

Optical and electrical properties of zinc oxide films prepared by spray pyrolysis

BENNY JOSEPH[†], K G GOPCHANDRAN, P K MANOJ, PETER KOSHY[‡]
and V K VAIDYAN*

Department of Physics, University of Kerala, Trivandrum 695 581, India

[†]Permanent address: Department of Physics, St. Joseph's College, Calicut 673 008, India

[‡]Regional Research Laboratory, Pappanamcode, Trivandrum 695 019, India

MS received 2 November 1998; revised 31 May 1999

Abstract. Zinc oxide thin films were prepared on glass substrates from an aqueous solution of zinc acetate by spray pyrolysis. These films were characterized using X-ray diffraction, scanning electron microscopy and optical transmission. The films were highly transparent to the visible radiation and electrically conductive. Films deposited at optimum conditions exhibited a resistivity of $3.15 \times 10^{-3} \Omega\text{m}$ along with a transmittance of 98% at 550 nm.

Keywords. Zinc oxide films; spray pyrolysis; transparent conducting films.

1. Introduction

Zinc oxide (ZnO) is a II–VI semiconductor. It has a bandgap of ~ 3.3 eV and its resistivity can be controlled by the deposition process to sufficiently low values. ZnO is a good candidate to substitute indium tin oxide ($\text{In}_2\text{O}_3 : \text{Sn}$) and tin oxide (SnO_2) in conductive electrodes of amorphous silicon solar cells due to the high stability of ZnO films in hydrogen plasma (Aktaruzzaman *et al* 1991). These characteristics along with nontoxicity and low cost of the constituent elements make ZnO very attractive for photovoltaic applications. These films have also applications in energy efficient windows, liquid crystal displays, optoelectronic devices, etc (Chopra *et al* 1983). Zinc oxide films have been prepared by different methods such as spray pyrolysis, evaporation, chemical vapour deposition and sol-gel technique (Roth and Williams 1981; Major *et al* 1983; Minami *et al* 1984; Yutaka Ohya *et al* 1996; Benny Joseph *et al* 1998). In the present work, highly transparent and conductive zinc oxide films were prepared by spray pyrolysis technique using an aqueous solution of zinc acetate.

2. Experimental

ZnO films were deposited on heated glass substrates by spraying an aqueous solution of zinc acetate (0.1 M). The solution was sprayed onto heated glass substrates held at constant temperature between 573 and 773 K with an

accuracy of ± 5 K. Compressed air was used as the carrier gas and spray rate of the solution was maintained at 6 mL/min. To enhance the conductivity, the as-deposited films were annealed at 573 K for 90 min under a vacuum of 10^{-5} mbar. Films from acetate solution having molarity 0.2 and 0.4 M were also deposited at optimum substrate temperature without changing the other process parameters. The apparatus and the deposition details have already been reported (Benny Joseph *et al* 1999).

Characterization of the films was carried out using a Philips PW1710 X-ray diffractometer and a JEOL 35C scanning electron microscope. Film thickness was measured by the Tolansky's interferometric method. The resistivity studies were carried out using the four-probe method and the transmission studies using a Shimadzu double beam spectrophotometer UV240.

3. Results and discussion

3.1 XRD studies

Figure 1 shows the X-ray diffraction patterns of zinc oxide films prepared at different substrate temperatures using 0.1 M zinc acetate solution. All the peaks in the diffraction patterns correspond to the hexagonal structure of ZnO and are indexed on the basis of ASTM data card 5-664. All the diffractograms of the prepared films clearly indicate polycrystalline nature of ZnO films with prominent diffraction from crystal planes such as (002), (101) and (100). At 573 K, the preferential orientation was along (100) crystal plane. For deposition temperature

*Author for correspondence

above 573 K, the preferential orientation was along (002) crystal plane. The calculated values of lattice constants are found to be close to those of the ASTM data reported for ZnO powder sample.

