

Substrate temperature influence on the properties of nanostructured ZnO transparent ultrathin films grown by PLD

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Abstract

Zinc oxide films of 40 nm thickness have been deposited on glass substrates by pulsed laser deposition using an excimer XeCl laser (308 nm) at different substrate temperatures ranging from room temperature to 650 °C. Surface investigations carried out by using atomic force microscopy have shown a strong influence of temperature on the films surface topography. UV–VIS transmittance measurements have shown that our ZnO films are highly transparent in the visible wavelength region, having an average transmittance of ~90%. The optical band gap of the films was found to be 3.26 eV, which is lower than the theoretical value of 3.37 eV. Besides the normal absorption edge related to the transition between the valence and the conduction band, an additional absorption band was also recorded in the wavelength region around 364 nm (~3.4 eV). This additional absorption band may be due to excitonic, impurity, and/or quantum size effects. Photoreduction/oxidation in ozone of the ZnO films lead to larger conductivity changes for higher deposition temperature. In conclusion, the ozone sensing characteristics as well as the optical properties of the ZnO thin films deposited by pulsed laser deposition are strongly influenced by the substrate temperature during growth. The sensitivity of the films towards ozone might be enhanced significantly by the control of the films deposition parameters and surface characteristics.

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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]. It is a quite important oxide which exhibits near ultraviolet emission and transparent conductivity. ZnO is piezoelectric due to its non-central symmetry, a property that

makes it a major candidate for building electromechanical coupled sensors and transducers [2]. ZnO is also one of the most widely applied oxide gas sensing materials [3]. It is sensitive to many sorts of gases at moderate temperatures and shows satisfactory stability [4–10]. ZnO gas sensor elements have been fabricated in various forms, like single crystals, sintered pellets and thin films. Thin films exhibit many advantages since they can be fabricated in small dimensions, at large scale and low cost and are widely compatible with microelectronics technology. As-deposited ZnO films are mainly polycrystalline and during the deposition process, a large number of grain boundaries are formed. Oxygen adsorbed on the grain's surface results in the extraction of conduction electrons from the near-surface region of the grain, a process that leads to an increase of

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grain-boundary barriers and grain-boundary resistance. These barriers can be reduced or increased via the reaction of the film with UV light or oxidizing gases, respectively [11], leading to a gas-sensing action. Gas sensing from ZnO thin films requires accurate control and comprehensive understanding of various parameters related to the film deposition process such as substrate temperature, kinetic energy of the deposition flux, deposition rate [12] and buffer gas pressure.

In our previous work we have shown that very thin ZnO films present better sensing response as compared to thicker ones [13]. In this work, we examine the influence of the growth temperature on nanostructural properties of ZnO ultrathin films prepared using the pulsed laser deposition (PLD) technique. Our investigation attempts to show the influence of deposition temperature on the ultrathin films surface parameters like surface grain size and roughness and correlate them with the optical as well as the electrical/sensing properties of the films.

2. Experimental details

A typical PLD deposition chamber was used for the deposition of 40 nm thick ZnO films [14], in oxygen atmosphere at different temperatures ranging from room temperature (RT) to 650 °C, using a XeCl Excimer Laser (308 nm) as the light source. The films were deposited onto silicon [1 1 1] and Corning 1737F glass substrates, the electrical contacts being deposited by thermal evaporation. The thickness of the films was measured using an Alphastep profilometer, while the surface characterization was performed with an atomic force microscope (AFM) Nanoscope III (Digital Co. Instruments, USA). In the present study the morphology parameters were determined using the scanning probe image processor (SPIP) image processing software for nano- and micro-scale microscopy. The RMS roughness of the surface is then defined as

$$\text{RMS} = \sqrt{\frac{\sum_{i=1}^N (z_i - z_{\text{ave}})^2}{N}}$$

where z_i is the current value of z , z_{ave} the mean value of z in the scan area and N is the number of points. Surface bearing index, S_{bi} is defined as the ratio of the RMS deviation over the surface height at 5% bearing area. Then, $S_{\text{bi}} = \text{RMS}/Z_{0.05} = 1/h_{0.05}$, where $h_{0.05}$ is the normalized surface height at 5% bearing area. A large surface bearing index indicates a good bearing property. For a Gaussian distribution of the height S_{bi} approaches 0.608 with increasing number of pixels. Moreover, the surface area ratio, S_{dr} , expresses the ratio between the surface area (taking the z height into account) and the area of the flat xy plane:

