Low temperature ZnO films deposited by SSCVD

G Escalante¹, H Juárez, M Pacio, G García, T Díaz, E Rosendo and A Coyopol
Centro de Investigación en Dispositivos Semiconductores, Universidad Autónoma de Puebla, 14 Sur and Av. San Claudio, San Manuel 72570, Puebla, México.

¹E-mail: gertrova@ece.buap.mx

Abstract: ZnO films were deposited by single source chemical vapor deposition (SSCVD) at low temperatures on glass substrates using zinc acetate as a source of Zn and oxygen gas as the oxidizing agent. The zinc acetate was sublimated on a resistance heated to 210ºC. The substrate temperature was varied from 200 to 300ºC every 50ºC with a deposition time of 5 min. X-ray diffraction results show that all deposited films are polycrystalline with an average grain size below 8 nm in all directions. The ZnO films showed a transmittance higher than 75% in the visible region.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap (3.3 eV) and a hexagonal wurtzite structure [1]. The ZnO films are widely used for a variety of applications such as transparent conductive oxide (TCO) [2], surface acoustic wave device (SAW) [3] and gas sensor [4] due to their structural, optical and electrical properties. So far, a variety of techniques such as sputtering [5], sol-gel [6], spray pyrolysis [7] and atmospheric pressure chemical vapor deposition (APCVD) [8, 9] have been used to deposit ZnO films. Over the past few years, there has been a growing interest in single-source chemical vapor deposition (SSCVD) because of its low-cost deposition system and high-quality films at moderate temperatures. This technique essentially consists of the precursor vaporization followed by the precursor decomposition/deposition [10-13].

In this paper, we report the low temperature deposition of ZnO films obtained with an SSCVD system at atmospheric pressure. Also, structural and optical characterizations of the deposited ZnO films are presented.

2. Experimental Procedure

Figure 1 shows a schematic diagram of the SSCVD system used for the deposition of ZnO films. The system consists of a vertical reactor made of quartz; it was implemented in the laboratory at Centro de Investigaciones en Dispositivos Semiconductores [14]. The ZnO films were deposited on glass substrates using dihydrate Zinc acetate (Zn(CH₃COO)₂·2H₂O), as a single precursor which was sublimated on a NiCr resistance heated to 210ºC using an AC power source (10 Vp, 60 Hz). A type-K thermocouple and a Eurotherm 2416 temperature controller were used to control the resistance temperature. The resistance was placed at 50 mm below the substrate. Additionally, an Oxygen gas (O₂) flow was used as oxidant agent and the flow rate was 50 sccm. On the other hand, the substrate was placed under the upper heater. The substrate temperature (Tₛ) during deposition was varied between 200ºC and 300ºC every 50ºC with a deposition time of 5 min.
The structural properties of the deposited ZnO films were studied using X-ray diffraction (XRD) in a Bruker D8 Discover diffractometer with a X-ray source of CuKα radiation (1.5406 Å) at 40kV and 40mA. The optical characterization was carried out using a UV-vis Thermo Scientific Evolution 600 spectrophotometer in the wavelength range from 200 to 800 nm. The thickness of the films was determined using an electromechanical stylus instrument.

3. Results and Discussion

Figure 2 shows the X-ray diffraction patterns of the deposited films. At a low deposition temperature of 200ºC, the film is polycrystalline and without preferential orientation. The diffraction peaks were observed in 31.68º, 34.34º and 36.16º corresponding to the (100), (002) and (101) planes, respectively [15]. However, there is a contribution when increasing the temperature to 250ºC; the deposited film has a preferred orientation in the (002) plane. Many researchers assume that the contribution is due to the low surface free energy in comparison to the (110) and (100) planes [16]. Nevertheless, the deposited ZnO film at 300ºC is polycrystalline without preferential orientation. At this temperature, the adhesion of particles increases from the gaseous phase reducing the oriented growth.

