

Thickness influence on surface morphology and ozone sensing properties of nanostructured ZnO transparent thin films grown by PLD

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Abstract

Transparent zinc oxide (ZnO) thin films with a thickness from 10 to 200 nm were prepared by the PLD technique onto silicon and Corning glass substrates at 350 °C, using an Excimer Laser XeCl (308 nm). Surface investigations carried out by atomic force microscopy (AFM) and X-ray diffraction (XRD) revealed a strong influence of thickness on film surface topography. Film roughness (RMS), grain shape and dimensions correlate with film thickness. For the 200 nm thick film, the RMS shows a maximum (13.9 nm) due to the presence of hexagonal shaped nanorods on the surface. XRD measurements proved that the films grown by PLD are *c*-axis textured. It was demonstrated that the gas sensing characteristics of ZnO films are strongly influenced and may be enhanced significantly by the control of film deposition parameters and surface characteristics, i.e. thickness and RMS, grain shape and dimension.

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1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor of wurtzite structure, with a direct bandgap of about 3.37 eV at room temperature [1]. Polycrystalline ZnO has found numerous applications, such as those related to surface acoustic wave devices [2], piezoelectric devices [3], varistors, planar optical waveguides [4], transparent electrodes [5,6], ultraviolet photodetectors [7], facial powders, phosphors [8], gas sensors [9–11], etc. Regarding the gas sensor applications, ZnO-based devices have attracted significant interest since they present sensitivity to various gases, high chemical stability, suitability for doping, non-toxicity and low cost. Furthermore, the

sensitivity of nanostructured ZnO-based devices is relatively high due to the grain-size effect [9].

For the development of high sensitivity ZnO-based gas sensors, it is necessary to realize the correlation between gas sensitivity and microstructure of ZnO thin films. While the semiconducting properties of ZnO are in general similar to those of conventional semiconductors, its defect chemistry seems to be quite different. Even without intentional doping, n-type behavior is often displayed due to the low formation enthalpy of donor-type intrinsic defects such as oxygen vacancies and zinc excess. ZnO-based gas sensing elements are normally prepared in polycrystalline form and during the deposition process, large numbers of grain boundaries are formed. The oxygen adsorbed on the grain surface extracts conduction electrons from the near-surface region of the grain, leading to grain-boundary barriers, which determine grain-boundary resistance. Reaction of a reducing gas or UV light

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with the adsorbed oxygen results in its removal, and thereby, in a reduction of the barrier. On the contrary, the presence of oxidizing gases in the ambient leads to a decrease in the concentration of electrons in the surface layer and an increase in the height of the intergrain barriers [12].

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 nano-, micro-structural feature properties, such as the surface grain size, roughness, and film crystallinity on the electrical/sensing properties of the films.

2. Experimental details

The deposition of the ZnO films was carried out in a typical PLD deposition chamber [13], in 100% oxygen atmosphere

substrate temperature 350 °C, using a XeCl Excimer Laser (308 nm). Films having a thickness in the range of 10 nm to 1 μm were deposited onto Corning 1737F glass substrates with Ni–Cr electrical contacts deposited by thermal evaporation. The thickness of the films was measured using an Alphastep profilometer, while the surface morphology (grain size and surface roughness) was determined with an atomic force microscope (AFM) NanoScope III (Digital Co. Instruments, USA) using normal silicon nitride tips (125 μm) in Tapping Mode, scanning the surface with the oscillating tip in its resonant frequency (200–400 kHz). In the present study, the RMS roughness of the surface is defined as: $RMS\ (nm) = [\sum(z_i - z_{ave})^2/N]^{1/2}$, 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. The grain radius and the features dimensions were then evaluated using the facilities of NanoScope III Program. X-ray