Figure 2 shows the X-ray diffraction patterns of ZnO films deposited at a substrate temperature of 723 K using precursor solutions of different molarities. The preferential orientation along (002) crystal plane is found to increase with zinc concentration in the precursor solution. More Zn is incorporated in films prepared at higher molarities due to oxygen insufficiency in the pyrolysis processes. The peak intensity ratio (P_{hkl}/P_{max}) gives a measure of preferential orientations in the films. The strongest peak corresponds to the (002) plane indicating that most grains have c-axis perpendicular to the surface. The high c-axis orientation at higher molarities of the

precursor solution can be explained as due to the combined effect of increase in Zn incorporation, increase in growth rate and reorientation effect (Goyal *et al* 1992; Agashe and Major 1996).

3.2 SEM studies

Figure 3 shows scanning electron micrographs of zinc oxide films grown at different substrate temperatures using 0.1 M zinc acetate solution. These micrographs show films of two distinct morphologies. At low substrate temperature (< 623 K), solid phase of the precursor is deposited with less transmittance (figure 3a). While micrographs of films formed at higher deposition temperatures show a uniform film nature with distinct

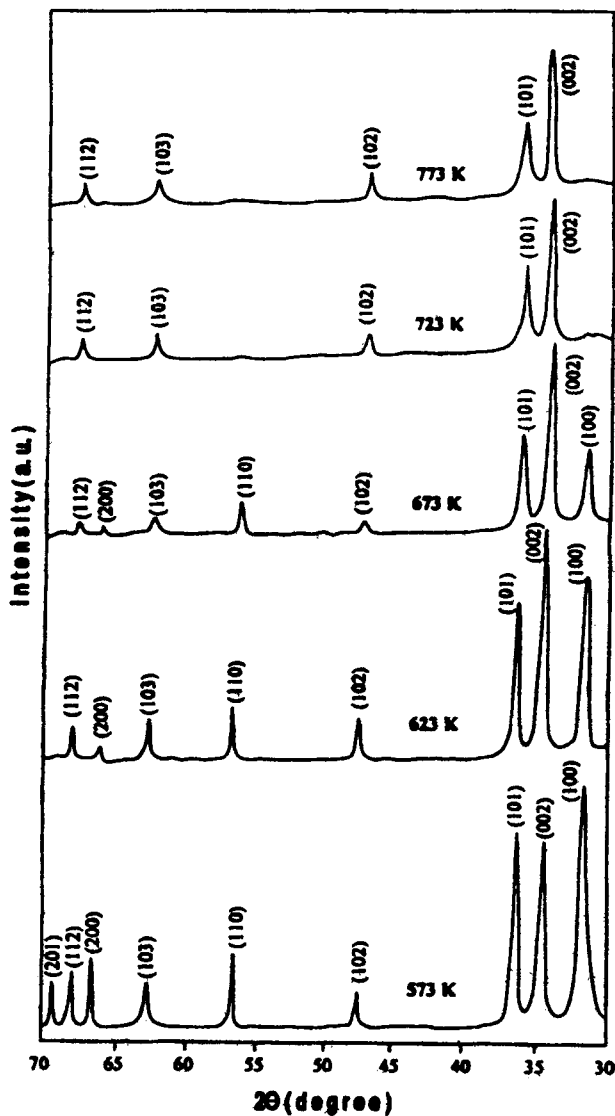


Figure 1. X-ray diffractograms of ZnO films deposited using 0.1 M zinc acetate precursor solution at different substrate temperatures.