$$S_{\text{dr}} = \frac{S_{3A}}{S_{2A}} = \frac{\left(\sum_{k=0}^{M-2} \sum_{l=0}^{N-2} A_{kl} \right) - (M-1)(N-1) \delta x \delta y}{(M-1)(N-1) \delta x \delta y} \times 100\%$$

where

$$A_{kl} = \frac{1}{4} \left[\sqrt{\delta y^2 + (z_{k,l} - z_{k,l+1})^2} + \sqrt{\delta y^2 + (z_{k+1,l} - z_{k+1,l+1})^2} \right] \times \left[\sqrt{\delta x^2 + (z_{k,l} - z_{k+1,l})^2} + \sqrt{\delta x^2 + (z_{k,l+1} - z_{k+1,l+1})^2} \right]$$

For a totally flat surface, the surface area and the area of the xy plane are the same and $S_{\text{dr}} = 0\%$. Finally, the fractal dimension, S_{fd} is calculated for the different angles by analyzing the Fourier amplitude spectrum; for different angles the Fourier profile is extracted and the logarithm of the frequency and amplitude coordinates calculated. The fractal dimension for each direction is then calculated as 2.0 minus the slope of the log–log curves [15].

The optical transmittance of the films was measured using a Varian Cary50 UV–VIS spectrophotometer with Varian data analysis tools. XRD measurements performed did not show any peaks due to the rather small thickness of the deposited films. Finally, the conductivity measurements were carried out in a homemade designed reactor [13]. For the photoreduction process, the samples were directly irradiated in vacuum by the UV light of a mercury pencil lamp. 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 was kept on so that it can induce ozone production. The overall treatment was lasting approximately 40 min, no further changes being observed in the conductivity after this time period. The same photoreduction/oxidation cycle was repeated for several times. For the conductivity measurements, an 1 V cm^{-1} dc electric field was applied to the films and the corresponding electrical current was measured using an electrometer. All conductivity measurements were carried out at room temperature. 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

AFM analysis (Fig. 1) revealed that all films displayed a granular, polycrystalline morphology, with an increasing tendency for texturing of the surface as the substrate temperature increases. The roughness of the grown films was found to be in the range 1.745–3.624 nm with an irregular variation with temperature as represented in Fig. 2a (square symbols). The dimensions of structure features on the ZnO films' surface were determined to be in the range 10–85 nm with a clear tendency to form grain agglomerations for films grown at higher temperatures. In order to fully characterize the surface properties evolution as a function of the growth temperature, the S_{dr} , S_{bi} and S_{fd} parameters were determined. Fig. 2a and b presents the influence of temperature on the parameter values. As it can be observed, increased growth temperature induces a general increase of the active surface as well as of the surface fractal dimension. Surface bearing index exhibits small variations around 0.56 in all films, a value close to 0.608 which corresponds to a Gaussian ideal distribution

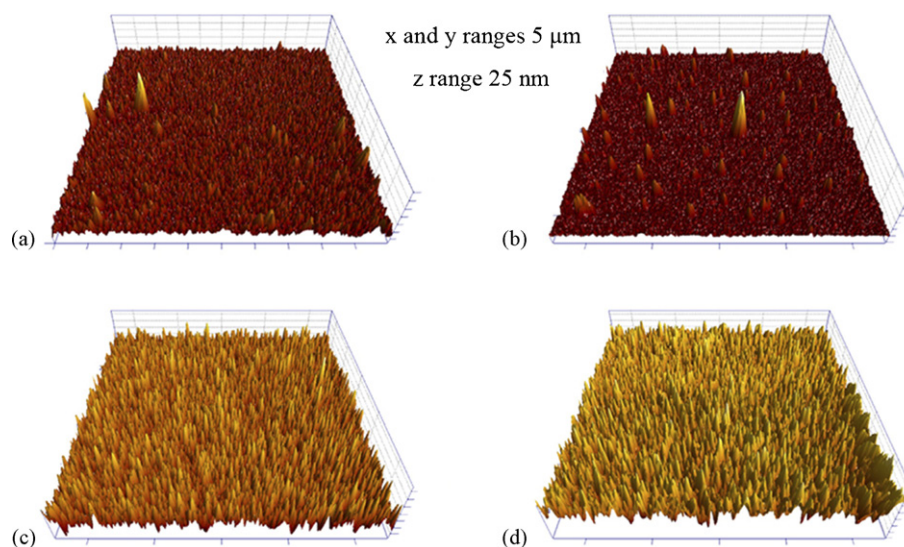


Fig. 1. 3D AFM images of films surface (scan size $5\ \mu\text{m} \times 5\ \mu\text{m}$) for various growth temperatures: (a) 150 °C, (b) 350 °C, (c) 450 °C, and (d) 650 °C.

