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THIN ZnO FILMS PRODUCED BY PULSED LASER DEPOSITION

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In this work, thin ZnO films have been produced by pulsed laser deposition on (001) SiO_2 substrates. The influence of the substrate temperature and oxygen pressure applied on the structural, morphological, and optical properties of the films were investigated. All ZnO films are textured along (002) direction. The increase of the substrate temperature enhances the diffraction peak intensity for all oxygen pressures applied. Highest intensity peak for a fixed temperature was obtained at pressure in the range 0.05 – 0.1 mbar. The increase of the substrate temperature at 0.1 mbar leads to deposition of smoother films with an average RMS value of 9 – 11 nm. The film morphology changes with the increase of oxygen pressure at fixed temperature. Highest optical transmission was achieved at room temperature. The increase of the oxygen pressure reduces the film transmission in the visible range of the spectra. The value of the measured waveguide losses strongly depends on the crystalline quality and surface roughness of the films. The optical losses decrease to a value lower than 3 dB/cm when temperature increases.

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1. Introduction

In the recent years, gas sensors based on optical detection have focused a high attention due to the possibility to operate at room temperature, to have very fast response time, and to measure lower gas concentrations compared to the traditional sensitive elements [1]. Optical sensors have been shown to be safety in explosive environment as well as being applicable even in unusual and extreme conditions. When gas components interact with the thin film surface, change of its physical or chemical properties is observed. A new possibility of improving the precise measuring of the gas concentration is revealed when the working mechanism is based on detection of the refractive index changes upon gas exposure.

Various basic materials such as ZnO, SnO_2, In_2O_3, TiO_2, SnO_2/NiO, metal acetylacetonates and etc. were tested and studied as sensing media [2-3]. ZnO is a promising candidate for such application due to its high transparency in the visible wavelength range and low electric resistance [4-6]. The ZnO sensing media have a strong response when react with reducing gas agent such as H_2, NO_x, NH_3, SO_x and etc.

Different deposition techniques can be used to prepare ZnO thin films, such as pulsed laser deposition (PLD), chemical vapor deposition, magnetron sputtering, sol – gel processing and etc. [5, 7-9]. PLD has been successfully used for growth of multicomponent oxides, primarily because the stiochiometry of the laser irradiated target can be reproduced in the film. The method is very attractive for the deposition of high quality optical films with losses less than 1 dB/cm suitable for waveguide applications [10].

The aim of this work is to produce quality ZnO thin films by pulsed laser deposition and to investigate the influence of the substrate temperature and oxygen pressure applied during the process

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on the structural, morphological, and optical properties of the films in respect to gas sensor applications.

2. Experimental

Preparation of the thin ZnO films was carried out by standard on – axis PLD setup. The experiments were performed by XeCl excimer laser (308 nm, pulse duration of 30 ns, repetition rate of 2 Hz). The laser fluence was kept at 2 J/cm^2. The vacuum chamber was pumped to a background pressure of 10^{-5} mbar. All the experiments were performed in oxygen atmosphere in the range of 0.05 – 0.3 mbar. (001) SiO_2 was used as substrates because of its low refractive index and high transparency in the visible and near infrared ranges of spectra. The films were grown at different substrate temperatures in the range of 25 – 500 °C. The substrate temperature was always kept below 573.5 °C, the temperature of the structural transformation on SiO_2. The target-to-substrate distance was 4cm. Home – made ceramic targets were used in the experiments. The targets were made from 99.99 % purity ZnO powder pressed at 6 MPa. The as - prepared targets were calcified at 500 °C for 4 h and then sintered at 1150 ºC for 12 h.

The crystal structure of the films was analyzed by XRD measurements with Co Kα radiation in θ - 2θ Bragg - Brentano geometry. The surface morphology of the films was studied by Atomic force microscopy (AFM). The optical transmission spectra of the films were investigated by CARY 5E Spectrophotometer. The refractive index and the thickness of the as – deposited films were determined by m - line spectroscopy using film – prism coupling. The optical waveguide loss measurements were performed by recording the attenuation of the scattered light of He – Ne laser along with the propagation path.

3. Results and discussions

XRD analyses show that all the films are textured along (002) direction independently on the substrate temperature and oxygen pressure applied. However, the temperature and pressure have an influence on the intensity and width of the diffraction peak. Fig. 1 shows XRD patterns of the ZnO films produced at fixed oxygen pressure of 0.1 mbar and substrate temperature from 25 to 500 °C. It is clearly seen that increase of the substrate temperature leads to the enhancement of the peak intensity. This behavior is valid for all oxygen pressure applied. The temperature dependence on the film quality can be interpreted mainly by the mobility of the atoms in the films at different temperatures. At low temperature, the vapor species have a low surface mobility and will be located at different positions on the surface. The low mobility of the species will prevent full crystallization of the films. This is the reason why the diffraction peak (002) of the films deposited at room temperature is slightly shifted. The increase of the substrate temperature over 150 °C is high enough to ensure such species mobility, which will arrange them at a suitable position in the crystalline cell. This result is in good agreement with previous work [12].

