International Journal of Physical Sciences Vol. 6 (18), pp. 4382-4387, 9 September, 2011
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS11.648
ISSN 1992 -1950 ©2011 Academic Journals

Full Length Research Paper

Electrical, structural and optical properties of ZnO thin films grown by pulsed laser deposition

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Accepted 20 June, 2011

We report the influence of oxygen partial pressure (PO_2) on the electrical, structural and optical properties of no-stoichiometric ZnO ($ZnO_{1-\delta}$) thin films grown by Nd:YAG pulsed laser deposition. We note that the electrical resistance of the $ZnO_{1-\delta}$ thin films is significantly modified by oxygen pressure; the electrical resistance decreases with the O_2 pressure in the range of 10 to 40 mTorr and reach a minimum resistance of $\rho \sim 2.1x10^{-2}$ Ω-cm at 30 mTorr increasing again after this pressure. These indicate that the increase/decrease of the electrical resistance is ascribed to the annihilation/formation of the residual donor-type defects in the $ZnO_{1-\delta}$ thin films, mainly due at the oxygen pressure. It is suggested that the decrease of the electrical resistance is due to the formation of oxygen vacancies (V_O) complex defects. X-ray diffraction shown that the oxygen pressure doesn't affect the main peaks positions which reflect the existence of hexagonal ZnO single phase and five principal peaks (100), (002), (101), (110) and (103) appeared in the films. The $ZnO_{1-\delta}$ thin films shown an average transmittance of ~85% with optical band gap of average value of ~3.3 eV.

Key words: Pulsed-laser deposition, zinc oxide, transparent conducting oxide, electro-optical properties.

INTRODUCTION

The simultaneous occurrence of high optical transparency (>80%) in the visible region and high electrical conductivity (>10^3 S-cm^{-1}) is not possible in an intrinsic stoichiometric material. Partial transparency and good conductivity can be achieved in thin films of a variety of materials. The easy option to obtain good transparent conductors is to create electron degeneracy in wide band gap oxide materials by controlling the non-stoichiometry or by adding dopants. These conditions can conveniently be created in oxides of indium, tin, zinc, cadmium and their alloys in thin film form. The unique property of the transparent conducting oxide films make them very useful in a large number of electric and optoelectronic applications such as resistors, electromagnetic shield coatings, transparent electrodes for solar cells, antireflection coatings, heat reflecting mirrors, gas sensors and protective coatings. The electrical and optical properties of these films depend mainly on the microstructure, stoichiometry and the nature of impurities present. It also depends on the deposition condition, substrate temperature and oxidation process that occur during and after the deposition. Each deposition technique has characteristic parameters which must be optimized to yield desirable properties. Doping is the most significant parameter which affects the electro-optical properties of

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Abbreviations: TCO, Transparent conductor oxides; **ZnO,** Zinc oxide; **UV,** ultraviolet; **PLD,** pulsed laser deposition; **PO_2,** partial pressure; **Ts,** substrate temperature; **XRD,** x-ray diffraction beam; **V_O,** oxygen vacancies.

the transparent conductor oxides (TCO). The large conductivity of oxide thin film is due to high electron concentration resulting from the deviation from the stoichiometry and doping effects. The deviation in stoichiometry is due to the anion vacancies and excess interstitial electrons.

Zinc oxide (ZnO) is an *n*-type semiconductor with a wide band gap of 3.3 eV, it shows high optical transmittance and a wide range of electrical conductivity values simultaneously. ZnO is used in many different application in both microelectronic and optoelectronic devices. As a consequence of it direct energy gap, ZnO absorbs ultraviolet (UV) radiation due to band-to-band transitions (Norton et al., 2004). Furthermore ZnO can be used as semiconducting gas sensor (Subramanyam et al., 2000) due to conductivity changes it exhibits when exposed to oxidizing gases such as ozone. Several techniques can be used to grow ZnO thin film, like pulsed laser deposition (PLD) (Villanueva et al., 2006), ion plating, spray pyrolysis (Olvera et al., 2007), metal-organic chemical vapor deposition (Tan et al., 2005), rf-and-dc magnetron sputtering, among others. Due to intrinsic and extrinsic defects, also it is possible with PLD technique to obtain ZnO films with a wide range of resistivity, from 10^{-4} to 10^{9}) cm (Ondo-Ndong et al., 2003). The properties of ZnO thin films are known to depend on deposition parameters such as substrate temperature (Li et al., 2003), type of substrate (Ondo-Ndong et al., 2003), pressure and gas atmosphere (Tvarozek et al., 2007) and thickness (Bouderbala et al., 2008). In particular the growth behavior including growth orientation (Zhang et al., 2007), microstructure and electrical properties (Gao and Li, 2004) of oxide films is very sensitive to the oxygen partial pressure (PO_2) used. Therefore, when one attempts to grow ZnO films of high quality using PLD, it is necessary to simultaneously consider both defect formation and film growth behavior in optimizing ambient PO_2 in the growth chamber.

