of the ZnO films was carried out in an Alcatel dc magnetron sputtering system using 99.999% pure metallic Zn and ZnO ceramic targets under different conditions. The base pressure in the chamber was $\leq 5 \times 10^{-7}$ mbar. Films with a thickness of about 100 nm were deposited onto Corning 1737F glass and silicon substrates in an oxygen–argon atmosphere. The deposition constant parameters were the total pressure (8×10^{-3} mbar), the substrate temperature at 27 °C (RT), and the film thickness. The depositions were done at two different plasma current settings ($I=0.44$ A and $I=0.25$ A). 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: $\text{RMS (nm)} = [\sum(z_i - z_{\text{ave}})^2 / N]^{1/2}$ 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 feature dimensions were evaluated using the Cross Section Analysis Menu facilities of NanoScope III Program. The crystal structure of the deposited films was determined by X-ray diffraction (XRD) using a Rigaku diffractometer with $\text{CuK}\alpha$ X-rays. The optical

transmittance was measured using a Varian Cary50 UV/Visible spectrophotometer with Varian data analysis tools.

The conductivity measurements were carried out in a special designed reactor [9] at room temperature in a home made system at FORTH. For photoreduction the samples were directly irradiated in vacuum by the UV light of a mercury pencil lamp at a distance of approximately 3 cm for 20 min in order to achieve a steady state. For the subsequent oxidation ozone was produced up-stream in the presence of UV and the chamber was backfilled with oxygen and ozone at a pressure of 560 Torr. This treatment lasted 40 min, after which no further changes of the conductivity could be observed. Finally, the chamber was evacuated and the photoreduction–oxidation cycle described above was repeated a few times. An electric field (1 or 10 $\text{V} \times \text{cm}^{-1}$) was applied during the whole cycling procedure to the samples and the electrical current was measured with an electrometer. Current–voltage (I – V) measurements were always performed before the cycling started in order to ensure the ohmic nature of the contacts.

3. Results and discussion

AFM imaging of the surfaces of ZnO thin films deposited at room temperature from metallic and ceramic targets, under varying Ar-to- O_2 flow ratios, are shown in Fig. 1. AFM characterization for the films deposited from a metallic target (Fig. 1a, b) revealed a granular, polycrystalline morphology