Fig. 2 shows the dependence of the diffraction peak intensity on the substrate temperature at different pressure of oxygen. Highest intensity peak was obtained at oxygen pressure in the range of 0.05 – 0.1 mbar for all substrate temperatures. Further increase of the O_2 pressure reduces crystallinity of the films. Two components have contribution to the actual surface temperature during growing of the films: the substrate heating by the heater and the kinetic energy of the vapor species impinging on the surface during the process. Since the first component was kept constant during the deposition process, the second one may have influence on the crystalline quality of the films. At higher O_2 pressure the kinetic energy of the growth species reduces because the laser ablated vapor species suffer more collisions with the gas molecules which results in lowering of the surface temperature and the film crystallinity decreases.

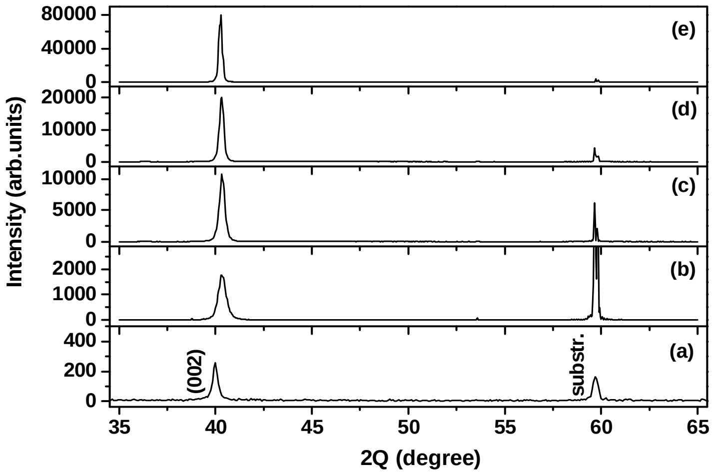


Fig. 1. XRD patterns of the ZnO films produced at 0.1 mbar oxygen pressure and different substrate temperature: (a) room, (b) 150 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C.

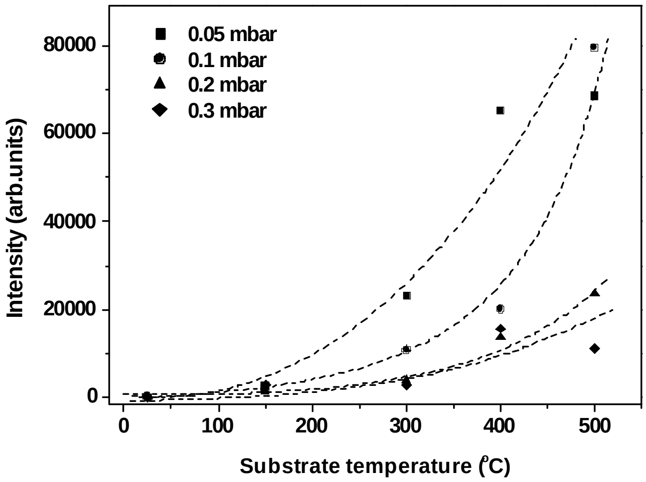


Fig. 2. Dependence of the diffraction peak intensity on the substrate temperature at different oxygen pressures.

It is well known that the sensitivity of the sensor media strongly depends on the grain dimension of the sensing material. The grain size was calculated using the Scherrer's equation. The estimated value strongly depends on the substrate temperature. Fig. 3 shows the influence of the out-of-plane diffracting domain size on the oxygen pressure applied at different substrate temperature. It is clearly seen that the grain size increases with the temperature raise. Moreover, the increase of the substrate temperature shifts the optimum pressure for achieving smaller grains towards higher pressures. This result correlates with the rise of the width of the XRD peaks with the O_2 pressure.