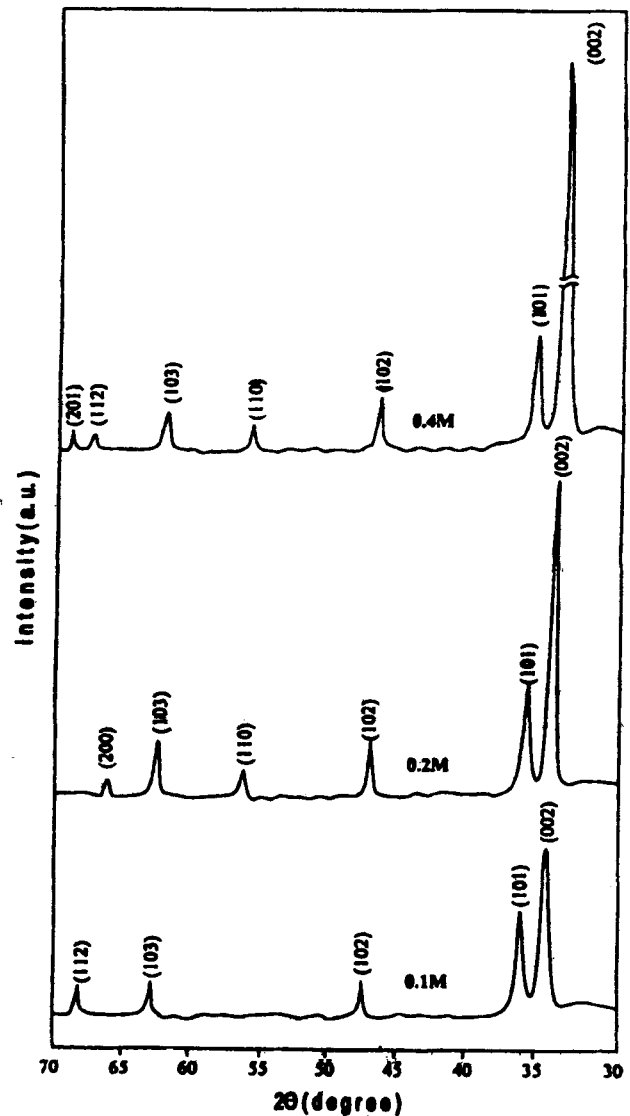


Figure 2. X-ray diffractograms of ZnO films prepared at a substrate temperature 723 K using zinc acetate precursor solutions of different concentrations.

grain boundaries. The films deposited at 773 K (figure 3b) consist of uniform crystallites in the form of small grains.

3.3 Electrical and optical properties

The electrical resistivity, transmittance, optical energy gap and figure of merit of ZnO films deposited from

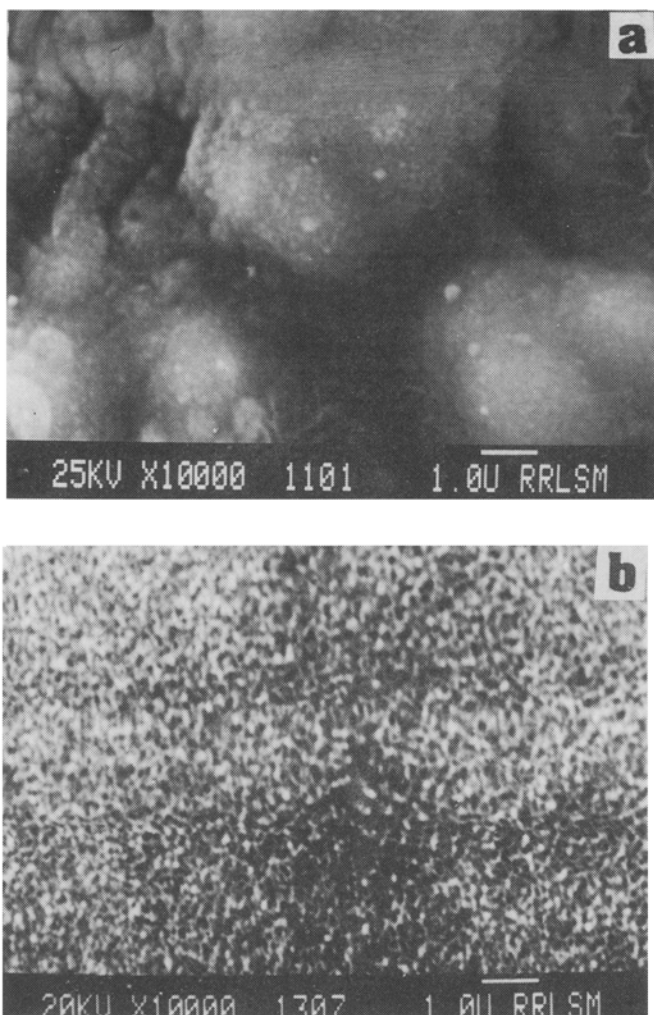


Figure 3. Scanning electron micrograph of zinc oxide thin films prepared at a substrate temperature (a) 573 and (b) 723 K using 0.1 M zinc acetate solution.

