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Full Length Research Paper

Structural, optical and electrical properties of ZnO thin films grown by radio frequency (rf) sputtering in oxygen atmosphere

Juan M. Camacho[1], R. Castro-Rodríguez[1], A. Iribarren[2], E. Chan y Díaz[3]*, A. Duarte-Moller[3] and P. Sánchez Santiago[3]

[1]Applied Physics Department, CINVESTAV-IPN, Unidad Mérida, 97310, Mérida, Yucatán, México.
[2]D.I.E.E.S. Instituto de Materiales y Reactivos, Universidad de La Habana, Zapata y G, Vedado, Plaza, Ciudad de la Habana 10400, Cuba.
[3]Centro de Investigación en Materiales Avanzados, Miguel de Cervantes Saavedra 120, Complejo industrial Chihuahua 31109, Chihuahua, Chih, México.

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Growth conditions for ZnO thin films were found for their potential use as a buffer layer in CdTe/CdS solar cells. Electrical, optical and structural properties were investigated as a function of the oxygen pressure during the growth of ZnO by radio frequency (rf) sputtering. The electrical behavior is explained in terms of the structural properties. Our results suggest that optimal oxygen partial pressure is 4 Pa for attaining a ZnO thin film as a buffer layer, with resistivity on the order of 10^3 Ω cm and an average of optical transmission of 89%.

Key words: Zinc oxide, transparent conducting oxide, buffer layer, solar cell, electrical resistance, optical transmission.

INTRODUCTION

It is well known that the effect of a high resistive transparent layer (HRT) as a buffer layer at the front contact improves the efficiency of CdTe/CdS solar cells. The primary effects of HRT are the decrease of shunts and the enhancement of the open-circuit voltage and fill factor. SnO_2, In_2O_3 and Zn_2SnO_4 are several HRT's that have been used as buffer layers. Recently, zinc oxide (ZnO) has been used by Mazzamuto et al. (2008) as a buffer layer into CdTe cells with resistivity of 10^3 Ω cm. However, there is not a detailed or systematic study about obtaining ZnO to be used as a buffer layer.

ZnO shows high optical transmittance and a wide range of electrical conductivity values simultaneously. Due to intrinsic and extrinsic defects, it is possible to obtain ZnO films with a wide range of resistivities, from 10^{-4} to 10^9 Ω cm by the radio frequency (rf) sputtering technique (Ondo-Ndong et al., 2003). The properties of sputtered ZnO thin films are known to depend on deposition parameters such as r.f. power, substrate temperature, type of substrate, pressure, gas atmosphere and thickness. In particular, the growth behavior including growth orientation (Zhang et al., 2007), microstructure and electrical properties (Gao and Li, 2004) of oxide films in rf-sputtering is very sensitive to the O_2 pressures used. Therefore, when one attempts to grow ZnO films of high quality by using r.f. sputtering, it is necessary simultaneously consider both defect formation and film growth behavior in optimizing ambient O_2 pressure in the growth chamber.

This work deals with the procedure to obtain optimum zinc oxide to be used as a buffer layer. We report results concerning the effect of oxygen partial pressure on the electrical, structural and optical properties of resistive ZnO thin films prepared by magnetron rf-sputtering.

EXPERIMENTAL

Zinc oxide thin films were grown on Corning glass by r.f. planar magnetron sputtering. The target was metallic zinc with 99.995% purity. The target-to-substrate distance was 60 mm. The substrate temperature (Ts) was 400°C. The chamber was evacuated up to a

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*Corresponding author. E-mail: enrique.chan@cimav.edu.mx. Tel: +52 (614) 439 1127. Fax: +52 (614) 439 4884.