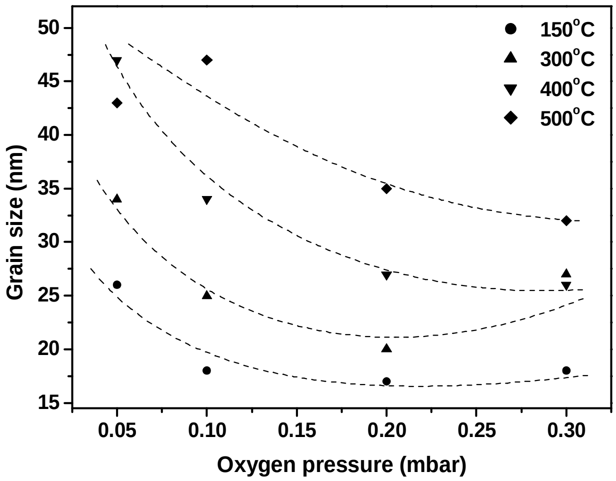
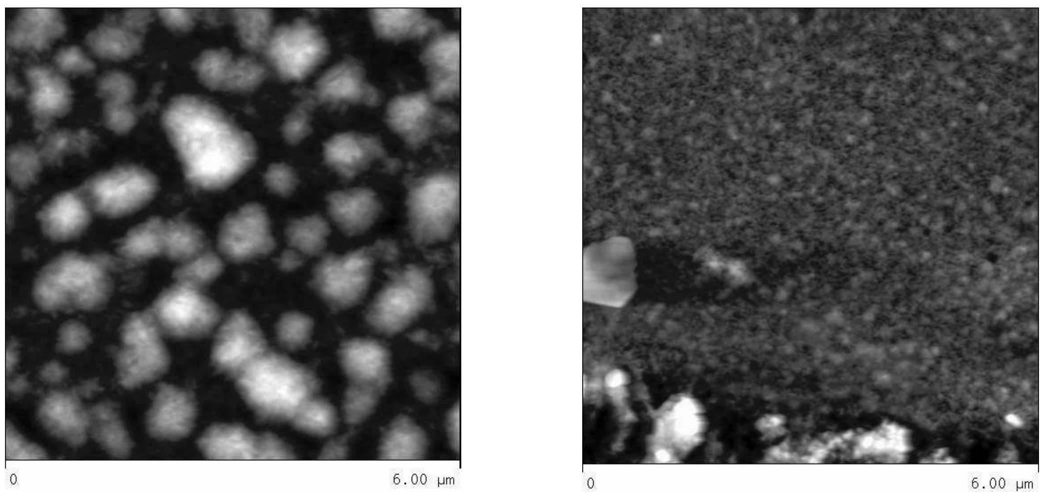


Fig. 3. Influence of the grain size of the films on the oxygen pressure applied at different substrate temperatures.

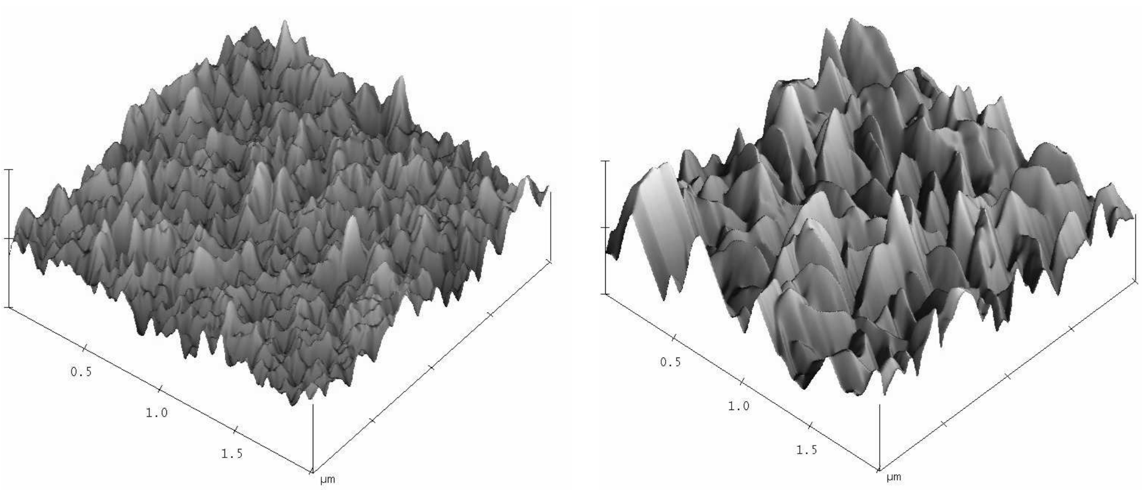
The morphology and the optical properties of the sensing thin films are also important characteristics for optical detection. Fig. 4 presents AFM images of the ZnO films produced at oxygen pressure of 0.1 mbar and two different substrate temperature. The surface of the films at lower temperature (150 °C) consists of a continuous background with large isolated islets (Fig. 4a). At higher temperature (500 °C), the number and size of the islets decrease (Fig. 4b). The highest RMS value of about 35 nm was obtained for the film prepared at 150 °C and 0.1 mbar. The increase of the substrate temperature at 0.1 mbar oxygen pressure leads to deposition of smoother films, which average RMS value is about 9 – 11 nm. The increase of the oxygen pressure at fixed temperature leads to change of the film morphology.

