Conduction mechanism in (ZnO/PVC) polymer nanocomposite

A Joy Singh

Department of Physics, S. Kula Women’s College, Nambol-795134, Manipur, INDIA
Email: joyarambam@gmail.com

Abstract: The electrical conductivity of ZnO nanoparticle doped PVC polymer of different concentrations and thickness has been investigated as a function if applied electric field and temperature. The LnJ versus $E^{1/2}$ plot for the pure sample shows transition field but for highly doped sample, the plot shows curvature for both low and high field, i.e., there is no transition field. This nonlinearity of the plot is due to space charge built up in the sample. The value of $\beta$ is calculated from the slope of LnJ versus $E^{1/2}$ plot and compared with the theoretical value. The result shows the Poole-Frenkel mechanism of conduction is operative.

1. Introduction:

The organic polymers that conduct electricity are called conducting polymers, such compound may have metallic conductivity or can be a semiconductor. The advantages of conducting polymers are their process ability mainly by dispersion. Conducting polymers are generally not plastic but like insulating polymer, these are organic materials. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers. The electrical properties can be fine-tuned using the method of organic synthesis and by advance dispersion techniques [1]. The most recent research in conducting polymers is to develop high conducting with stability and acceptable processing attributes. So, for most well studied conducting polymers are (i) nitrogen containing polymers, i.e., Polypyrroles, polyaniline. (ii) Sulphur containing polymers, i.e., Polythiophenes, Poly(3,4-ethylenedioxythiophene), Poly(p-phenylenesulfide) and (iii) other polymers i.e. Polyacetylenes, Poly(p-phenylene vinylene), Polyethylene terephthalate etc.

The ZnO material is a wide band gap 3.3eV (at room temperature) n-type semiconductor. Advantages associated with large band gap includes higher breakdown voltage ability to sustain large electric field, lower electronic noise, high temperature and higher power operation. The band gap of ZnO can further be tuned to 3-4 eV by alloying magnesium oxide or cadmium oxide [2].

ZnO exhibits a diverse group of growth morphologies in the nano regime that has made this material a promising candidate in the field of nanotechnology. Nanostructured ZnO exhibits novel electrical, mechanical, chemical and optical properties which are believed to be due to the surface confinement effects or nanostructures in one dimension. These one-dimensional objects are of great importance to understand some basic physics
related phenomena in the low dimensional system to form the basis of next generation higher performance nanodevice [3].

As ZnO has high electron mobility and wide band gap so, ZnO nanoparticle is doped in PVC film, electrical property of the nanocomposite film will change from the pure PVC film. In the present study, an attempt is made to investigate the conduction mechanism in pure PVC, (having excellent electrical insulation property as mentioned above), film and ZnO nanoparticle doped PVC film at different applied voltage, temperature and doping concentrations.

2. Experimental

(1) Formation of pure film
For the present study, PVC granules are collected from Reliance Industry, Surat, India and Cyclohexanone from S D Fine Chem. Ltd Mumbai, India, form a solution (4 gram of PVC and 20 cc of cyclohexanone). The solution was kept at room temperature for one week for complete dissolution. The solution was poured on the glass plate to make thin film. The glass plate was placed over a pool of mercury for perfect levelling so as to ensure uniform thickness. The system was allowed to evaporate at room temperature in dust free chamber for 6 days and the film was detached from the glass plate. Thus, we get pure (PVC + cyclohexanone) film.

(2) Preparation of nanocomposite film
After formation of solution as above, ZnO nanoparticles collected from Material Science Laboratory, B N College, Patna, were doped with different quantities i.e., 0.00325 gm/cc, 0.00653 gm/cc and 0.01303 gm/cc. The mixture (PVC + ZnO) were stirred by Magnetic stirrer (Eltect-MS 205) for 8 hr and the mixture were poured on the glass plate and proceed as mentioned above. Thus, we get ZnO nanoparticle doped PVC film. The thickness of different samples were 0.035 cm, 0.0175 cm, 0.03 cm and 0.019 cm.

(3) Measurement of conductivity:
The sample was sandwich between two electrodes having area 5.067 x 10⁻⁴ sq. m under light constant pressure in the sample holder and placed inside the temperature-controlled bath, Ultra-thermostat. The different potential is applied across the sample by the power supply (EHT-11) supplied by Scientific Equipment, Roorkee. The value of potential across the sample is varied from 0 to 1400 volt by an interval of 100 volt at constant temperature. The potential drop across 1 MΩ resistor is recorded by digital multimeter. The same operation is repeated for different values of temperature from room temperature 300 K to 373 K by an interval of 10 K. In order to make uniform heating the sample is kept at constant temperature for 30 minutes for each consecutive reading. The conductivity measurement is same as that reported earlier.

3. Result and discussion

The plot of LnJ versus E¹/² (figure 1-4) show that mechanism of conduction for different applied field and temperature. For the pure PVC field (sample A), is almost linear upto 1.5x10⁴ V/m and this applied field the plot is linear with stiffer than that in the lower field. Similarly, for the ZnO nanoparticle doped PVC film at the rate of 0.0065 gm/cc (sample B) and 0.00326 gm/cc (sample D) the plot is almost linear beyond the applied field 1.849 x10⁴ V/m and 2.05x10⁴ V/m respectively with greater stiffer to that lower field. For different rate of ZnO nanoparticle doping the transition field are different also due to the doping on pure PVC film the transition field are shifted from the pure PVC film. The samples are under the action of applied `filed are just to that in vacuum diode-space charge limited
current [4]. If ZnO nanoparticle is doped 0.0130 gm/cc the plot shows the curvature for both low and high field i.e., there is no transition field. The nonlinearity of the plot is due to space charge build up in the sample [5]. Generally, in polymers the Ln J versus E$^{1/2}$ plot for different temperature, show straight line in high electric field region, in which JαE$^{1/2}$, the case of hot electrode i.e., energy required by the field is greater than the thermal energy. The Schottky and Poole-Frenkel mechanism of conduction are dominant process of conduction in insulator or semiconductor at high field [6,7]. Heavy reliance has been made on the measured slope of LnJ versus E$^{1/2}$ for the interpretation of the experimental data.

