Thermally stimulated discharge conductivity study of zinc oxide thermoelectrets

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Abstract. The present work deals with transmission electron microscopy (TEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermally stimulated discharge current (TSDC) study of inorganic metal oxide (ZnO) nanoparticles and its thermoelectrets. The thermoelectrets were prepared by applying different electric polarizing field (E_p) at constant polarizing temperature (T_p), for constant polarization time (t_p). The TSDC study was carried out in the temperature region of 313–473 K. It was observed that the conductivity of ZnO samples increases with the increase in temperature and polarizing field. The dependence of TSDC data on polarizing agents, i.e. field and temperature shows Arrhenius type of behaviour and is explained on the basis of variable range hopping mechanism.

Keywords. ZnO nanoparticles; DSC; thermoelectrets; TSDC.

1. Introduction

As we all know, any material in its nano form is more demandable than in its bulk form, because at nano level, the material undergoes a drastic change in its properties and has versatile applications. Recently, nanoparticles (NPs) of metal oxides have been the focus of a number of research efforts due to the unusual physical properties that are expected on entering this size regime. Control and manipulation of the morphology of the NPs will ultimately dictate the electrical and optical properties of the final devices (Wu *et al* 2006).

Zinc oxide (ZnO) is a semiconductor compound characterized by wide band gap (3.37 eV) and a larger excitation binding energy (60 meV). Moreover, ZnO is very important material because of its interesting properties, such as dielectric, piezo-electric, pyro-electric, semiconducting, acousto-optic, optical, electro-optical, nonlinear optical, photo-electrochemical and electrical properties (Chu *et al* 2000). These properties make ZnO, a promising material to be used in ultraviolet light-emitting diodes, photo-detectors, solar cells and surface acoustic wave devices (Salama and Hammad 2009). The applications of ZnO for the above devices are associated with the transport mechanism of charge carriers in this material. For the effective functioning of these devices, the study and knowledge of transport mechanism is very important.

An electret is a piece of dielectric material that is capable of storing charges in a quasi-permanent state and finds an important place in several areas including signal transmission and reception. The ZnO NPs electrets were prepared by thermal polarization method. The thermally stimulated discharge current (TSDC) technique is much less employed to characterize electrical behaviour of inorganic dielectric materials. However, it is a powerful tool in the study and quantification of defects, and more important to study the transport of charge carriers, i.e. oxygen vacancies. This paper reports the study of temperature dependence of conductivity of ZnO NPs along with the TSDC study. The conduction mechanism in ZnO NPs is found to be *via* activated type and variable range hopping conduction processes.

2. Materials and method

The hexagonal wurtzite structured ZnO NPs with average crystallite size about 80 nm were successfully synthesized by simple chemical solution method followed by combustion. Detailed preparation technique and properties of as-prepared NPs was reported elsewhere (Golchha *et al* 2011). The morphology of NPs was observed with a TEM, Hitachi H-7100 transmission electron microscopy. X-ray diffraction (XRD) data of the as-synthesized ZnO NPs was collected using Phillips Holland, XRD system PW 1710 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm). Differential scanning calorimetry (DSC) was used to obtain the thermal properties of oven-dried

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ZnO NPs. DSC measurements were carried out using a Netzsch DSC 200F3 PC instrument in the temperature region from room temperature to 450 °C, with heating rate of 10 °C/min in nitrogen atmosphere.

In order to measure the electrical properties, ZnO NPs were grounded into fine powder and the pellets of diameter 1.16 cm were fabricated using a manual hydraulic press machine. The pellet was then annealed at 500 °C for 1 h before current measurements. The thickness of the sample was measured by the compound microscope in conjunction with an oculometer having least count of 15.38 μm , similar to method reported by Sangawar *et al* (2006). The thickness of the sample was kept constant throughout the work and was of the order of 0.1692 cm.

Before TSDC measurement, polarization of sample was carried out by first heating them to a specific polarizing temperature, $T_p = 353$ K and then subjecting the sample to different electric polarizing fields, E_p (0, 1, 2 and 3 kV/cm) using a stabilized 'Labin' d.c. voltage source, for a constant polarizing time, t_p . After polarization, the sample was cooled to room temperature under continuing electric stress. Total polarization time, t_p , was adjusted to 2 h in each case. The sample was then short-circuited for 20 min to remove frictional and stray charges, if any.