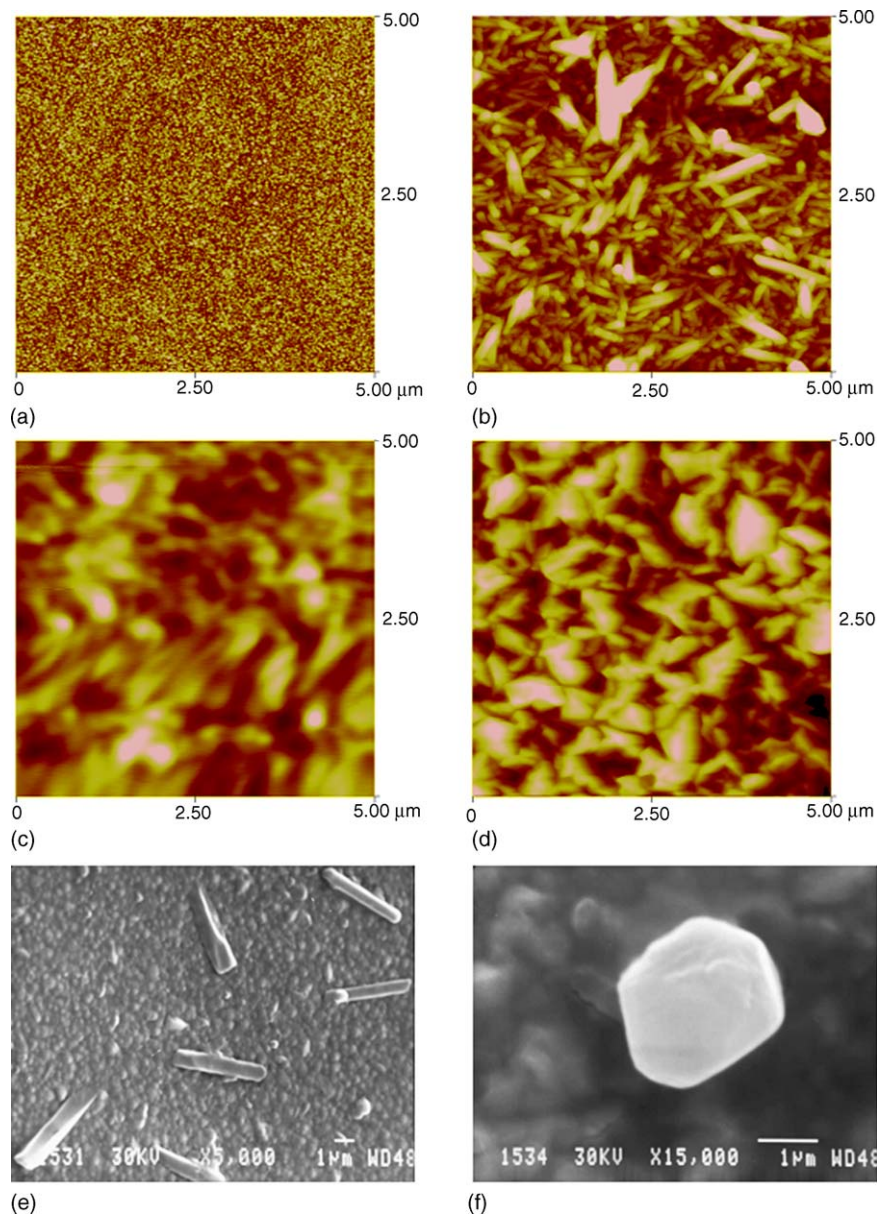


Fig. 1. AFM images of films surface (scan size 5 μm × 5 μm) for various thicknesses (a) 100 nm, (b) 200 nm, (c) 400 nm, (d) 1 μm and SEM images of (e) nanorods on a 1 μm thick film (f) hexagonal shaped grain on a 700 nm thick film.

diffraction (XRD) by using a Rigaku diffractometer with Cu K α X-rays determined the crystal structure of the deposited films. Finally, the conductivity measurements were carried out in a homemade special designed reactor [14]. For the photo-reduction process, the samples were directly irradiated in vacuum by the UV light of a mercury pencil lamp, placed at a distance of approximately 3 cm for a period of 15 min, time required to obtain steady state conditions. For the subsequent oxidation, the chamber was filled with oxygen at a pressure of 560 Torr and the samples were shielded from the lamp, which however was kept on, so that it can act as a UV source for ozone production. The above-described treatment was lasting almost 45 min, no further changes being observed in the conductivity after this time period. Finally, the chamber was again evacuated and the same photo-reduction/oxidation cycle was repeated for several times. For the conductivity measurements, a dc electric field (1 or 10 V cm⁻¹) was applied to the films during the whole procedure and the corresponding electrical current was measured using an electrometer. All conductivity measurements were carried out at room temperature using the two-point configuration. Current–voltage (*I*–*V*) measurements were always performed before the sensing cycle, in order to check the Ohmic nature of the contacts.