In the present work, studies have been made on the physical characteristics of ZnO thin films. These films have been grown by using PLD in a vacuum coating chamber. We report results concerning the effect of oxygen partial pressure on the electrical, structural and optical properties of ZnO thin films.

EXPERIMENTAL PROCEDURE

Non-stoichiomteric ZnO ($ZnO_{1-\delta}$) thin films (71-22 nm thick) were deposited on glass substrates (Corning No. 7059) using a Nd:YAG laser λ=1064 nm, 10 ns full width at half maximum at a repetition rate of 5 Hz under the conditions listed in Table I. The laser was focused through a 50 cm focal length lens onto a rotating target at a 45° angle of incidence. The targets were prepared from solid reaction of ZnO powder to sintered one solid disk of 5 mm of thickness and diameter of 15 mm. The films were deposited at substrate temperature (Ts) of 300°C in PO_2 ranging between 10 and 40 mTorr. The substrates were cleaned in an ultrasonic cleaner for 10 min with acetone and then methanol.

The structural properties were determined by measurements in the grazing incidence geometry with an inclination of 1º in the x-ray diffraction beam (XRD) by using CuKα wavelength monochromatic radiation (λ=1.5405 Å). Acquisition conditions were: a beam of 40 kV with 35 mA and with an aperture diaphragm of 0.2 mm, using a D5000 Siemens X-ray diffractometer. The thickness (d) of the films was measured by a surface profilometer Dektak-8, Veeco. The electrical properties were determined at room temperature by Van der Pauw-Hall method. For a uniform thickness, the electrical resistivity (ρ) can be determined using the relation $\rho = R_S d$, where R_S is the sheet resistance. All sheet resistance and resistivity values were also determined as the average of three measurements of three different films deposited at same conditions. The optical transmittance measurements were carried out using visible near-IR spectrophotometer equipment. The band gap (E_G) was determined by extrapolating the straight regions from plots of the square of the absorption coefficient α^2 versus photon energy ($h\nu$) (Tauc et al., 1966).

RESULTS AND DISCUSSION

The resistivity of the TCO film depends strongly on the chamber oxygen pressure as well as the stoichiometry of the film (Miller and Haglund, 1966). Oxygen provides the background gas necessary for the optimal PLD growth of complex oxides, and equilibrates the energetic species of the emerging atomic/ionic constituents ablated from the target (Zheng and Kwok, 1993). This can be explained by the nature of PLD. In PLD, the surface of the substrate is covered by atoms and ions pulsed from the target. It has been found that laser-generated atom and ion beams travel toward the substrate with a time duration of about 10 ps and with peak velocities of ~10^6 cm/s (Zheng et al., 1989). Different atomic species travel at different speeds. However, these velocities eventually equilibrate due to the many collisions between fast and slow atoms. These collisions take place between energetic atoms and the ambient O_2. The film stoichiometry is directly related to the velocity distributions of various atoms (Wu et al., 1999). When the densities of various atoms on the substrate surface are uniform and the coverage rates are the same, there is a much better chance of forming a stoichiometry compound. At low oxygen pressures, although the same species leave the target, the density of various species will not be uniform when they arrive on the surface of the substrate and it is most favorable the non-stoichiometry compound.

In general, electron conduction in the *n*-type oxide semiconductors is generated from interstitial or substituted cations and/or vacancies (Chopra et al., 1983). At the optimal PO_2 range of 10 to 40 mTorr, energetic atoms and ions with a uniform velocity distribution of various species, combine to produce non-stoichiometric ZnO and produce oxygen vacancies and/or interstitial cations. Figure 1 shows a plot of the electrical properties as a function of oxygen deposition pressures for $ZnO_{1-\delta}$ thin films at room temperature. As can be see in Table 1, $ZnO_{1-\delta}$ compounds are more favorable in the PO_2 between 10 to 40 mTorr, the electrical resistivity

Table 1. Nd:YAG PLD growth conditions for $ZnO_{1-\delta}$ films.