After the electret formation, the sample was placed in the sample holder of brass electrodes (M–S–M sandwich configuration) and then placed in a controlled temperature furnace for TSDC study. The sample was thermally discharged in the temperature region of 313–473 K at a uniform rate of 2 °C/min and the corresponding current was measured across the sample using a Digital Nanometer DPM III, supplied by Scientific Equipments, Roorkee. The method for conductivity measurement was the same as that reported earlier (Sangawar and Moharil 2012).

Figure 1. TEM image of ZnO nanoparticles.

3. Results and discussion

3.1 Tunneling electron microscopy (TEM) analysis

Morphology of synthesized ZnO NPs observed using TEM image is presented in figure 1. It shows that the synthesized ZnO NPs have spherical morphology with some tetragonal NPs.

3.2 XRD analysis

Figure 2 shows the XRD pattern of the as-prepared ZnO NPs. The diffraction peaks appeared at $2\theta = 31.70^\circ$, 34.40° , 36.20° , 47.50° and 56.60° , which corresponds to (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) planes in hexagonal wurtzite structure consistent with the bulk ZnO (JCPDS card no. 36-1451) (Cheng-Hsien 2007; Nirmala *et al* 2010). As shown in the XRD data, the (1 0 0) direction in figure 2 is the preferred orientation for the synthesized ZnO NPs. The strong and sharp peaks reveal the highly crystallite nature of NPs. The average crystallite size was found to be about 80 nm, calculated using the Scherrer formula

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

where D is the crystallite size, λ the wavelength of X-ray, β the FWHM in radian and θ the peak angle.

3.3 DSC analysis

A DSC thermogram is shown in figure 3. It reveals endothermic peaks when the decomposition occurs. The curve shows small endothermic peaks around 143 and 171.5 °C. These peaks are attributed to the evaporation of water and

Figure 2. XRD pattern of ZnO nanoparticles.

Figure 3. DSC curve of ZnO nanoparticles.

decomposition of organics. While endothermic peaks 403.4 °C probably represents the removal of oxalate species (Chen *et al* 2008; Pillai *et al* 2008; Telipan *et al* 2011).

3.4 D.C. electrical conductivity

Thermal treatment to the respective sample modifies their structural characteristics and consequently, their electrical properties. The temperature dependence of d.c. electrical conductivity ($\sigma_{d.c.}$) of ZnO nano-powder pelleted samples was obtained by measuring the current across the sample as a function of temperature (in the range of 313–473 K) at different poling fields, i.e. 0, 1, 2 and 3 kV/cm. Figure 4 shows the thermograms ($\log \sigma$ vs $10^3/T$ plot) of the ZnO samples.

The values of electrical conductivities have been obtained using the relation

$$\sigma = [(I \times t)/(V \times A)], \quad (2)$$

where I is the current, V the voltage, t the thickness and A the cross-sectional area.

From figure 4, it is observed that the d.c. electrical conductivity of polarized ZnO samples (thermoelectrets) is higher than the unpolarized ZnO sample. For all the samples, conductivity increases with polarizing field.

It is also observed that the conductivity increase with increase in temperature, represents semiconducting nature. It can be noticed that the conductivity increases with the temperature obeying the well-known Arrhenius equation

$$\sigma = \sigma_0 \exp \left[\left(-\frac{E_a}{kT} \right) \right], \quad (3)$$

where σ is the electrical conductivity at any temperature, σ_0 the pre-exponential factor, E_a the activation energy,

Figure 4. Plots of $\log \sigma$ vs $1/T \times 10^3$.

Table 1. Activation energy values.

Field (kV/cm)	E_a values (eV)	
	LTR	HTR
0	0.144	0.205
1	0.147	0.232
2	0.150	0.310
3	0.161	0.409

which corresponds to the energy difference between the donor level and the conduction level, k the Boltzmann constant and T the absolute temperature (Hossain *et al* 2008; Natsume *et al* 2000).