0.1 M zinc acetate precursor solution at various substrate temperatures are presented in table 1. The resistivities of as-deposited films have been high. This is probably due to the grain boundary effects, since the films are polycrystalline in nature. Also, since air was used as the carrier gas, it is quite likely that a large number of oxygen molecules are chemisorbed in the film both at the grain boundaries and on the surface. The chemisorption of oxygen will produce potential barrier, which hinders the electrical transport causing a reduction in conductivity.

In order to enhance the conductivity, the zinc oxide films were annealed at 573 K for 90 min under a vacuum of 10^{-5} mbar. During film deposition, large number of oxygen ions (O_2^-) were chemisorbed and incorporated at the grain boundaries and also on the surface of the film producing potential barriers which hinder the electrical transport. On vacuum annealing, the chemisorbed O_2^- ions in the films desorb from the samples donating an electron to the atom ($O_2^- \rightarrow O_2 + e$) causing the resistivity to fall drastically (Fujita and Kwan 1959; Mark and Chang 1976). Thus, the conductivity increase due to vacuum annealing can be attributed to increase of carrier concentration and lowering of grain boundary potential. The lowest resistivity obtained in the present investigation was $3.15 \times 10^{-3} \Omega m$ for films deposited with 0.1 M zinc acetate precursor solution at a substrate temperature of 723 K.

Figure 4 depicts the optical transmission spectra of the films deposited using precursor solution of molarity 0.1 M at various deposition temperatures. The transmission measurements were recorded in the range 300–900 nm. The intrinsic absorption in a semiconductor occurs for wavelengths in the vicinity of the energy gap. The absorption coefficient ' α ' is calculated using Lambert's law.

$$\alpha = [\ln(1/T)]/t, \quad (1)$$

where T is the transmittance and t the thin film thickness. Figure 5 shows the typical variation of absorption coefficient ' α ' with photon energy for films deposited at a substrate temperature 723 K. The absorption has its maximum value at a low energy and decreases with optical energy in a manner similar to the absorption edge of semiconductors. Assuming that transition becomes

Table 1. Electrical and optical properties of ZnO films.

Solution concentration (M)	Substrate temperature (K)	Thickness (nm)	Resistivity (Ωm)	Transmittance at 550 nm (%)	Φ_{TC} (S)	Bandgap (eV)
0.1	573	300	7.5×10^{-2}	25	0.38×10^{-11}	3.14
	623	275	3.0×10^{-2}	40	0.96×10^{-9}	3.19
	673	200	3.2×10^{-3}	86	0.14×10^{-4}	3.26
	723	175	3.15×10^{-3}	98	0.45×10^{-4}	3.26
	773	150	3.3×10^{-3}	98	0.37×10^{-4}	3.26

