



Studies on A.C. Conductivity of Spray Deposited ZnO Thin Films

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Abstract

Zinc oxide thin films were prepared by chemical spray pyrolysis technique using $Zn(CH_3COO)_2$ as precursor solution. Structural analyses of the films performed with XRD confirmed that all the films were of zinc oxide having polycrystalline nature with (101) as preferred plane of orientation. A.C. conductivity of zinc oxide thin films measured in the frequency range of 1Hz to 0.1MHz and in the temperature range of 300K to 433K. The experimental studies on a.c. conductivity of ZnO thin films reveal that correlated barrier hopping (CBH) model is the most suitable model to explain the a.c. conduction mechanism in the ZnO thin films. Based on this model, the polaron binding energy (W_m), the height of Coulomb barrier (W) and the characteristic relaxation time (τ_0) have been calculated. The values of W_m and W increase as the film thickness decreases, whereas the values of τ_0 decrease with decreasing film thickness.

Key words : ZnO films, Sputtering, a.c. Conductivity, CBH Model.

Introduction

Zinc oxide (ZnO) is a II-VI compound semiconductor with a wide direct bandgap of 3.3 eV at room temperature. Thin films of ZnO have been used in many important applications, such as solar cells, surface acoustic wave (SAW) devices, heat mirror coatings and more recently as solid-state gas sensors (Sahay et al., 2005; Sahay, 2005). Zinc oxide thin films can be prepared by various methods such as magnetron sputtering; plasma enhanced chemical vapour deposition (PECVD), spray pyrolysis, pulsed laser deposition, sol-gel process, vacuum evaporation etc. (Sahay et al., 2005; Sahay, 2005; Nanto et al., 1986; Koshizaki and Oyama, 2000; Nagaraju and Kripamidhi, 2006) and more importantly it is being considered as a potential candidate in new frontiers of research like spintronics (Rouning et al., 2004) In the present investigation, thin films of ZnO were prepared by spray pyrolysis technique, which is simple and involves low cost equipments.

Though studies on d.c. conductivity in ZnO material have received considerable attention of

researchers, there have been only a few studies on their a.c. transport properties. A.C. conductivity is an immensely important parameter, used to characterize the dielectric properties of materials. Measurement of a.c. conductivity of semiconductors has been extensively used (Tewari et al., 2009) to understand the transport mechanism in these materials to investigate the nature of defect centers, since they play a major role in the conduction process. A.C. measurements provide information about the interior of the materials in the region of relatively low conductivity. This measurement also helps to distinguish between localized and free band conduction. In the case of localized conduction, the a.c. conductivity increases with frequency, while in the free band conduction the conductivity decreases with frequency.

In this work, we report the results of a.c. conductivity measurements carried out on the ZnO films prepared by spray pyrolysis in the frequency range (1Hz to 0.1MHz) and in the

temperature range 300 to 433 K. The results have been analyzed in the light of the existing theories with a view of understanding the conduction mechanism involved.

Experimental Details

The films were prepared on conducting glass substrates, which were placed on the surface of a substrate heater when sprayed. The substrate heater was an electrically controlled block furnace. The spraying solution used was of 0.1 M concentration of high purity zinc acetate dehydrate (Merck, India) prepared in distilled water. The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle, with the help of compressed air as carrier gas. The schematic representation of the spray system is given in Fig. 1. The various process parameters used in the film deposition are listed in table 1. During the course of spray, the substrate temperature was monitored using a chromel-alumel thermocouple with the help of a Motwane digital multimeter (Model: 454). Further details of the procedure are reported elsewhere (Sahay et al., 2007).

