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Thermally stimulated discharge conductivity study of zinc oxide thermoelectrets

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The *dc* electrical conductivity of ZnO nanoparticles and its thermoelectrets have been studied in the present paper. Thermal stability of ZnO nanoparticles has been investigated by DSC. The thermoelectrets were prepared by polarizing the sample by applying different polarizing fields (E_P) at constant polarizing temperature (T_P) for constant polarization time (t_p). The thermally stimulated discharge current (TSDC) studies have been made on ZnO sample at a constant heating rate in the temperature region 313-473 K. It has been observed that the conductivity of ZnO nanoparticles has been increased with increase in temperature and field. The thermograms are plotted between log σ and temperature ($10^3/T$). The dependence of TSDC data on polarizing agents i.e. field and temperature is explained on the basis of theoretical predictions.

Keywords: ZnO nanoparticles, Differential scanning calorimetry, Thermoelectrets, Thermally stimulated discharge current

1 Introduction

Any material in its nano form is more demandable than in its bulk form because in nano level the material undergoes a drastic change in its properties and has versatile applications. Recently, nanoparticles of metal oxides have been the focus of a number of research efforts due to the unusual physical properties that are expected upon entering this size regime. Control and manipulation of the morphology of the nanoparticles will ultimately dictate the electrical and optical properties of the final devices[1].

ZnO is a semiconductor compound characterized by wide band gap (3.37 eV) and a larger excition binding energy (60 meV). Moreover, zinc oxide is very important material due to the many interesting properties inherent in this material, such as dielectric, piezo-electric, pyroelectric, semiconducting, acousto-optic, optical, electro-optical, nonlinear optical, photo-electrochemical and electrical properties[2]. These properties make ZnO a promising material to be used in ultraviolet light-emitting diodes, photo-detectors, solar cells and surface acoustic wave devices[3]. Thus, ZnO material has been increasingly studied for many years due to its excellent physical properties. The application of the ZnO material for the above devices is associated with the transport mechanism of charge carriers in this material. For the effective functioning of these devices,the 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 to study and quantification of defects and more importantly to study the transport of charge carriers i.e., oxygen vacancies. In the present paper, the study of temperature dependence of conductivity of ZnO nanoparticles along with the TSDC study. The conduction mechanism in ZnO nanoparticles is found to be via activated type and variable range hopping conduction processes.

2 Materials and Methods

The hexagonal Wurtzite structured zinc oxide nanoparticles (ZnO NPs) with average crystalline size about 80 nm were successfully synthesized by a simple chemical solution method followed by combustion. Detailed preparation technique and properties of as-prepared NPs was reported elsewhere[4]. Differential Scanning Calorimetry (DSC) was used to obtain the thermal properties of oven-dried ZnO nanoparticles. DSC measurements were carried out using a Netzsch DSC 200F3 PC instrument from room temperature up to 450°C with heating of 10°C/min in nitrogen atmosphere.

In order to measure the electrical properties, ZnO nanoparticles 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 occulometer having a least count of 15.33 μm similar to method reported[5]. The thickness was kept constant throughout the work and is of the order of 0.1686 cm.

Before TSDC measurement, polarization of sample was carried out by first heating them to a specific polarizing temperature Tp = 353 K and then subjecting them to different electric polarizing field Ep (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. Then, the field was switched off. The total time of polarization t_p was adjusted to be 2 h in each case. The samples were short-circuited for 20 min to remove frictional and stray charges, if any.

After the electret formation, the M-S-M sandwich configuration using a sample holder of brass electrodes was placed in a controlled temperature furnace. The sample was thermally discharged 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, in the temperature region 313-403 K. The method for conductivity measurement was the same as that reported earlier[6].

3 Results and Discussion

3.1 DSC analysis

A plot of DSC curve is shown in Fig. 1. DSC graph reveals endothermic peaks when decomposition occurs. The curve shows small endothermic peaks around 143°C and 171.5°C. These peaks are attributed to the evaporation of water and decomposition of organics. While endothermic peaks 403.4°C probably represent the removal of oxalate species. Our results are found to be in good agreement [7-9].

3.2 DC electrical conductivity

Thermal treatment to the respective sample modifies their structural characteristics and consequently, their electrical properties. The temperature dependence of *dc* electrical conductivity (σ_{dc}) of ZnO pelleted powder samples studied by measuring the current as a function of temperature in range 313-473 K at different poling fields i.e. 0, 1, 2 and 3 kV/cm. Figure 2 shows the thermograms (logσ-$10^3/T$ plot) of the ZnO sample.

The values of electrical conductivities have been obtained from:

$$\sigma = [(I \times t) / (V \times A)] \quad \ldots(1)$$

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

From Fig. 2, it is observed that the *dc* electrical conductivity of ZnO sample (without preparing thermo-electrets i.e. 0 kV/cm in graph) is lower than the ZnO thermo-electrets. For all the samples, conductivity increases with increase in temperature, represents semiconducting behaviour. It is also observed that conductivity also increases with increasing polarizing field.