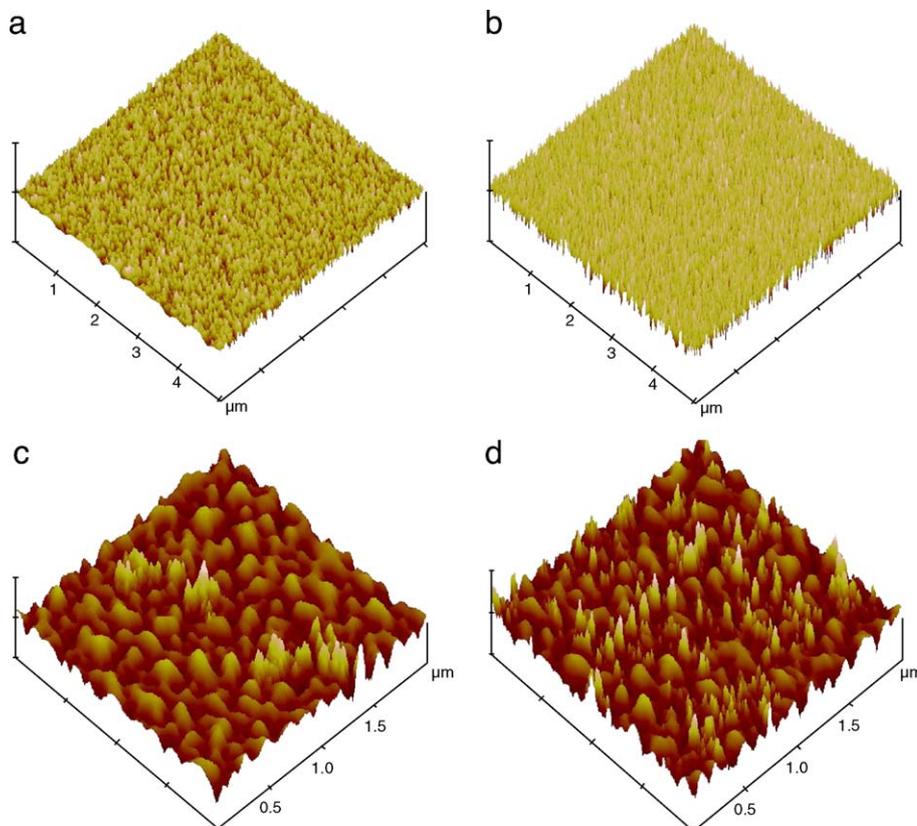


Fig. 1. AFM 3D images of as-deposited ZnO thin films at room temperature with Ar ratios of respectively (a) 0%, z-range 50 nm/div (b) 27% from Zn metallic target, z-range 50 nm/div (c) 100%, z-range 30 nm/div (d) 90% from ZnO ceramic target, z-range 30 nm/div.

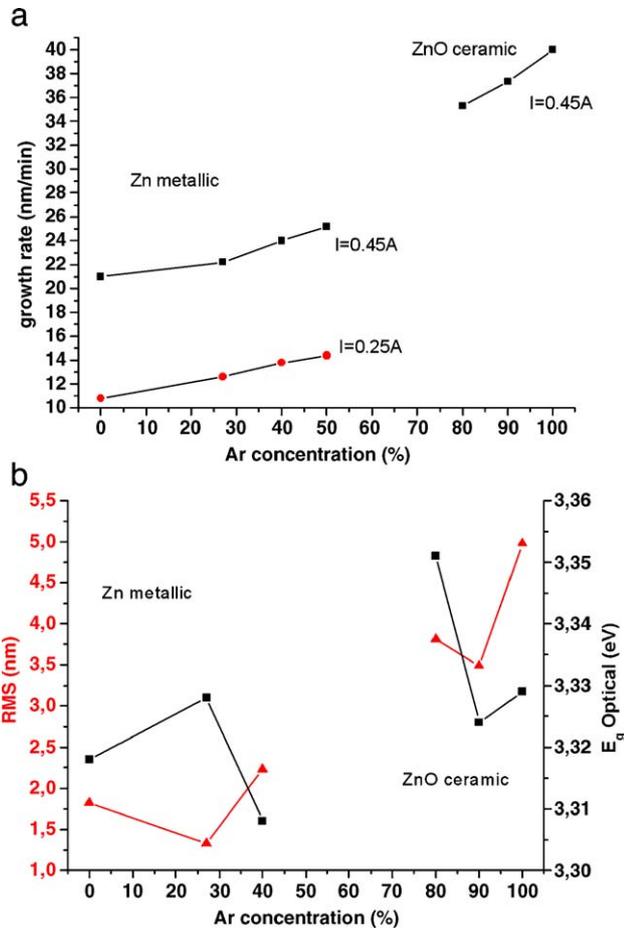


Fig. 2. (a) Film growth rates versus Ar concentration in plasma, (b) optical band gap (squares) and RMS variations (triangles) versus Ar concentration in plasma.