Table 1 : Spray parameters of deposition

Spray parameter	Value
Zinc acetate solution concentration	0.1 M
Nozzle-substrate distance	50 cm
Solution flow rate	4.5 ml/min
Gas pressure	3 kg/ cm ²
Substrate temperature	410 ± 5 °C

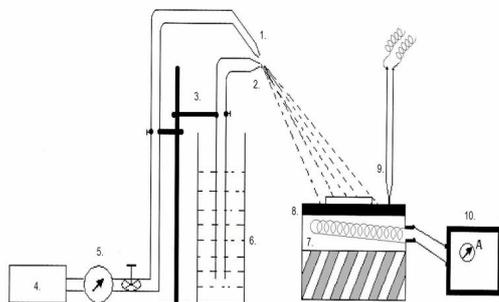


Fig.1: Schematic representation of the spray system

[(1) – air output nozzle;(2) – spray nozzle; (3) – iron stand; (4) –air compressor; (5) –pressure regulator and gauge; (6) – spray solution container; (7) – block furnace; (8) – substrate; (9) –

thermocouple; (10) – temperature control unit.]

Results and Discussions

When aerosol droplets arrived close to the heated glass substrates, a pyrolytic process took place and a highly adherent film of ZnO formed [16]: on the substrates. The films thus prepared were almost clear and transparent in physical appearance, and undergone for structural analysis. Fig.2 shows the X-ray diffraction (XRD) patterns of the different ZnO films. The observed XRD patterns are analyzed using X’Pert HighScore software. The films were found to match with the ICDD reference pattern of Zinc Oxide. All the films were found to be polycrystalline in nature, possessing hexagonal wurtzite structure with the strongest peak corresponding to the plane (101).other peaks corresponding to the planes (002),(102),(103),(112) and (104) were also present with relatively lower intensities.

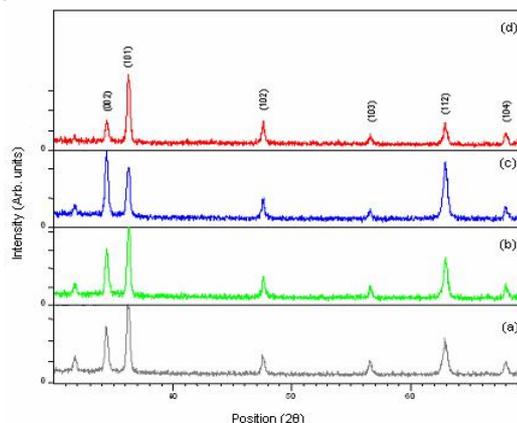


Fig. 2 : XRD pattern.of ZnO Thin films deposited of thicknesses temperatures (a) 212 (b) 261 (c) 307 (d) 373 nm.

the a.c. conductivity ($\sigma(\omega)$) of different thin ZnO films were measured in the frequency range 10Hz to 0.1MHz and in the temperature range 300 = T = 433K. The variation of a.c. conductivity with frequency for the ZnO thin films is shown in Fig. 3 It is seen that the a.c. conductivity increases with the increase of frequency and temperature.

The a.c. conductivity is found to depend on the frequency as (Tewari et al., 2009; Sahay et al., 2008; Bhatnagar and Bhatia, 1990)

$$\sigma(\omega) = A\omega^s \quad (1)$$

where, exponent s is found to be temperature dependent and has a value $s = 1$, A being a constant independent of frequency but dependent on temperature and ω is angular frequency.

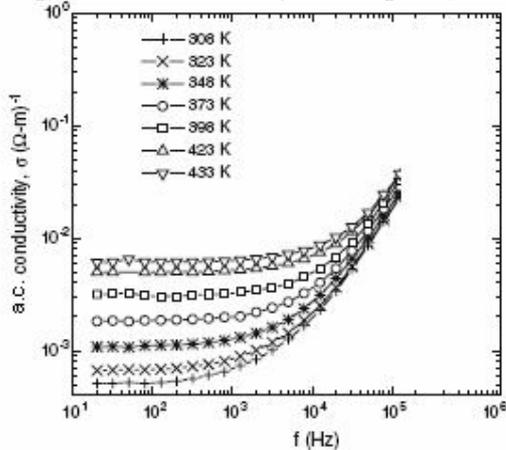


Fig. 3 : Variation of A.C. conductivity with frequency at different constant temperature

Fig.3 shows the frequency dependence of a.c. conductivity of a typical ZnO film at different fixed temperatures on a log-log scale. It is clear that at all temperature the conductivity increases with increasing frequency having different slopes over three frequency regions. This type of variation is indicative of localized conduction. Contrary to this, in case of free band conduction the a.c. conductivity decreases with frequency (Anwar and Hogarth, 1990). Also, the of a.c. conductivity is found to increase with increase in temperature. This rise of $\sigma_{a.c.}$ with temperature is attributed to thermal activation which allows the hopping of carriers between different localized states.