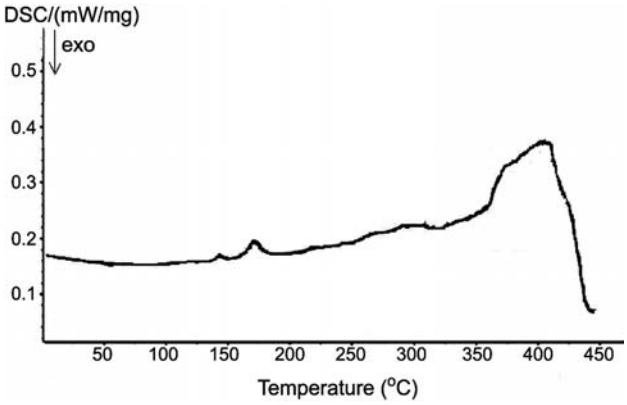

Fig. 1 — DSC curve of ZnO nanoparticles

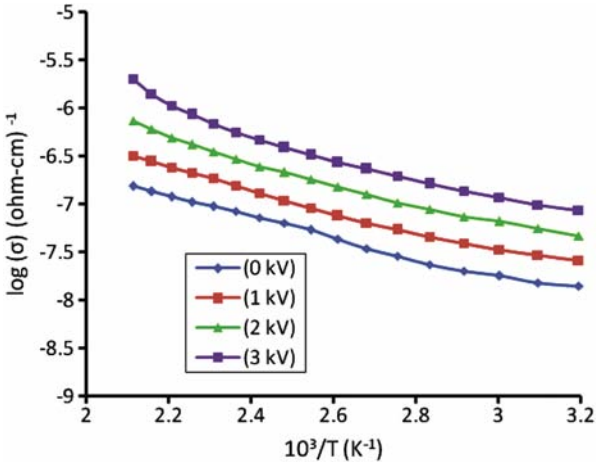

Fig. 2 — Plots of logσ versus $1/T \times 10^3$

Table 1 — Activation energy values

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

It can be noticed that the conductivity increases with the temperature obeying the well-known Arrhenius equation:

$$\sigma = \sigma_0 \exp\left[\left(-\frac{E_a}{kT}\right)\right] \quad \ldots(2)$$

where σ is the electrical conductivity at any temperature, σ_0 the pre-exponential factor, E_a is the activation energy, which corresponds to the energy difference between the donor level and the conduction level, K is the Boltzmann constant and T is the absolute temperature[10,11]. Thermograms represent Arrhenius-type electrical conductivity behviour for ZnO samples.

The activation energy values have been calculated from the slope of thermograms in two temperature regions-low temperature region (LTR) and high temperature region (HTR) and are presented 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 which was attributed to the increase of ionized oxygen vacancy V_o with the increase of temperature.

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[12]:

$$\sigma = \sigma_{h0} \exp\left[\left(-\frac{T_0}{T}\right)\right]^{1/4} \quad \ldots(3)$$

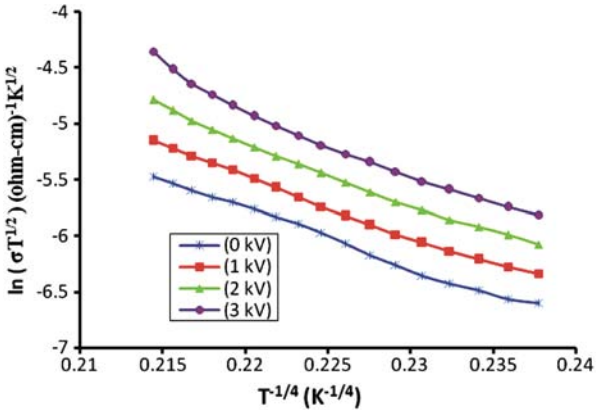

Fig. 3 — Plot of ln ($\sigma T^{1/2}$) versus $T^{1/4}$

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

$$\sigma_{h0} = \frac{3e^2 \nu_{ph}}{(8\pi)^{1/2}} \left[\frac{N(E_F)}{\alpha kT}\right]^{1/2} \quad \ldots(4)$$

$$T_0 = \left[\frac{16\alpha^3}{kN(E_F)}\right] \quad \ldots(5)$$

where ν_{ph} ($\approx 10^{13} s^{-1}$) is the phonon frequency at Debye temperature, k is Boltzmann's constant, N (EF) is the density of localized electron states at Fermi level and α is inverse localization length of the localized state. From Eqs (4) and (5), we have:

$$\ln(\sigma T^{1/2}) \propto T^{-1/4} \quad \ldots(6)$$

Figure 3 shows the plot of ln ($\sigma T^{1/2}$) with $T^{-1/4}$ for ZnO thermo-electrets indicating that the dominant mechanism of conduction is variable range hopping.

ZnO crystals exhibit strong *n*-type conductivity due to intrinsic defects[13,14] (oxygen vacancy and interstitial zinc atoms). 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[15].

Thus with TSDC technique, when the ZnO NPs samples were polarized under a constant electrical field, *E*p, at an elevated temperature, *T*p, the possible defects that exist in the system responded to this field stress to form a metastable state of the charge or dipole distribution. The samples when cooled to a lower temperature, T_0, freeze in those polarized defects. Subsequently, the electric field was removed,

and the samples were heated at a constant heating rate. As the temperature increases, the thermal energy excites the lattice vibrations, and these activate charge motion or aligned dipoles, resulting in the relaxations of those charge distributions or polarized states, and gives rise to a current in the external circuit, which was recorded as TSDC.

4 Conclusions

Differential Scanning Calorimetry (DSC) revealed that ZnO NPs are thermally stable. The electrical conductivity of ZnO nanoparticles in the temperature range 313-473 K was studied and found to be increased with increasing temperature as well as applied 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 ZnO thermoelectrets were found to be increased with increasing temperature as well as polarizing field.

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