Laser	Nd:YAG (λ=1064 nm)
Laser density energy	2 Jcm^{-2} $shot^{-1}$
Repetition rate	5 Hz
Target to substrate distance	50 mm
Target rotation	30 rpm
Target	ZnO powder 99.99% (disk with thickness of 5 mm and diameter of 15 mm).
Substrate	Corning No. 7059
Substrate temperature (Ts)	300ºC
Background pressure	10^{-6} Torr
Gas pressure	between 10 and 40 mTorr
Ablation Shots	3000

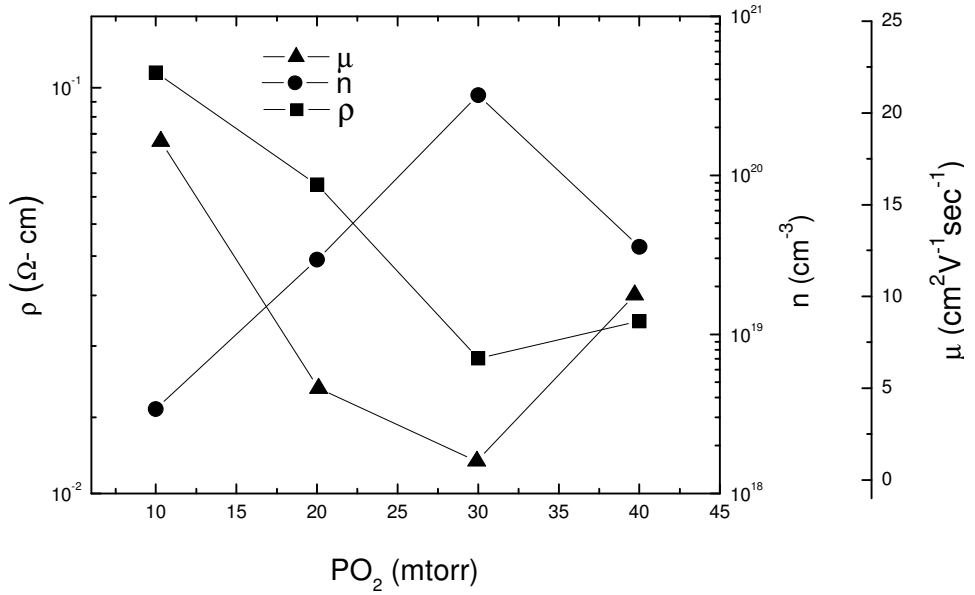

Figure 1. Variations in resistivity, carrier concentration, and carrier mobility as functions of oxygen pressure for $ZnO_{1-\delta}$ deposited at deposition temperature of 300ºC.

decrease from ρ~1.1x10^{-1} Ω-cm at 10 mTorrr reaching a minimum value of ρ~2.1x10^{-2} Ω-cm. The mechanism responsible for the conductivity changes in $ZnO_{1-\delta}$ thin films is the formation and annihilation of oxygen vacancies. To films grown in these range of PO_2 (10 to 40 mTorr), the average Hall coefficient, measured by Van der Pauw electrode configuration, gave around of –0.61 cm^3C^{-1}, suggesting that the conduction is *n*-type. Combining the Hall coefficient and conductivity measurements resulted in an average carrier density of *n*~9.6x10^{19} cm^{-3} and average Hall mobility of the electrons of ~8.6 $cm^2V^{-1}s^{-1}$ as can see in the Figure 1.

The obtained XRD patterns for the $ZnO_{1-\delta}$ thin films are shown in Figure 2 at different PO_2. The XRD patterns of the films are consistent with the pattern of ZnO powder reported in standard JCPDS data file and show a preferred growth orientation along the *c*-axis, that is, (002) plane, which is perpendicular to the substrate. The lattice constants of these films are calculated from the obtained values of *d*-spacing and their corresponding (*hkl*). The average values of the lattice constants are found to be (*a* = *b* = 3.24 Å and *c* = 5.23 Å) which are close to the standard value of hexagonal form of ZnO powder. The PO_2 doesn't affect the main peaks positions, which reflect the existence of ZnO single phase. Five principal peaks (100), (002), (101), (110) and (103) are appeared in the films. The intensities of these planes are increased gradually by increasing of the PO_2 still to 30 mTorr. In contrast the film grown at 40 mTorr, these intensities of the peaks are decreased. The crystal size of $ZnO_{1-\delta}$ thin