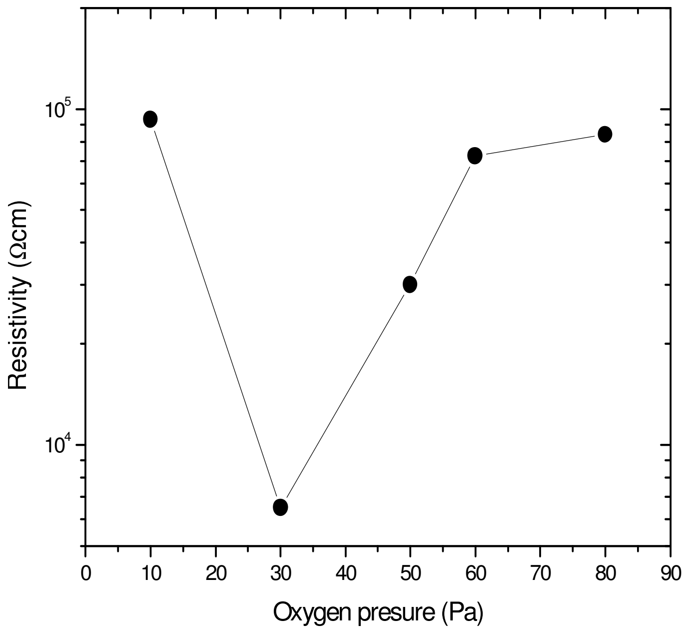

Figure 1. Dependence of electrical resistivity for ZnO films as a function of the oxygen partial pressure. For all cases, the total deposition pressure was 13.3 Pa.

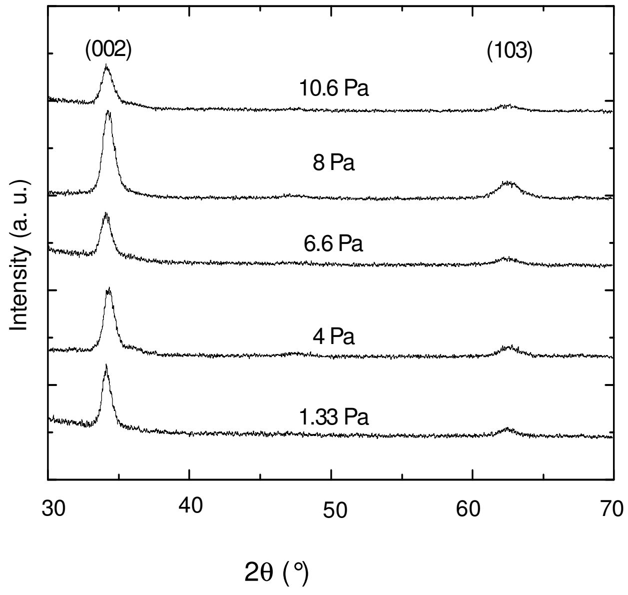

Figure 2. XRD patterns of ZnO films for different oxygen partial pressure.

base pressure below 10^{-6} Pa. Argon (Ar) and oxygen (O_2) were used as reactive gases. Variation of oxygen partial pressure was from 1.33 to 10.67 Pa and for all cases the total deposition pressure ($Ar+O_2$) was 13.33 Pa. Parameters such as target bias and rf-power (80 W) were held constant during deposition. Calibration was done with a Dektak 8 profile-meter in order to obtain reliability on the deposited thickness. The deposition time for all films was 30 min. The resistivity and optical transmittance values were determined as the average of three measurements of three different films deposited at same conditions.

Analysis of the resulting thin films was accomplished using a standard four-probe resistivity, X-ray diffraction (XRD) and optical transmittance measurements. The XRD measurements were made using Cu *K*α radiation (0.15418 nm) in a D5000 Siemens X-ray Diffractometer.

RESULTS AND DISCUSSION

Resistivity

The measured thickness was independent of oxygen pressure and in average was 120 nm for the films. The dependence of electrical resistivity (ρ) of the ZnO films as a function of the oxygen partial pressure when Ts = 400 °C is shown in Figure 1. As we can see, the electrical resistivity (ρ) of these films was sensitive to the presence of environmental oxygen. In this case, ρ decreases when the oxygen pressure increases, reaching a minimum at 4 Pa ($\rho = 6.5 \times 10^3$ Ω cm), and ρ increases at higher oxygen pressures (> 4 Pa), reaching 8.4×10^4 Ω cm at 10.67 Pa. A similar behavior has been seen in others works with ZnO grown by PLD (Look et al., 1999).