The activation energy values in low temperature region (LTR) and high temperature region (HTR) have been calculated from the slope of thermograms and are shown in table 1. E_a values for all the samples are found to be lower in LTR as compared to HTR. In both the temperature regions, E_a values are found to be increased with increase in polarizing field and temperature. This can be due to the energy gap width at low temperature region is lower than that of the high temperature region, which was attributed to the increased ionized oxygen vacancy V_O with the increase in temperature (Salama and Hammad 2009).

At low temperature, when the mobility of the charge carriers is low, the charges may be largely localized in shallow traps. However, at high temperature, the charge carriers with high mobility are shifted to deeper traps. The number of such trapped charge carriers increases with the polarizing field. Thus, as the temperature increases, mobility of the charge carriers also increases; consequently shifting the excess charges to deeper traps.

Figure 5. Plot of $\ln(\sigma T^{1/2})$ vs $T^{-1/4}$.

The release of charge carriers from such traps requires more energy.

Variable range hopping (VRH) is also considered as one of the major carrier-transport mechanism proposed for inorganic semiconductors. Hopping refers to tunneling transition from occupied to unoccupied localized status. In the VRH conduction mechanism, the electrons hop between the levels that are close to Fermi level irrespective of their spatial distribution. So in this type of hopping conduction, the hopping distance is not constant as in the nearest-neighbour hopping. The relation of conductivity with temperature for VRH is given by (Mott and Davis 1979)

$$\sigma = \sigma_{h0} \exp \left[\left(-\frac{T_0}{T} \right) \right]^{1/4}, \quad (4)$$

where σ_{h0} and T_0 are given by the following expressions

$$\sigma_{h0} = \frac{3e^2 \nu_{ph}}{(8\pi)^{1/2}} \left[\frac{N(E_F)}{\alpha kT} \right]^{1/2}, \quad (5)$$

$$T_0 = \left[\frac{16\alpha^3}{kN(E_F)} \right], \quad (6)$$

where ν_{ph} ($\approx 10^{13} \text{ s}^{-1}$) is the phonon frequency at Debye temperature, k Boltzmann's constant, $N(E_F)$ the density of localized electron states at Fermi level and α the inverse localization length of the localized state.

From (5) and (6), we have

$$\ln(\sigma T^{1/2}) \propto T^{-1/4}. \quad (7)$$

Figure 5 represents the plot of $\ln(\sigma T^{1/2})$ vs $T^{-1/4}$ for ZnO thermoelectrets indicating that the dominant mechanism of conduction is variable range hopping.

ZnO crystals exhibit strong *n*-type conductivity due to intrinsic defects (oxygen vacancy and interstitial zinc atoms) (Zhou *et al* 2004; Pearton *et al* 2005). These defects introduce donor states in the forbidden band slightly below the conduction band and hence, result in the conducting behaviour of ZnO. The electrical conductivity is thus controlled by the intrinsic defects generated during synthesis (Sawalha *et al* 2009).

Moreover, ZnO is piezoelectric material and the origin of the piezoelectricity lies in its crystal structure, in which the oxygen and zinc atoms have tetrahedral bonding. In such a non-centrosymmetric structure, the centre of positive and negative charges can be displaced due to external pressure-induced lattice distortion. This displacement results in local dipole moment, thus, a macroscopic dipole moment appears over the whole crystal (Wang 2004).

Thus, while polarizing the ZnO NPs samples with polarizing electric field, E_p , at an elevated temperature, T_p , the possible defects that exist in the system respond to this field stress to form a meta-stable state of the charge or dipole distribution. Whereas, cooling the sample to a lower temperature T_0 , freeze in those polarized defects. In TSDC process, the electric field was removed, and the sample is thermally discharged at a constant heating rate. As the temperature increases, the thermal energy excites the lattice vibrations, activates charge motion or aligned dipoles, resulting in the relaxations of those charge distributions or polarized states, and gives rise to a TSD current in the external circuit.

4. Conclusions

Differential scanning calorimetry (DSC) revealed that ZnO NPs were thermally stable. The d.c. electrical conductivity of ZnO NPs and its thermoelectrets in the temperature range from 313 to 473 K, found to be increased with increasing temperature as well as polarizing field. The activated type of conduction as well as Mott's variable range hopping conduction mechanisms were found to be dominating. In addition, the activation energy of ZnO thermoelectrets were found to be increased with increasing temperature as well as polarizing field.

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