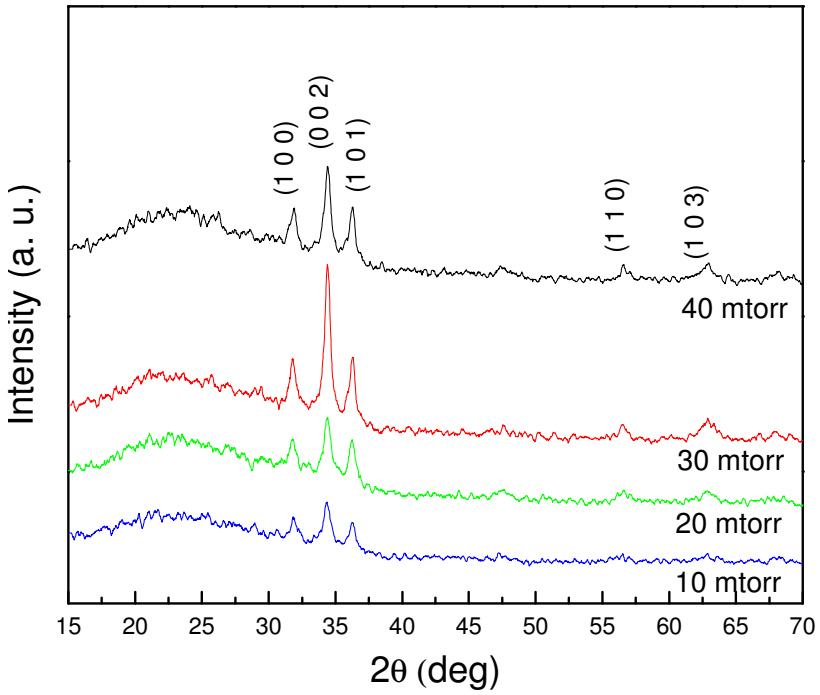

Figure 2. XRD peaks for $ZnO_{1-\delta}$ films grown at 300ºC under different PO_2.

Table 2. Structural properties of $ZnO_{1-\delta}$ films as a function of PO_2.

PO_2 (mTorr)	Cristal size (nm)	a=b (Å)	c (Å)	V (Å^3)
ZnO	-	3.2498	5.2066	47.63
10	16.93	3.2399	5.2553	47.78
20	15.08	3.2483	5.2212	47.71
30	18.03	3.2467	5.2168	47.62
40	17.03	3.2433	5.2371	47.71

films were calculated using Scherrer formula:

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad (1)$$

Where D is the mean grain size, β is the full width at half maximum of the diffraction line in radians, θ is the diffraction angle and λ is the wave length of X-ray (1.542 Å). The crystal size and volume of the unit cell of the films grown are shown in Table 2 as function of the PO_2. The average of the grains size was about 16.76 nm. The average of the volume of the $ZnO_{1-\delta}$ unit cell was approximately 47.71 Å^3 while the standard volume of the ZnO unit cell reported is 47.63 Å^3. These indicate an expansion in the $ZnO_{1-\delta}$ unit cell as a consequence of the annihilation of oxygen vacancies (V_O) in the lattice and the interstitials sites formation. However, the film deposited at PO_2 = 30 mTorr shown a minor volume of the unit cell than the ZnO powder, by indicating a compression of the unit cell due at the V_O formation. From Figure 3, we can see that the thickness of the films decrease from 71 to 22 nm as increasing of the PO_2, this reduction can be attributed primarily to collision of the ablated Zn and oxygen particles with the ionized gas plasma during deposition.

The transmittance versus wavelength for the $ZnO_{1-\delta}$ thin films is shown in Figure 4 at different PO_2. It is observed that the films are highly transparent with sharp absorption edge at λ = 380 nm (UV region) and average transmittance of ~85%. The optical band gap values are obtained from the plot $(\alpha h\nu)^2$ vs $h\nu$ by extrapolating the linear portion of the plot to $(\alpha h\nu)^2 = 0$. The inset in Figure 4 shows the optical band gap for $ZnO_{1-\delta}$ thin films at 30 mTorr, similar results were measurements in the others films. The calculated optical band gap has no