X-ray diffraction

Figure 2 shows the XRD spectra of the ZnO thin films deposited at different oxygen pressures. No evidence for the existence of metallic zinc or other phases than the hexagonal wurtzite structure of ZnO was found. The films shown a preferred growth orientation along the c-axis, plane (002), which is perpendicular to substrate and a marginal contribution of the (103) planes was observed. The d-space from (002) peak, extracted from the XRD patterns had an average value of 5.235 nm which are higher than of the standard powder sample.

The change of d-space for (002) peak could be due to the interstitial zinc and it suggests that the unit cell might be elongated along the c-axis, and there is stress in the plane. This characteristic is evidence that the stress generated in the film during deposition had certain influence on the electrical properties. Gao and Li (2004) found that good conductivity in ZnO thin films was related with d-space close to the standard powder sample, while films with poor conductivity has large d-space value. Zhang et al. (2007) found the c-axis preferential orientation is sensitive to the variation of oxygen partial pressure in the growth.

Figure 3 shows the full width at half-maximum (FWHM) of the (002) diffraction peak for the films deposited at different oxygen pressures. Increasing the oxygen partial pressure, the FWHM value increases, which implies that crystal quality degrades with an increase in the oxygen pressure? The crystallite size (D) of this sample (Figure 3), can be estimated by using the Scherrer formula:

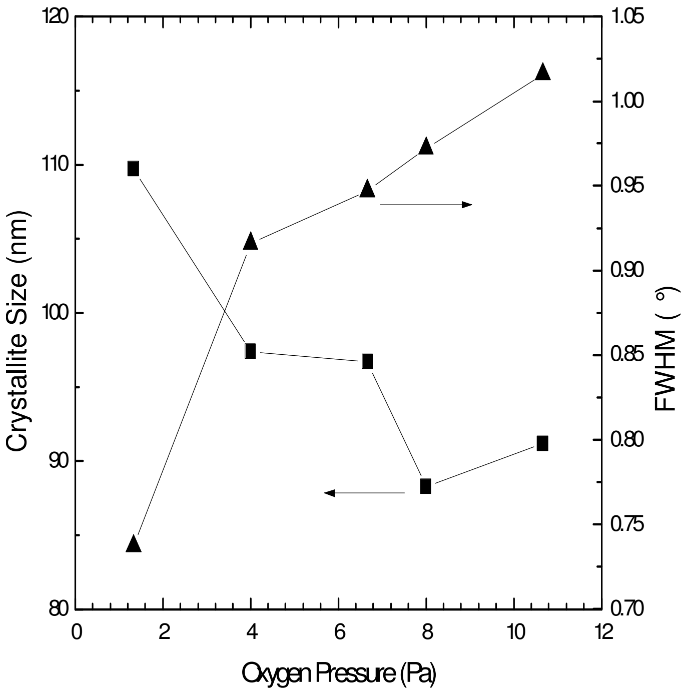

Figure 3. FWHM's of (002) diffraction peaks and calculated crystallite sizes of ZnO thin films grown at different oxygen pressures.

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

where λ is the X-ray wavelength, θ the Bragg diffraction angle in degrees, and β the FWHM of the (002) peak in radian. As can be seen, the crystallite size decreases while oxygen pressure increases. The film crystallinity was affected by the kinetics of atomic arrangements during deposition. For a high crystallinity film, simply stated, there must be sufficient time for deposited atoms to undergo surface diffusion to thermodynamically stable sited before being covered by the next layer atoms. The energy of deposition flux is controlled by means of the ambient gas pressure; higher pressure causes lower deposition energy and small crystallite sizes; a lower pressure causes high deposition energy and causes large crystallite sizes (Ellmer et al., 2008). We thus speculate that this behavior is result from the energy of the deposition flux caused by the O_2 pressure. Thus, the crystallite size of ZnO films decreases with increasing oxygen pressure. This behavior is similar to those found in previous reports (Sayago et al., 2005a, b; Kim and Lee, 2004).