3. Results and discussion

SEM and AFM analysis (Fig. 1) revealed that all films grown at a temperature of 350 °C displayed a granular, polycrystalline morphology, with an increasing tendency for nano-, micro-rod formation as the thickness of the film increases. For the characterization of these films, it is important to determine their RMS roughness. The roughness of the grown films was found to be in the range 0.6–13.9 nm (Fig. 2). It can be noted that RMS increases with film thickness up to 200 nm. However, for films over 700 nm thickness, an irregular increase in the RMS with values over 70 nm was observed (not shown in Fig. 2), a behavior related to the presence of nano- or micro-features on the surface of the films, as it can be seen in Fig. 1e and f. The dimensions of the rods and structure features on the ZnO films'

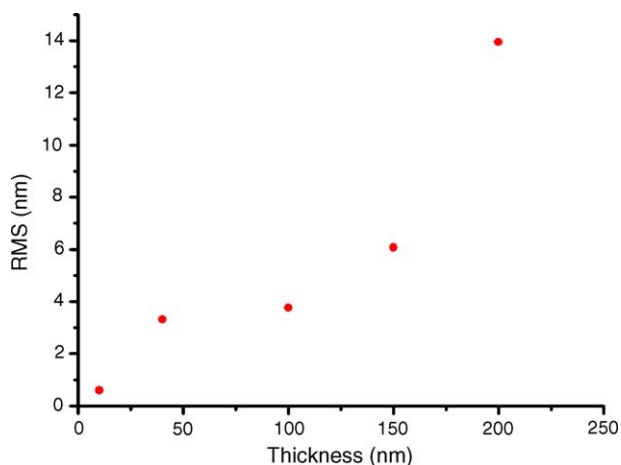


Fig. 2. Variation of the RMS roughness from AFM scan area of 5 $\mu\text{m} \times 5 \mu\text{m}$ with film thickness.

surface were determined to be in the range 10–200 nm for films with a thickness lower than 400 nm (Fig. 1b and c). For thicker films the rods were 1–3 μm long and their dimensions and shape strongly depended on the deposition parameters and the thickness of the film (Fig. 1d–f).

From the XRD 2θ – ω scans it is revealed that all deposited films are *c*-axis textured and show the (0 0 2) and the (0 0 4) basal plane reflections of wurtzite ZnO, in agreement with previous reports [15–18]. Fig. 3a shows the 2θ – ω scans for films with various thicknesses (100–400 nm), recorded in the vicinity of the (0 0 2) reflection plane and plotted on a semi-logarithmic scale. The broadening of this particular peak can be used to determine the crystallite size (*d*), which is inversely proportional to the Full Width at Half Maximum (FWHM) of the peak according with Scherer's formula:

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2} \cos \theta} \quad (1)$$

In Eq. (1), β is the FWHM of the (0 0 2) peak width in radians, β_0 the width introduced by the instrumental broadening, $K = 0.9$, $\lambda = 0.154056$ nm and θ is the peak position [19].

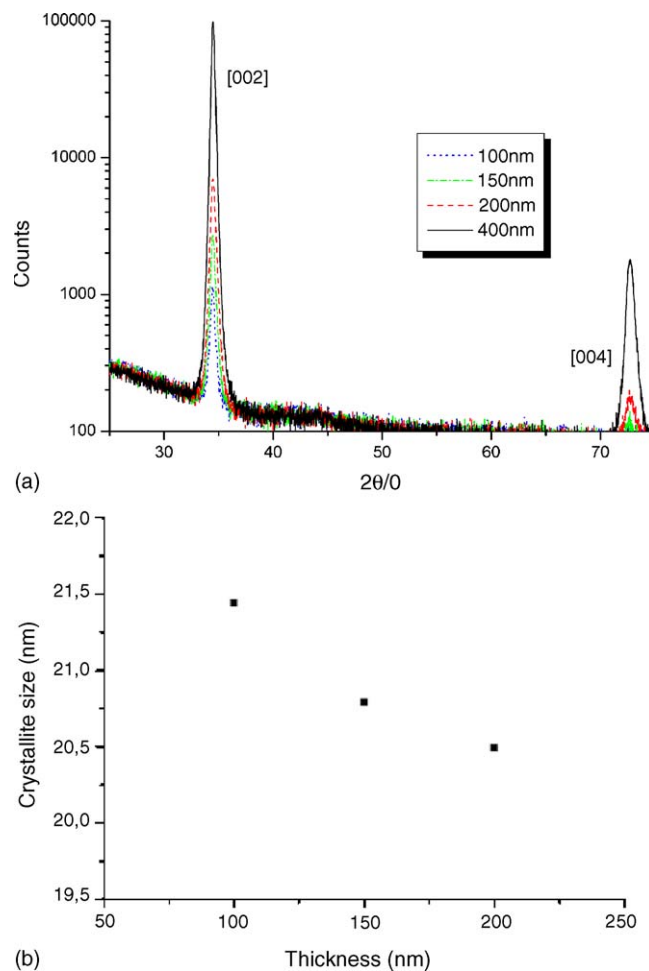


Fig. 3. (a) XRD 2θ – ω scans of ZnO films for various thicknesses and (b) variation of crystallite size calculated by the Scherer formula with film thickness.