The grain size (D) was calculated using the Scherrer formula [17]

\[
D = \frac{0.9 \lambda}{B \cos \theta}
\]

where \( \lambda \) is the wavelength (Cu Kα = 1.5406 Å), \( \theta \) is the Bragg's diffraction angle and \( B \) is the full width at half maximum (FWHM) of the diffraction peak. The inset of figure 2 shows that the values for the grain size obtained from the ZnO films are smaller than 8 nm. In addition, this shows that the grain size increases with the rise in the deposition temperature.
Figure 3 shows the transmittance spectra of deposited ZnO films in the temperature range from 200 to 300ºC. The transmittance spectrum shows that all films have values higher than 75% in the visible region. The transmittance spectrum for the film deposited at 200ºC shows a shoulder near to the UV region, this behavior can be related to the thin thickness and porosity of the film. Although the thickness increases in the case of the deposited films at 250 and 300ºC, the percent transmittance in the visible region is maintained and the transmittance in the UV region disappears. This behavior is due to the fact that the film is densified when the temperature is increased [18].

The optical band gap of the deposited films was calculated using the relation

$$\alpha hv = A(hv - E_g)^{n/2}$$

where $\alpha$ is the absorption coefficient, $hv$ is the photon energy, $A$ is a constant, $E_g$ the optical band-gap energy and $n = 1$ (for semiconductor of direct transition) [19]. In the inset of figure 3, the relationship between $(\alpha hv)^2$ and $hv$ is plotted. The $E_g$ value can be obtained by extrapolating the linear portion to the energy axis. The measured optical band gap values were in the range of 3.21 to 3.28 eV which is very close to the band gap of intrinsic ZnO [1].

![Figure 3. Transmittance spectra and plots of $(\alpha hv)^2$ as a function of the energy (E) for ZnO films deposited at 200, 250 and 300ºC with thicknesses of 270, 380 and 690 nm, respectively.](image)

4. Conclusions

ZnO films were deposited on glass substrates using the SSCVD technique at low temperatures. The films were deposited in the range from 200 to 300ºC without treatment annealing. The ZnO film deposited at 250ºC shows a greater crystalline quality associated with a high preferential orientation in the (002) plane. When the deposition temperature rises, the grain size increases. The optical transmittance in the visible region of the ZnO films shows that all films have a transmission (over 75%). Finally, it is shown that the percent of transmittance in the visible region of the deposited ZnO films depends on the films thickness and their densification.

Acknowledgment

The authors wish to acknowledge M.C. René Pérez Cuapio for his assistance in the realization of the X-ray diffraction.
References
[1] Özgür Ü et al 2005 J. Appl. Phys. 98 041301
[2] Jeong S H, Park B N, Yoo D G, Boo J H and Jung D 2007 J. Korean Phys. Soc. 50 3 622-25
[3] Chen X, Liu D, Chen J and Wang G 2009 Smart Mater. Struct. 18 115021
[4] Malik A, Sêco A, Nunes R, Vieira M, Fortunato E and Martins R 1997 Mat. Res. Soc. Symp. Proc. 471 47
[5] Nunes P, Costa D, Fortunato E and Martins R 2002 Vacuum 64 293-97
[6] Ohyama M, Kozuka H and Yoko T 1997 Thin Solid Films 306 78-85
[7] Goyal D J, Agashe C, Takwale M G, Marathe B R and Bhide V G 1992 J. Mater. Sci. 27 4705
[8] Haga K, Katahira F and Watanabe H 1999 Thin Solid Films 343-344 145-47
[9] Pacio M, Juárez H, Escalante G, García G, Díaz T and Rosendo E 2010 Mater. Sci. Eng. B 174 38-41
[10] Dai L P, Deng H, Zang J D, Mao F Y, Chen J J and Wei M 2008 J. Mater. Sci. 43 312-15
[11] Deng H, Gong B, Petrella A J, Russell J J and Lamb R N 2003 Sci. China Ser. E 46 4 355-60
[12] Deng H, Russell J J, Lamb R N, Jiang B, Li Y and Zhou X Y 2004 Thin Solid Films 458 43-46
[13] Petrella A J, Deng H, Roberts N K and Lamb R N 2002 Chem. Mater. 14 10 4339-42.
[14] Escalante G 2010 Design and fabrication of SSCVD system CIDS-UAP México
[15] International Centre of Diffraction Data, PDF: 00-036-1451
[16] Nguyen H T, Hartmann A J and Lamb R N 1999 J. Phys. Chem. B 103 4264
[17] Klug H P, Alexander L E 1974 X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, (John Wiley & Sons. New York) p.p 687.
[18] Aslan M H, Oral A Y, Mensur E, Gül A and Basaran E 2004 Sol. Energy Mater. Sol. Cells. 82 543-52
[19] Davis E A, Mott N F 1970 Philos. Mag. 22 903-16.