with grain size decreasing and roughness increasing as the oxygen partial pressure in the plasma decreases. This characteristic behavior was observed for two different plasma current settings namely $I=0.44$ A and $I=0.25$ A. However, in the case of films grown from a ceramic target (Fig. 1c, d) the surface had a complete different morphology, which was mainly dominated by grain agglomerations and very tall features. The grain size, derived as described above from the AFM measurements, varied from 50 to 20 nm for ZnO deposited from a metallic target. For ZnO films deposited from a ceramic target, agglomeration dimensions varied from 500 to 50 nm. The subgrain dimensions were measured and found to be in the range of 10–50 nm. Since the plasma current is correlated with the growth rate in the sense that high plasma current corresponds to a high deposition rate, the above microstructural changes are directly attributed to the film growth rate variation. At the same time, the growth rate increases when the O₂ concentration decreases due to the presence of Ar atoms in the plasma (Fig. 2a). For films grown from a metallic target, we observed that films deposited at higher O₂ ratio (Fig. 1a) have shown bigger, better-formed grains, formed by the aggregation of many small particles, whereas those deposited at higher Ar ratio (Fig. 1b) had a uniform grain distribution and smaller size. These observations may be attributed to the introduction of

oxygen in the plasma, which could also generate high-energy oxygen neutral atoms. It is generally believed that the formation of grain agglomerations in the film deposited under the introduction of oxygen gas might be due to re-sputtering of high-energy neutral oxygen atoms [10]. As oxygen content in the plasma gas increases, re-sputtering effect by high-energy neutral oxygen atoms can increase. Subsequently it might accelerate grain growth (or aggregation of particles) and thus change the surface topology of the film at the initial stage of the film growth process. For films grown from a ceramic target, the growth rate had a remarkable increase compared with the metallic target case due to the high Ar ion concentration in the plasma. The surface roughness variations of the ZnO thin films deposited at different O₂/Ar ratios are shown in Fig. 2b (triangles). The scan area for surface roughness was $5 \times 5 \mu\text{m}$. One can observe that the surface roughness (RMS) generally increased with increasing Ar concentration in the plasma for both target materials.

The as-deposited ZnO thin films were found to be highly transparent in the visible wavelength region with an average

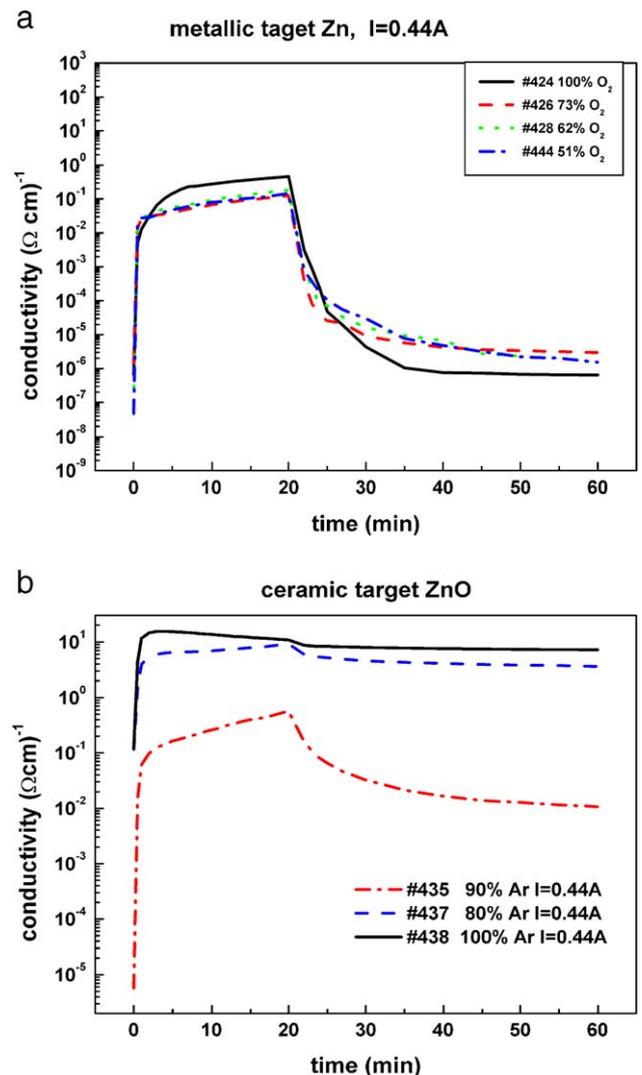


Fig. 3. Photoreduction/oxidation curves for 100 nm films grown from (a) Zn metallic target, (b) ZnO ceramic target.