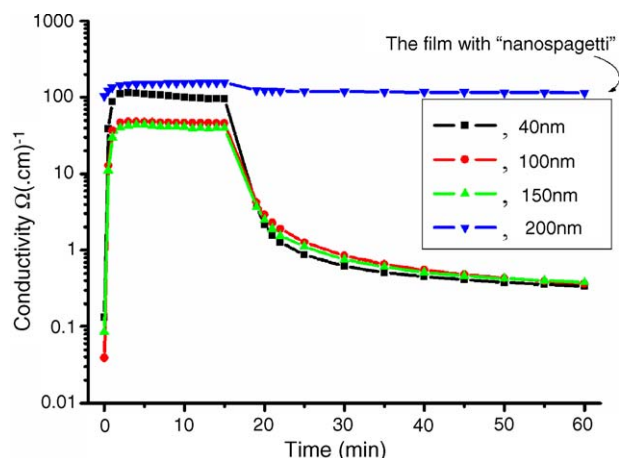


Fig. 4. Conductivity changes under UV photo-reduction (starts at 0 min) and ozone oxidation (starts at 15 min, lasts for 45 min) for films of different thicknesses.

The mean crystallite dimensions calculated from Eq. (1) are of the order of 20 nm and their variation with film thickness is presented in Fig. 3b. It is observed that the crystallite size reduces slightly for films up to 200 nm (21.4, 20.8, 20.5 nm).

The film sensitivity to ozone is in general correlated to oxygen stoichiometry and film microstructure. Conductivity changes in the ZnO films under reduction and/or oxidation are related to the formation and annihilation of oxygen vacancies. The irradiation of the samples with UV photons having energy larger than the Zn–O bonding energy can result in the transformation of a bound oxygen atom to a gaseous one, a process that changes the number of the free oxygen vacancies. In general, all films studied show high conductivity values (~ 0.1 – $100 \Omega^{-1} \text{ cm}^{-1}$), which indicates high carrier concentration due to the presence of oxygen vacancies and/or Zn interstitials. Henley et al. have reported recently such high conductivity values for pulsed-laser deposited ZnO films [20]. The results of the photo-reduction and oxidation treatments are presented in Fig. 4. As it can be seen, the reduction of the films resulted in an increase of conductivity of about two to three orders of magnitude, for films with low thickness (≤ 150 nm). The subsequent oxidation in ozone has led to a drop of conductivity by two orders of magnitude. It should be mentioned here that the observed behavior was completely reversible through many cycles of photo-reduction and oxidation. However, the conductivity of the 200 nm thick film was kept almost constant ($\sim 100 \Omega^{-1} \text{ cm}^{-1}$). This behavior could be attributed to the presence of nano-features on the film's surface. Comparing the variation of conductivity (Fig. 4) with that of the surface RMS from the AFM measurements (Fig. 2), it can be noted that as the RMS increases the conductivity change after O_3 exposure decreases (for a thickness ≤ 150 nm). The bulk crystallite dimensions also slightly decrease with increasing film thickness (Fig. 3b). The lateral grain size increase with thickness observed by AFM could be due to the formation of surface grains by the agglomeration of a number of smaller crystallites. As a result, the grains on the surface of thicker films contain more grain boundaries leading to the observed decrease in conductivity change after O_3 exposure for thickness values

up to 150 nm. Consequently, ZnO films, with a thickness up to 150 nm, could be potentially applied for ozone detection and their sensitivity towards ozone could be significantly enhanced by controlling their surface morphology.

4. Conclusions

ZnO films grown by PLD on glass substrates present a granular, polycrystalline morphology. Surface RMS increases with film thickness, the films with large thickness presenting a tendency for nanostructured formation. Photo-reduction treatment results in up to three orders of magnitude increase of the conductivity while ozone oxidation of films with a thickness up to 150 nm results in a conductivity drop by two orders of magnitude. Films with a higher thickness display no conductivity changes, and thus no sensitivity due to the high concentration of nano-features on the surface. This behavior was reversible through many cycles of photo-reduction and oxidation. Therefore, ZnO films grown by PLD could be used for ozone detection and their sensitivity can be improved by controlling the deposition parameters and surface microstructure.

Acknowledgments

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