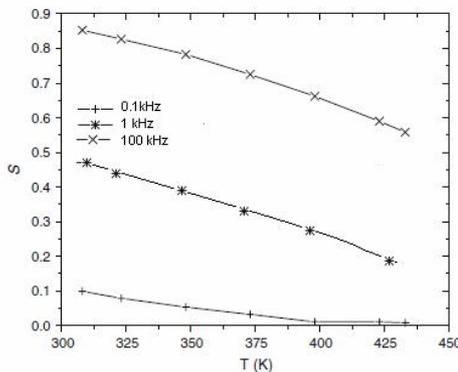


Fig.4 : Variation of the exponent s with temperature

The frequency exponent s and coefficient A were obtained from the least square fits of the data with the Eq. (1), considering A and s to be the fitting

parameters. The variation of frequency exponent s as a function of temperature for different samples is shown in Fig. 4 Different theoretical models have been developed to explain the frequency and temperature dependence of a.c. conduction in materials (Pollak and Geballe, 1961; Pollak and Pike, 1972). According to hopping theory developed by Pollak and Geballe (PG), if hopping of charge carriers takes place between localized states with random distribution, the ac conductivity is directly proportional to ω^s where $0.5 < s < 1$ [20-21]. It is known that the low values of s indicate multihopping process, while high values of s indicate single hopping process. This theory also predicts an increase in activation energy with decreasing frequency at higher temperatures. Further, Jonscher (Jonscher, 1972) showed that for hopping systems, it was possible to generate a range of power law relations with exponent s ranging from zero to unity. He also found that s decreased with temperature and was frequency dependent. According to small polaron quantum mechanical tunneling model, the exponent s is an increasing function of temperature.

It is also evident from the s vs. T plots in Fig. 4, that s gradually decreases with temperature in contrast to the electron tunneling model which predicts s to be temperature independent. Small polaron tunneling model (SPTM) is also not found to be suitable to explain the a.c. conductivity behaviour of the ZnO films, as it predicts increase of s with increasing temperature.

The CBH model (Ghosh, 1990) considers the hopping of two electrons from a D^- to a neighbouring D^+ centre over the potential barrier between them. It predicts that s should be less than 1, decreasing with increasing temperature. In the CBH model, the electrons in charged defect states hop over the Coulombic barrier whose height (W), is given by

$$W = W_m - (ne^2 / \pi\epsilon\epsilon_0 r) \quad (2)$$

where W_m is the maximum barrier height, ϵ_0 the bulk dielectric constant, ϵ_0 the permittivity of free space, r the distance between hopping sites and n the number of electrons involved in a hop ($n = 1$ and $n = 2$ for the single polaron and bipolaron processes, respectively)

The a.c. conductivity is given by

$$\sigma(\omega) = \frac{\pi^3 \epsilon \epsilon_0 N N_p \omega (R_\omega)^6}{6} \quad (3)$$

Where, R_ω is the inter-site separation. The frequency exponent is expressed as

$$s = 1 - \frac{6kT}{W_m + (kT \ln(\omega\tau_0))} \quad (4)$$

In the present studies, the values of s was found to be 0.11 to 0.02 for the lower frequency (100 Hz) and 0.49 to 0.2 for the middle frequency range (1 kHz) and from 0.9 to 0.55 for higher (100 kHz) frequency range. However, we observed that s increases with frequency but decreases with temperature. This trend was observed throughout the frequency range (10 Hz to 100 kHz). The observed variation of s in this investigation is in good agreement with the CBH model. Hence this model is the most suitable one for explaining carrier transport mechanism in the ZnO thin films.

The conduction parameters calculated as per CBH model are as listed in Table 2.