Fig. 5 shows the AFM images of the ZnO films prepared at 300 °C and different oxygen pressure. It is clearly seen that the increase of the oxygen pressure enhances the porosity of the surface and RMS value.



(a) (b)

Fig. 4. AFM images of the ZnO films produced at 0.1 mbar oxygen pressure and two substrate temperatures:(a) 150 °C and (b) 500 °C.



(a) (b)

Fig. 5. AFM images of the ZnO films prepared at 300 °C and two oxygen pressures:
(a) 0.05 and (b) 0.3 mbar.

All the films are transparent in the visible and near IR range of spectra. Highest optical transmission of about 85 - 92 % was obtained [11]. The highest values of the optical transmission were achieved at room temperature. It is worth pointing out that the increase of the substrate temperature leads to the shift of the transmission cut-off edge to the long wavelengths (Fig. 6). This result is in good agreement with this previously reported data [12]. As it was deduced by XRD analyses, the increase of the substrate temperature leads to the better crystallinity of the films. The quantity of the free charges in the structure will decrease with enhancement of the film crystallinity. Consequently, the optical band gap width will decrease. This means that the absorption edge should be shifted towards the longer wavelengths. The oxygen pressure applied also has negative effect on the film transparency. The optical transmission has a tendency to decrease with increasing oxygen pressure. This result is due to the higher roughness achieved when higher O_2 pressure was applied during the film deposition.

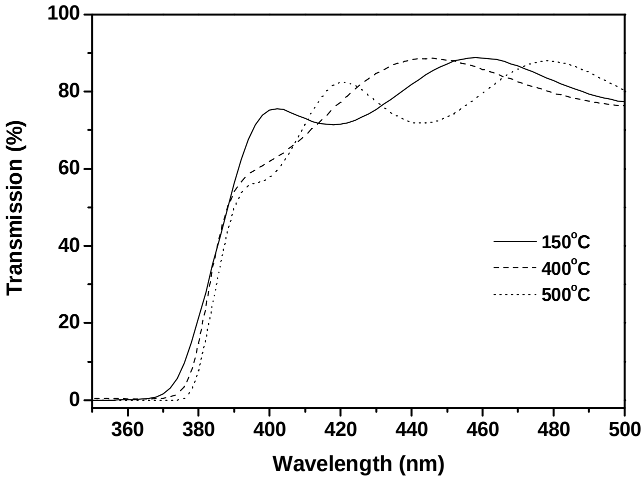


Fig. 6. Optical transmission spectra of the ZnO films at different substrate temperatures.

The m-line spectroscopy was used to determine the refractive index and the thickness of the films. Thin mode lines with good contrast were observed for most of the films. ZnO has a hexagonal structure, which means that the refractive index has different values for TE and TM waves. The values in the range of 1.97 - 1.99 for TE and 1.98 - 2.01 for TM were obtained, which are closed to those of the bulk material. The measured film thickness was in the range of 450 – 650 nm. The waveguide effect was observed in all films presented in this work. The value of the measured waveguide losses strongly depends on the crystallinity and surface roughness of the films. As it was demonstrated by AFM measurements, smoothest films suitable for waveguide propagation were deposited at lowest oxygen pressures applied – 0.05 mbar. The increase of the temperature enhances the quality of the crystalline structure and surface morphology, which decreases the optical scattering by the film surface. As a result, optical losses lower than 3 dB/cm were measured. It is well known that gas sensitivity of the sensing media increases with the decrease of the grain size. As it was discussed above, the grain size becomes lower when substrate temperature is reduced. Grain size of 30 nm and optical losses of 1.3 dB/cm were achieved in the films deposited at 300 °C and 0.05 mbar oxygen pressure. These films are a good candidate for gas sensor application.

4. Conclusion

Highly textured thin ZnO films have been produced by pulsed laser deposition. The diffraction peak intensity and the grain size increases with the substrate temperature raise for all oxygen pressure applied. The higher the substrate temperature is the smoother the films at fixed oxygen pressure. Highest values of the optical transmission were achieved at room temperature. The increase of the oxygen pressure decreases the film transmission in the visible range. Small grain size of about 30 nm and low optical losses of about 1.3 dB/cm were achieved for the films deposited at 300 °C and 0.05 mbar. These films are good candidates for gas sensor application.

Acknowledgments

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