(Fig. 2a, stars). Therefore, it can be concluded that the film surfaces are quite homogeneous.

The as-deposited ZnO thin films were found to be highly transparent in the visible wavelength region (Fig. 3a) with an average transmittance of 90%, the absorption edge in the UV region depending on film growth temperature. The optical energy gap E_g was derived assuming a direct transition between the edges of the valence and the conduction band. Then, the variation in the absorption coefficient with the photon energy $h\nu$ is given by $\alpha(h\nu) = A\sqrt{h\nu - E_g}$. “Tauc” plots of α^2 versus $h\nu$ can give the optical band gap value E_g , by extrapolation of the linear region of the resulting curve. The calculated values of the direct optical energy gap were found to be in the range 3.20–3.26 eV, depending on the growth temperature. Fig. 3b (square symbols) presents the variation of

the optical energy gap as a function of deposition temperature. As it can be observed, the energy gap varies slightly with growth temperature, a response attributed to the variation of the film density (bulk crystallite dimension) with temperature. In addition, quantum size effects may be involved due to nano-features on the films [2].

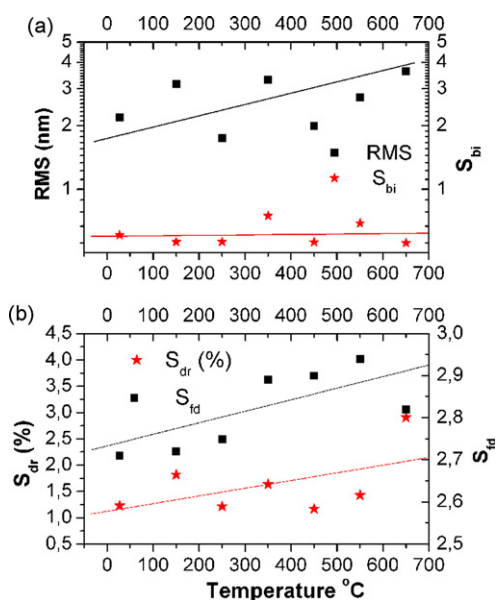


Fig. 2. Variation of the surface parameters with growth temperatures: (a) RMS and S_{bi} and (b) S_{dr} and S_{td} .

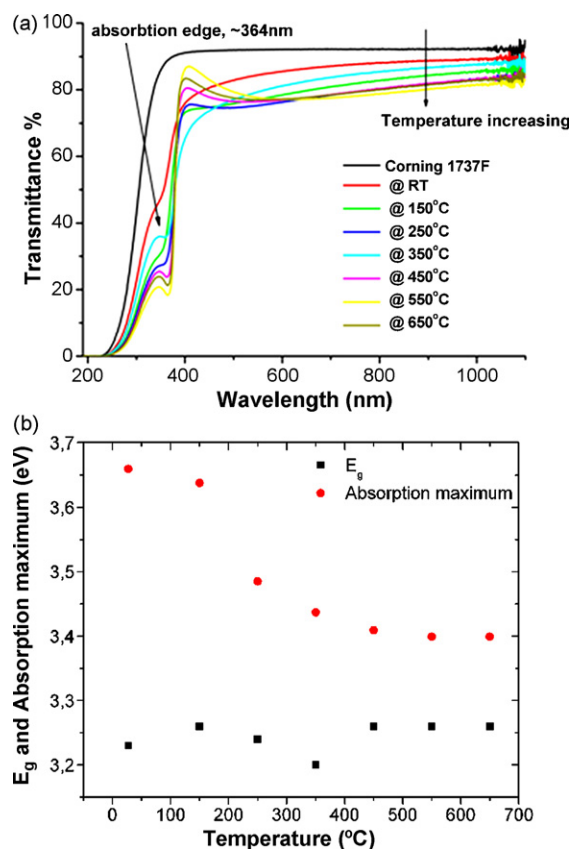


Fig. 3. Variation of the optical properties with growth temperature: (a) UV–VIS transmittance and (b) optical band gap variation and peak position changes for the additional absorption band.