Table 2 : CBH conduction parameters

Thickness (nm)	212	261	307	373
W_m (eV)	0.57	0.49	0.42	0.33
W (eV)	0.140	0.102	0.022	0.062
τ_0 (μ s)	90.9	195	443	658

The values of W , W_m and τ_0 calculated for ZnO thin films of different thicknesses are and listed in Table 2. It is seen from Table. 2 that the values of W_m and W increases as the thickness decreases whereas the values of τ_0 decrease with decreasing thickness. This is attributed due to the increase of defects and disordered regions in the films on reducing the thickness.

Conclusion

ZnO thin films were deposited by spray pyrolysis technique. The structural characterisation of the films with XRD confirmed formation of polycrystalline ZnO films. The measurement of a.c. conductivity and its dependence with temperature and the nature of the frequency exponent s revealed that the Correlated barrier hopping model is the most suitable for describing the a.c. conduction mechanism in ZnO thin films. Finally other conduction parameters have been interpreted on the basis of CBH model.

References

- Anwar, M.; Hogarth, C.A. (1990). A.c. conduction in evaporated MoO₃/SiO₂ amorphous thin films. *J. Mater. Sci.* 25(9): 3906-3909
- Bhatnagar, V.K.; Bhatia, K.L. (1990). Frequency dependent electrical transport in bismuth-modified amorphous germanium sulfide semiconductors. *J. Non-Cryst. Solids* 119: 214-231
- Elliot, S.R.(1977). A theory of a.c. conduction in chalcogenide glasses. *Philos. Mag. B* 36: 1291-1304
- Ghosh, A.(1990). Transport properties of vanadium germanate glassy semiconductors. *Phys. Rev. B* 42: 5665-5676
- Jonscher, A.K. (1972). Frequency-dependence of conductivity in hopping systems. *J.Non-Cryst. Solids.* 8(10): 293-315
- Koshizaki, N.; Oyama, T. (2000). Sensing characteristics of ZnO-based NO_x sensor. *Sensors and Actuators B.* 66: 119-121
- Nagaraju, D.J.; Krupanidhi, S.B.(2006). dc and ac transport properties of Mn-doped ZnO thin films grown by pulsed laser ablation. *Mater. Sci. Eng. B* 133:70-76
- Nanto, H.; Minami, T.; Takata, S.(1986). Zinc-oxide thin-film ammonia gas sensors with high sensitivity and excellent selectivity. *J. Appl. Phys.* 60(2): 482-485
- Pollak, M.; Geballe, T.H. (1961). Low-Frequency Conductivity Due to Hopping Processes in Silicon. *Phys. Rev.* 122: 1742-1753
- Pollak, M.; Pike, G.E. (1972). ac Conductivity of Glasses. *Phys. Rev. Lett.* 28: 1449-1451
- Ronning, C.; Gao, P.X.; Ding, Y.; Wang, Z.L.; Schwen, D. (2004). Manganese-doped ZnO nanobelts for spintronics. *Appl. Phys. Lett.* 84(5): 783-786
- Sahay, P.P.; Tewari, S.; Jha, S.; Shamsuddin, M. (2005). Sprayed ZnO thin films for ethanol sensors. *J. Mat. Sci.* 40(18): 4791-4793
- Sahay, P.P.(2005). Zinc oxide thin film gas sensor for detection of acetone. Zinc oxide thin film gas sensor for detection of acetone. *J. Mat. Sci.* 40(18): 4383-4385
- Sahay, P.P; Tewari, S.; Nath, R.K. (2007). Optical and electrical studies on spray deposited ZnO thin films. *Cryst. Res. Technol.* 42: 723-729
- Sahay, P.P; Tewari, S.; Nath, R.K.; Jha, S.; Shamsuddin, J. (2008). Studies on ac response of zinc oxide pellets. *J. Mater. Sci.* 43(13): 4534-4540
- Tewari, S.; Bhattacharjee, A.; Sahay, P.P. (2009). Structural, dielectric, and electrical studies on thermally evaporated CdTe thin films. *J. Mater. Sci.* 44(2): 534-540
- Wang, R.; King, L.L.H.; Sleight, A.W. (1996). Highly conducting transparent thin films based on zinc oxide. *J. Mater. Res.* 11(7):1659-1664