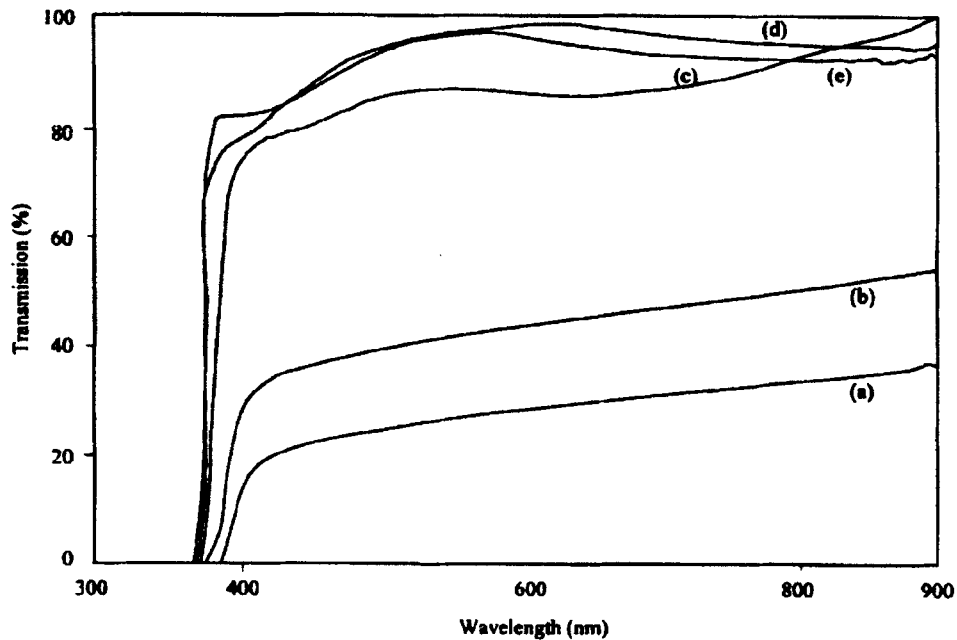


Figure 4. Transmission spectra of zinc oxide films deposited using 0.1 M zinc acetate precursor solution at different substrate temperatures: (a) 573, (b) 623, (c) 673, (d) 723 and (e) 773 K.

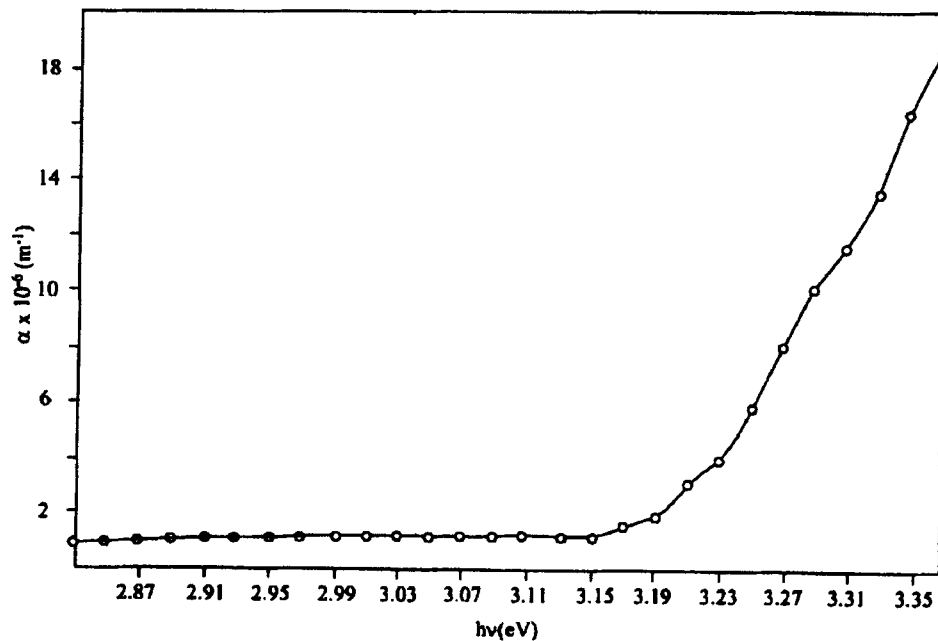


Figure 5. Typical variation of absorption coefficient ' α ' with photon energy $h\nu$ for ZnO films deposited at 723 K using 0.1 M zinc acetate precursor solution.

constant at the absorption edge, the absorption coefficient ' α ' for directly allowed transition for simple parabolic scheme can be ascribed as a function of incident photon energy as (Ables 1992),

$$\alpha h\nu \propto (h\nu - E_g)^{1/2}, \quad (2)$$

where E_g is the optical bandgap. Figure 6 gives the typical plot of $(\alpha h\nu)^2$ vs $h\nu$ for zinc oxide films prepared at 723 K using 0.1 M zinc acetate precursor solution. When the linear portion of the graph is extrapolated to zero, the intercept of the $h\nu$ -axis gives the bandgap. Table 1 gives bandgap values with deposition temperature for ZnO films