transmittance of 90%. The optical energy gap E_{gap} was derived assuming a direct transition between the edges of the valence and the conduction band, for which the variation in the absorption coefficient with the photon energy $h\nu$ is given by

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

In Eq. (1), E_{gap} denotes the optical energy gap between the valence and the conduction band. “Tauc” plots of α^2 versus $h\nu$ give by extrapolation of the linear region of the resulting curve, the optical band gap value E_{gap} . The calculated values of the direct optical energy gap varied between 3.31 and 3.35 eV for ZnO thin films depending on target composition and Ar/O₂ ratio. The variations of the optical energy gap could be attributed to changes in the film defect density. In Fig. 2b (squares), the dependence of the optical energy gap on Ar/O₂ ratio for ZnO films grown at RT is depicted. It is observed that films deposited from a ceramic target show in general a larger E_{gap} , which can be attributed to the Burstein–Moss shift (BM shift) due to the filling of the lowest levels of the conduction band with carriers in degenerate semiconductors [11]. Moreover, higher O₂ concentration in the plasma leads to more carriers and larger E_{gap} for both target materials.

The XRD measurements revealed that all deposited films are polycrystalline and show a preferred growth orientation along the *c*-axis, i.e. (002) plane, which is perpendicular to the glass substrate. All the 100 nm thick ZnO films deposited at RT exhibit also the (103) diffraction peak.

The effect of the target material and the O₂/Ar gas ratio on the conductivity changes under ozone exposure was studied. In general, the films sputtered from a ceramic target exhibit higher conductivity values (~ 0.1 – $10 \Omega^{-1} \text{cm}^{-1}$), which are in accordance with already reported values for rf sputtered ZnO films [12]. It seems that sputtering from a ceramic target leads to higher carrier concentration and thus to an increased conductivity. The conductivity results are in agreement with the optical measurements that revealed higher E_{gap} for the films sputtered from a ceramic target due to the presence of carriers inside the conduction band (BM shift). The photoreduction treatment resulted in an increase of the conductivity of up to seven orders of magnitude for ZnO thin films sputtered from a metallic target and only up to three orders of magnitude for ZnO thin films sputtered from a ceramic target. Subsequent ozone oxidation leads to conductivity changes of up to six orders for the ZnO films sputtered from a metallic target and up to one order for ZnO thin films sputtered from a ceramic target as shown in Fig. 3a, b. This behavior was completely reversible through many cycles of photoreduction and oxidation treatments. The surface-to-volume ratio is smaller in the case of ZnO films deposited from a ceramic target due to the presence of big agglomerates on the surface (Fig. 1c, d). This results in

the decreased sensitivity for those films, which is observed in Fig. 3b. [7] On the contrary films sputtered from a metallic target display smaller grains and thus show higher surface-to-volume ratio leading to increased sensitivity to ozone according to Barsan and Weimar [13].

4. Conclusions

The effect of plasma gas flow ratio (Ar to O₂) on the morphology of ZnO thin films and their correlation with the optical properties and conductivity changes of the films were investigated. AFM and XRD characterization of the films revealed polycrystalline morphology with roughness increasing as the argon partial pressure increases. The surface of the films grown from ceramic targets had a complete different morphology, which is mainly dominated by grain agglomeration and the presence of very tall features. ZnO films sputtered from a metallic target in pure oxygen plasma show smaller grains, smaller E_{gap} and as-deposited conductivity values. Moreover, they exhibit better sensitivity to ozone due to larger surface-to-volume ratio. On the contrary films sputtered from a ceramic target at high Ar concentration in the plasma show larger E_{gap} , better conductivity and much worse sensitivity to ozone.

Acknowledgments

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