The carrier concentration is related to oxygen vacancies or zinc interstitials. At low pressure for the oxygen partial pressure, the number of oxygen vacancies or zinc interstitials is high due to the fact that there are few oxygen atoms which may occupy oxygen vacancies or zinc interstitials (oxygen pressure < 4 Pa). By increasing oxygen pressure, the number of oxygen atoms which may occupy oxygen vacancies or zinc interstitials are increasing and consequently a deterioration on the carrier's concentration (one oxygen vacancy contributes to two conduction electrons) and the resistivity increases (oxygen pressure > 4 Pa) by increasing the oxygen pressure. These led to a lower value for the electrical resistance. On the other hand, by increasing the oxygen pressure, the crystallite size decreases, thereby increasing the electrons scattered in the grain boundary; as a consequence, ρ increases. Then, the presence of punctual defects like oxygen vacancies gives a reduction in the resistance, however at the same time the crystallite size decreases as a function of the oxygen partial pressure which leads to increase in ρ. These two factors provide the electrical behavior observed in the ZnO films (Look et al., 1999).

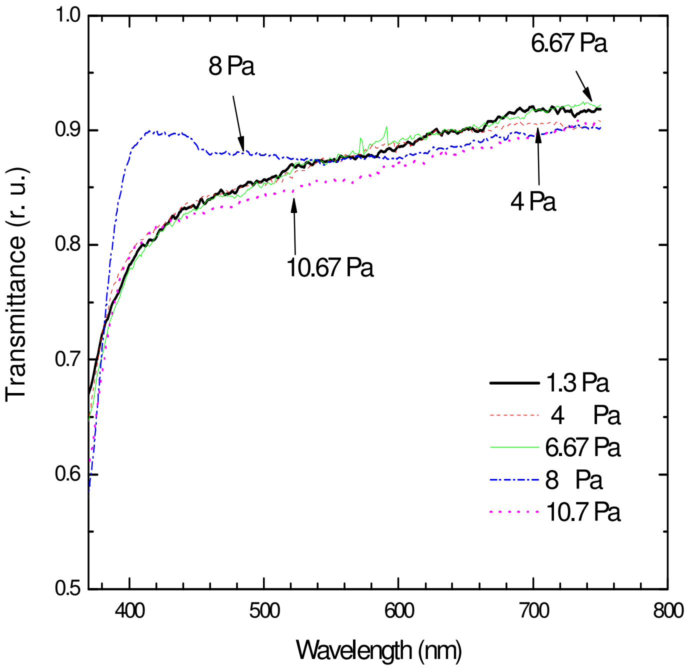

Figure 4. Optical transmission spectra of ZnO thin films.

Optical transmission

Figure 4 shows the optical transmission spectra of ZnO samples in the 360 to 800 nm region. All films showed an average transmission of 89% in the visible region. The optical band gap energy values, E_g, were calculated by extrapolation of the linear region of the plot of square of the absorption coefficient as a function of the photon energy. The values were from 3.1 to 3.2 eV. However, these values are lower than those expected due to the fact that they are strongly influenced by the band tails, which have high tail parameters estimated from the experimental curve to be in the range $E_0 \approx 100$ to 370 meV. The values of E_0 indicate that the samples are highly defective, which agrees with the little grain size that induces more grain boundary defects and wide FWHM's of the diffractograms that suggest structural disorder(Iribarren et al., 1999).

The HRT layer must be highly transparent; the optical transmission for these films did not change for all conditions, and, however, it was not the same for the electrical resistivity.

The recommended resistivity for buffer layer must be around 10^3 Ω cm; we could establish that the optimal growth conditions in our system to obtain adequate ZnO buffer layer were attained for 4 Pa of oxygen and 9.33 Pa of argon (total pressure = 13.33 Pa), which lead to a samples with $\rho = 6.5 \times 10^3$ Ωcm and 89% optical transmission.

Conclusion

ZnO was grown by rf-sputtering deposition using metallic zinc as target material. XRD scans of the ZnO samples indicated that ZnO (002) crystals were predominantly grown under ambient oxygen pressures from 1.33 to 10.67 Pa. The lowest resistivity and high optical transmission were obtained for ZnO films grown in our system with 4 Pa of oxygen partial pressure and 9.33 Pa argon pressure. Growth conditions of zinc oxide were found for its potential use as a buffer layer in CdTe/CdS solar cells.

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