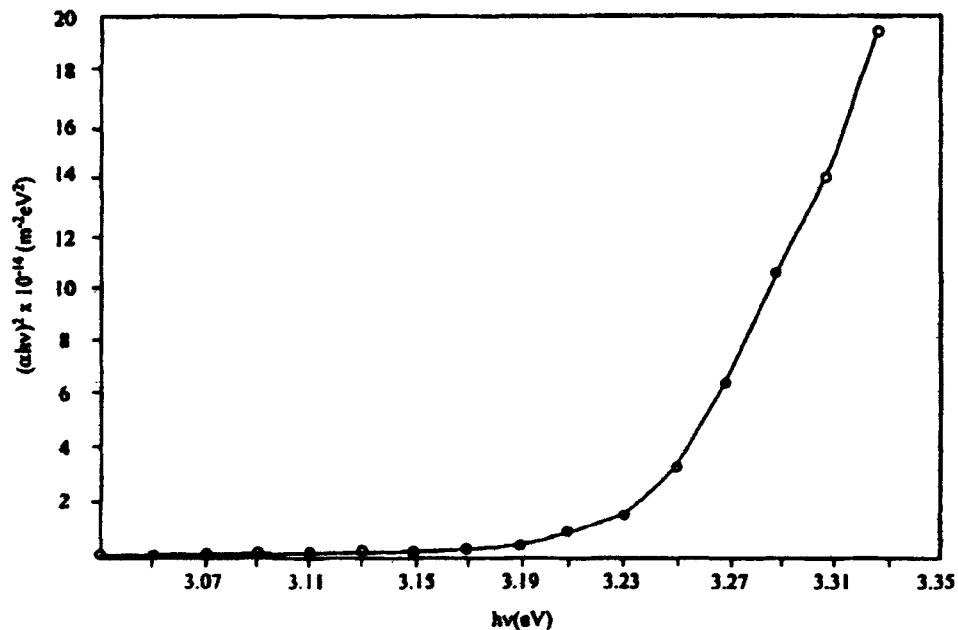


Figure 6. A typical plot of $(\alpha hv)^2$ vs hv for ZnO film deposited at 723 K using 0.1 M zinc acetate precursor solution.

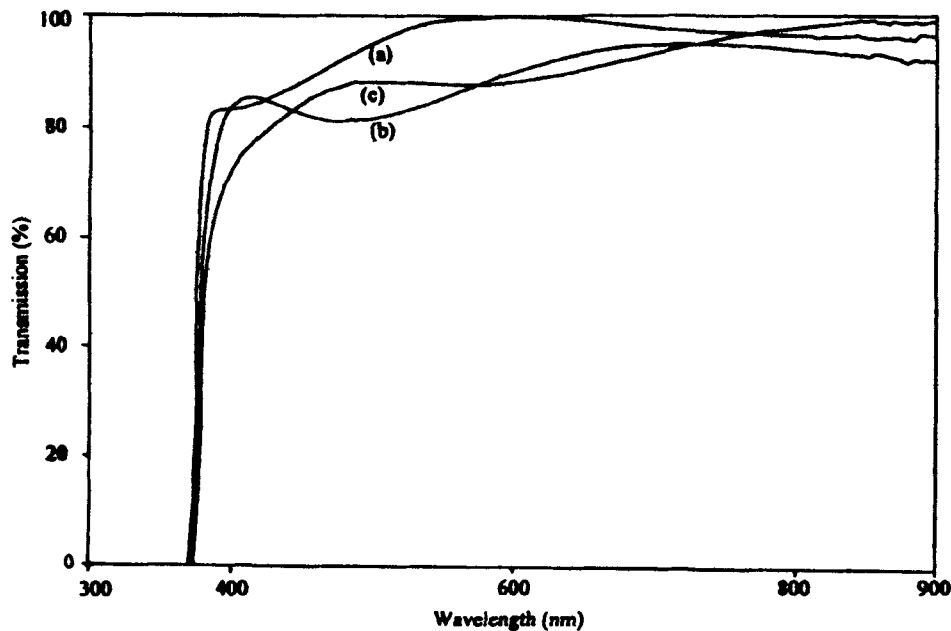


Figure 7. Transmission spectra of ZnO films deposited at 723 K using precursor solution of molarities (a) 0.1, (b) 0.2 and (c) 0.4 M.