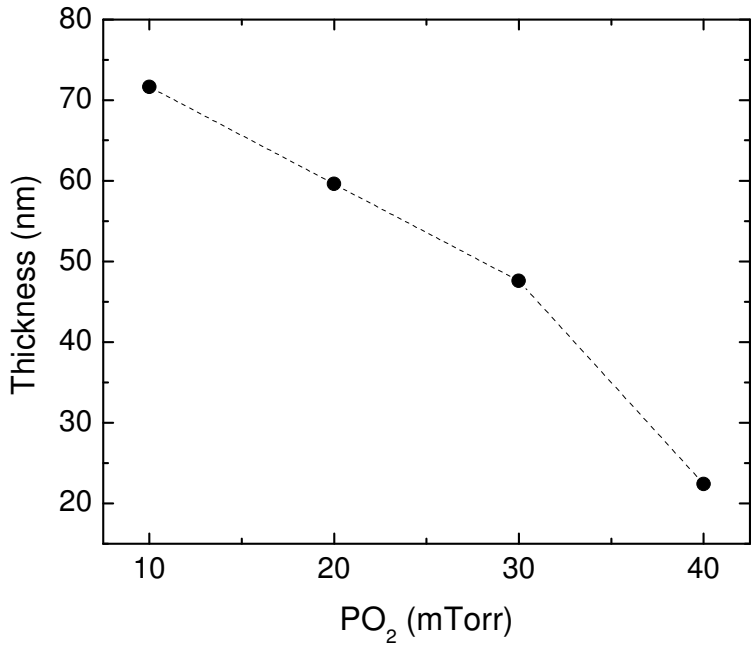

Figure 3. Thickness for the PLD $ZnO_{1-\delta}$ films as a function of the PO_2.

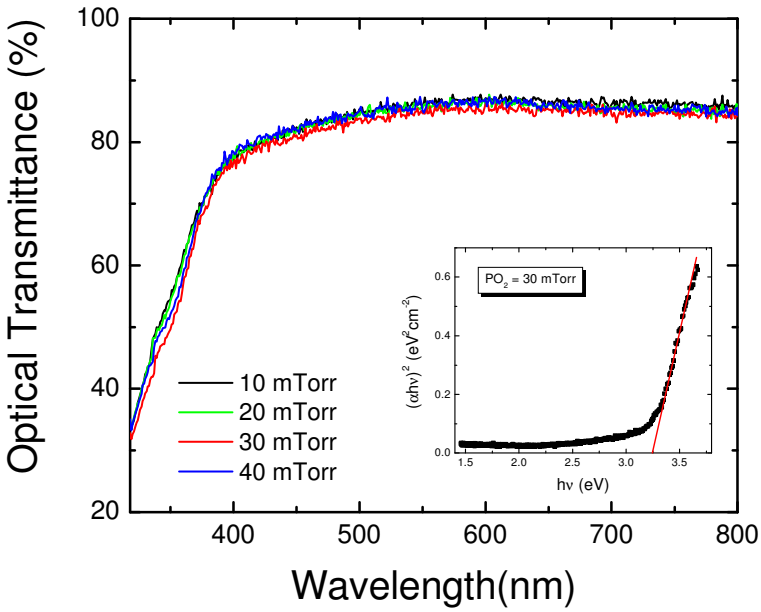

Figure 4. Optical transmittance spectra of $ZnO_{1-\delta}$ films under different PO_2.

change with PO_2; its average value is ~3.3 eV.

CONCLUSION

Electrical, structural and optical properties of no-stoichiometric ZnO ($ZnO_{1-\delta}$) thin films grown by Nd:YAG pulsed laser deposition were studied in function of the PO_2 in the range of 10 to 40 mTorr. The electrical resistance of the $ZnO_{1-\delta}$ thin films decreases with the oxygen pressure reaching a minimum resistance of $\rho \sim 2.1 \times 10^{-2}$ Ω-cm at 30 mTorr. The increase/decrease of the electrical resistance is ascribed to the annihilation/ formation of the oxygen vacancies (V_O) complex defects.

XRD patterns showed the existence of hexagonal ZnO single phase and the optical transmittance in the VIS range of the $ZnO_{1-\delta}$ thin films, shown an average transmittance of ~85% with optical band gap of average value of ~3.3 eV.

ACKNOWLEDGMENTS

The authors would like to thank Oswaldo Gómez, Mario Herrera, Daniel Aguilar, and Wilian Cauich for technical assistance, also to Mrs. Lourdes Pinelo for secretarial assistance. This work has been supported under Project No. 59996 CONACYT/México. E. Chan y Díaz acknowledges also CONACyT/México for his scholarship in the Advanced Materials Research Center, (CIMAV), from Chihuahua, National Laboratory of Nanotechnology at CIMAV and Partial Financial support: Secretaría de Educación Pública, PRONABES/632/2010, México. CONACYT/México.

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