ZnO Thin Films Prepared by Pulsed Laser Deposition

M. G. Tsoutsouva¹, C. N. Panagopoulos^{1*}, D. Papadimitriou², I. Fasaki³, M. Kompitsas³, N. Galanis⁴, D. E. Manolakos⁴

¹ Laboratory of Physical Metallurgy, National Technical University of Athens, Zografos, 15780, Athens, Greece
 ² National Technical University of Athens, Department of Physics, GR-15780 Athens
 ³Theor. and Phys./Chem. Institute, National Hellenic Research Foundation, 48 Vas. Konstantinou Ave., 11635, Athens, Greece
 ⁴Laboratory of Manufacturing Technology, National Technical University of Athens, 9 Iroon Polytechniou Avenue, 15780 Athens, Greece

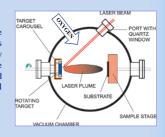
Introduction

Zinc oxide (ZnO) is a highly applicable and widely used II-IV semiconducting material with several attractive properties such as the wide band gap (3,37eV), high chemical stability and good photoelectric and piezoelectric properties. It is used in various technological domains such as surface acoustic wave devises, gas sensors, optical devices and transparent window layer in CIS, CGS solar cells. Various transparent conducting oxides (TCO) such as ITO.and SnO2 have been reported for their solar cell applications but ZnO has been considered to be the most promising TCO material in view of cost and properties.

Many techniques have been used to deposit ZnO films such as sputtering, evaporation, chemical vapour deposition (CVD), sol-gel, molecular beam epitaxy (MBE) and pulsed laser deposition PLD. Among these techniques, PLD is a very efficient method to deposit high quality and well crystallized films at lower temperature than other methods. This is due to the high energy of the ablated particles in the laser-produced plasma plume.

Experimental Procedure

ZnO films were deposited on glass substrates employing a typical homemade PLD system. All glass substrates were cleaned in an ultrasonic bath with acetone for 10 min before deposition. A UV pulsed KrF excimer laser operated at 248nm with pulse frequency 10 Hz, pulse duration 10 ns and fluence 2.6 J/cm² was used to evaporate the metallic Zn target. The metallic zinc disk (Aldrich 99,9% purity), with diameter 2,5cm and thickness 0,5cm was placed parallel 5 cm away from the substrate. To avoid fast drilling, the target was placed on a vacuum compatible, computer-controlled XY stage synchronized with the pulsed laser. The deposition chamber was initially evacuated to a base pressure 10^{-4} Pa, the substrate temperature was determined in situ during growth with a thermocouple placed below the substrate. At a fixed deposition time of 2 hours, the ZnO films were deposited at the substrate temperatures of 100 and 300 $^{\circ}$ C with oxygen partial pressures (flow) of 5, 10, 20, 30, 40 and 50 Pa.



Results and Discussion

Structural Properties

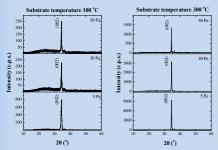


Figure 1: X-ray diffraction patterns of ZnO films grown at different oxygen pressures and two different substrate temperatures.

The increase of substrate temperature is shown to increase the ZnO (002) diffraction peak intensity (figure 1). It is believed that the temperature rise accelerates the migration of adatoms to the energy favorable positions, resulting in the enhancement of crystallinity of the ZnO films.

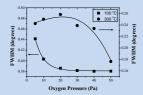


Figure 2: FWHM of the X-ray diffraction patterns for (002) peak of

The FWHM value of (002) peak is observed to decrease with increasing oxygen pressure from 5 to 50 Pa (figure 2). ZnO is always deviated from stoichiometry and presents intrinsic defects such as zinc interstitials and oxygen vacancies, especially at Zn-rich or O-deficient atmospheres. The number of these intrinsic defects could be decrease by the increase of partial-oxygen pressure, so the ZnO film becomes better crystalline [1].

Figure 3: The dependence of RMS roughness of ZnO films, on substrattemperatures and oxygen pressures during deposition.

The surface roughness of ZnO films (figure 3) is seen to increase with increasing oxygen pressure during deposition. This tendency is similar to other reported investigations [2, 3].

Optical Properties

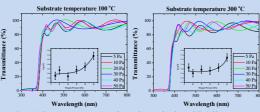


Figure 4: Transmittance spectra and optical energy bandgap of ZnO films

For the selected experimental conditions all the produced ZnO films show high transmission up to 90% in the visible region. The increase in oxygen pressure inhibits the evaporation of O atoms and favors the combination of Zn and O atoms during the deposition process. Accordingly the oxygen vacancy concentration is reduced as oxygen pressure increases, resulting in the increase of the optical band gap $E_{\rm o}$ [4]

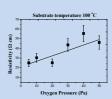
References

[1] J.-L. Zhao, X.-M. Li, J.-M. Bian, W.-D. Yu, Z.-D. Gao, J. Cryst. Growth, 276 (2005) 507

[2] S.S. Kim, B.T. Lee, Thin Solid Films 446 (2004) 307
 [3] Z.G. Zhang, F. Zhou, X.Q. Wei, M. Liu, G. Sun, C.S. Chen, C.S. Xue, H.Z. Zhuang, B.Y. Man, Physica E 39 (2007) 253

[4] L. Sun, W. Cheng, F. Lin, X. Ma, W. Shi, Physica B, 381 (2006) 109
[5] Y. Maa, G.T. Dua, T.P. Yanga, D.L. Qiub, X. Zhangb, H.J. Yanga, Y.T. Zhanga, B.J. Zhaoa, X.T. Yanga, D.L. Liua, J. Cryst. Growth, 255 (2003) 303
[6] F.K. Shana, G.X. Liua, W.J. Leea, G.H. Leea, I.S. Kima, B.C. Shina, Y.C. Kimb, J. Cryst. Growth, 277 (2005) 284–292

Electrical Properties



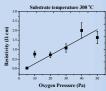


Figure 5: Dependence of ZnO resistivity on oxygen pressure and substrate temperature.

For both substrate temperatures, the electrical resistivity of ZnO films increases with increasing oxygen pressure from 5 to 50 Pa. With increasing oxygen pressure, the concentration of V_0 decrease, leading to a higher electrical resistivity of ZnO thin films[5]. It is also found that the resistivity decreases with increasing substrate temperature. This phenomenon may be due to the enhancement of film crystallinity with increasing temperature and consequently the electron mobility increases [6].

Conclusions

- The surface roughness of the deposited oxide films, was observed to be in the range of 2-9 nm.
- The ZnO films exhibited high transmittance of 90% in the visible region at oxygen pressures ranging from 5 to 50 Pa. The energy band gap and the thickness of the films calculated from the transmittance spectra were about 3.27 eV and 500 nm, respectively.
- The electrical resistivity of the ZnO films was found to decrease with increasing substrate temperature and decreasing oxygen pressure.