prepared using 0.1 M zinc acetate precursor solution. The bandgap energy changes from 3.14 to 3.24 eV, when the substrate temperature increases from 573 to 773 K. The effect of bandgap widening is attributed primarily to the Moss–Burstein shift in semiconductors (Burstein 1954; Moss 1954). The optical bandgap obtained is in good agreement with reported values (Roth and Williams 1981;

Chris Eberspacher *et al* 1986). The refractive index was calculated from the transmission data (Swanepoel 1983). The refractive index values lie between 1.807 and 2.038 in the visible range. Figure 7 represents the transmission spectra of the films deposited at 723 K using different precursor solution molarities. The variation of optical bandgap of the film with thickness was not appreciable.

The deposition using 0.1 M zinc acetate precursor solution at the substrate temperature 723 K yielded a highly transparent and conductive zinc oxide film.

Most of the electronic applications require the film to have low absorption in the visible region and high dc conductivity. Using a quantity called figure of merit (Haacke 1976) which is defined as

$$\phi_{TC} = T^{10}/R_{\square} \quad (3)$$

often ranks the performance of a transparent conducting film. Here, T is the transmittance and R_{\square} the sheet resistance. The values of ϕ_{TC} obtained for ZnO films prepared at different substrate temperatures using 0.1 M zinc acetate solution are given in table 1. The highest value of the figure of merit obtained was 0.45×10^{-4} S for films deposited at a substrate temperature of 723 K.

4. Conclusions

Zinc oxide films were successfully deposited on glass substrates by spray pyrolysis technique. The resistivity and transmittance of the films depend on the deposition temperature. Films deposited at optimum conditions have exhibited a low resistivity of $3.15 \times 10^{-3} \Omega\text{m}$ along with a transmittance of 98% at 550 nm.

Acknowledgement

The authors wish to acknowledge the State Committee on Science, Technology and Environment, Government of Kerala for financial assistance.

References

- Ables A 1992 *Optical properties of solids* (Amsterdam: North Holland)
- Agashe C and Major S S 1996 *Thin film characterization and applications* (eds) K Narayanadass and D Mangalraj (New Delhi: Allied Publishers)
- Aktaruzzaman A F, Sharma G L and Malhotra L K 1991 *J. Mater. Sci. Electron.* **2** 152
- Benny Joseph, Gopchandran K G, Manoj P K, Abraham J T, Peter Koshy and Vaidyan V K 1998 *Indian J. Phys.* **A72** 99
- Benny Joseph, Gopchandran K G, Thomas P V, Peter Koshy and Vaidyan V K 1999 *Mater. Chem. Phys.* **58** 71
- Burstein E 1954 *Phys. Rev.* **93** 638
- Chopra K L, Major S and Pandya D K 1983 *Thin Solid Films* **102** 1
- Chris Eberspacher, Alan L Fahrenbruch and Richard H Bube 1986 *Thin Solid Films* **163** 1
- Fujita Y and Kwan T 1959 *J. Res. Inst. Catal.* **7** 24
- Goyal D J, Agashe C, Takwale M G, Marathe B R and Bhide V G 1992 *J. Mater. Sci. Lett.* **11** 708
- Haacke G 1976 *J. Appl. Phys.* **47** 4086
- Major S, Banerjee A and Chopra K L 1983 *Thin Solid Films* **108** 333
- Mark P and Chang S C 1976 *Oxide and oxide films* (New York: Dekker)
- Minami T, Nanto H and Takata S 1984 *J. Electrochem. Soc.* **23** L280
- Moss T S 1954 *Proc. Phys. Soc. London* **B67** 775
- Roth A P and Williams D F 1981 *J. Electrochem. Soc.* **128** 2684
- Swanepoel R 1983 *J. Phys. E. Sci. Instrum.* **16** 1215
- Yutaka Ohya, Hisao Saiki, Toshimasa Tanaka and Yasutaka Takahashi 1996 *J. Am. Ceram. Soc.* **79** 825