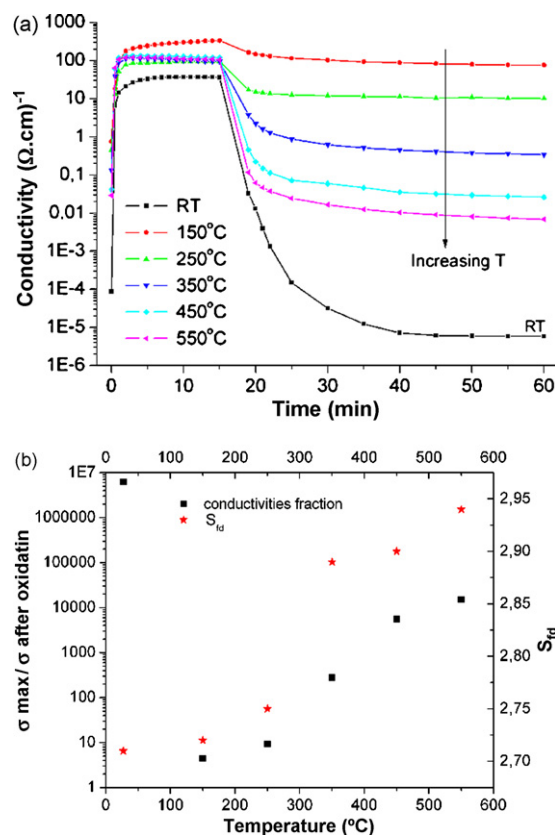


Fig. 4. (a) Conductivity changes under UV photoreduction and ozone oxidation for films grown at different temperatures. (b) Conductivity changes from photoreduced to ozone oxidized state compared with surface fractal dimension variation.

Except the absorption edge at ~ 3.26 eV, an additional absorption band was observed at ~ 3.4 – 3.65 eV, its actual position also dependent on growth temperature. The presence of such an absorption band has been also reported for nanostructured ZnO, and it is attributed to size effects [16] and excitonic phenomena [17]. The increase of the growth temperature was found to cause a red shift of the maximum of this band, as shown in Fig. 3b (circular symbols).

Regarding the sensitivity of ZnO films to ozone, this is in general correlated to oxygen stoichiometry and film microstructure [18]. Furthermore, the 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. The results of the photoreduction and oxidation treatments of the deposited films are presented in Fig. 4a. It is obvious that the reduction of the as-deposited films resulted in an increase of conductivity up to six orders of magnitude, the actual response depending on growth temperature. The subsequent oxidation in ozone leads to a drop of conductivity by one to six orders of magnitude, a behavior completely reversible through many cycles of photoreduction and oxidation. The dependence of the conductivity changes on the growth

temperature can be attributed to the evolution of the surface morphology of the films with growth temperature. This can be seen in Fig. 4b, which presents the variation of conductivity changes under ozone exposure (square symbols) with that of the parameter S_{fd} obtained from the AFM measurements (star symbols). Both conductivity changes and S_{fd} increase similarly with temperature for all cases, except for the film grown at RT. This leads to the conclusion that the fractal dimension of the ZnO films, which gives an indication of the surface-to-volume ratio of the films, varies almost linearly with the conductivity changes caused by the photoreduction/oxidation process. Roughness as well as the surface area ratio, S_{dr} , and the fractal dimension, S_{fd} , increase at higher deposition temperatures, resulting in larger conductivity changes of the PLD grown ZnO films and thus to better sensitivity to ozone.

4. Conclusions

ZnO thin films of 40 nm thickness grown by PLD at different substrate temperatures present a granular, polycrystalline morphology. The films grown at higher temperatures show a tendency for the formation of nanostructures. The optical band gap of the films was found to be ~ 3.23 – 3.26 eV, which is lower than the theoretical value of 3.37 eV. An additional absorption band was also recorded at ~ 3.4 – 3.65 eV, which red shifts with increasing deposition temperature. Photoreduction/ozone oxidation treatment results in up to six orders of magnitude change in the conductivity of the films. The increase in deposition temperature results in higher film roughness, surface area ratio and fractal dimension of the films, leading to larger conductivity changes.

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