It was found experimentally that, emission current increases with increasing field strength at the cathode, which is contradictory to that independence of current in thermionic emission. Schottky showed that a lowering of the work function due to an increase in the applied field was responsible for such a behaviour. Hence due to high field Schottky emission of electron occurs from the metal contact at the negative potential into the conduction band of the dielectric. This mechanism corresponds to thermal activation of electron over the metal insulator interface barrier with added effect that the applied field reduce the higher of the barrier. Considering the origin of the surface barrier, Schottky argued that, there are two regions (1) polarization field and (2) an image field. The Schottky effect is associated with the barrier on the surface of the metal and insulating material, whereas the Poole- Frenkel emission associated with the barrier in the bulk of the material. In both effect the restoring force is due to coulomb interaction between the escaping electrons and the positive charges, they differ in that, the positive image charges are mobile with Schottky emission and fixed for Poole- Frenkel barrier. Hence lowering of barrier is greater for Poole- Frenkel than that of Schottky emission.

Current density for Schottky(S) and Poole- Frenkel (PF) process follows the relation Lamb D R (1967).

$$J = J_o \beta^{1/2} e^{\frac{\beta E}{kT}}$$  \hfill (1)

Where

$$J_o = A T^2 \exp \left( \frac{\beta}{kT} \right)$$ \hfill (Schottky mechanism)

$$J_o = \frac{\sigma o V}{d}$$ \hfill (Poole- Frenkel mechanism)

T= absolute temperature  
k = 1.36x 10^{-23} J/K Boltzmann constant  
$\sigma_o$ = low field conductivity  
V= applied field  
d = thickness of the sample

$$\beta(s) = \sqrt{\frac{e^2}{4\pi \varepsilon_o \varepsilon}}$$ \hfill (Schottky constant)

$$\beta(pf) = \sqrt{\frac{e^2}{4\pi \varepsilon_o \varepsilon}}$$ \hfill (Poole- Frenkel constant)

$\varepsilon_o$ = permittivity of free space  
$\varepsilon$ = permittivity of the material.

From equation (1) it is suggested that the plot of LnJ versus E$^{1/2}$ is linear with slope $\beta/kT$. The values of $\beta$ were calculated from the plot (putting k = 1.36x 10^{-23} J/K) for all temperature.
Figure 1. Variation of LnJ vs $E^{1/2}$ for sample (A)

Figure 2. Variation of LnJ vs $E^{1/2}$ for sample (B)

Figure 3. Variation of LnJ vs $E^{1/2}$ for the sample (C)

Figure 4. Variation of LnJ vs $E^{1/2}$ for the sample (D)
If ZnO nanoparticle is doped to pure PVC film the value of LnJ is increase with $E^{1/2}$. As PVC is partially syndiotactic material, with sufficient irregularity structure that crystallinity is quite low, i.e., almost amorphous in nature. The presence of amorphous region gives rise to localized state. As there are many localized states, the release or excitation carriers in these states dominant the conduction process. The dopant ZnO present in sufficient quantity remarkably affect the position of Fermi level. The molecules of the dopant enter either in the amorphous regions of the polymer or at the disordered regions chain folds. If molecules of the dopant are present at low concentration, they will give rise to additional molecular sites for trapping of charges. Such localized site formed by dopant molecules can be defined in molecular terms using the difference in ionization potential as an indication of trap depth. If dopant concentrations are increase, the dopant molecule starts bridging in separating the two localized states and lowering the potential barrier, that facilitating the transfer of charge carrier between the two localized states, the dopant ZnO has high mobility also n-type semiconductor so if it is doped to pure PVC the energy level lies just below the conduction band, i.e. the width of the band gap is decreased, which result electrons move into the conduction band with increased of applied field.

Theoretical values of $\beta(s)$ and $\beta(ps)$ were calculated from equation (2) and (3) using $e=1.6 \times 10^{-19}$C, $\varepsilon=3.0$ and $\varepsilon_o=8.85 \times 10^{-12}$ F/m.

4. Conclusion

The present experimental investigation reveals that ZnO nanoparticle doped PVC film operates the Poole- Frenkel mechanism of conduction within intermediate range of temperature.

Acknowledgements

The author expresses sincere thanks Prof. N.A. Karimi for stimulate discussion and thanks to Material Science Laboratory, Department of Physics, B N College Patna for supplying ZnO nanoparticles.

References

[1] Nalwa, H.S., (2000) Hand book of Nanostructured Materials and Nanotechnology. Academic Press, New York, 5: 501-575.
[2] Ozgur, U., Aliivov Ya, I., Lin, C., (2005) A comprehensive review of ZnO materials and devices. J. Appl. Phys, 98, 4.
[3] Bahadur, H., Srivastava, A.K., (2007) Nano-structured ZnO films by sol-gel process. Indian J Pure & Appl Phys. 45, 395.
[4] Mott, N.F., Gurney, R.W., (1964) Electronic Process in Ionic Crystal. Dover Publication Inc. New York.
[5] Aldert, V. D. Z., (1957) Solid State Physical Electronics, Pentice Hall. New York 483.
[6] Lamb, D. R., (1967) Electronic Conduction Mechanism in Insulating Films. Methun & Co, London.
[7] Sangawar, V.S., Dhokne, R.J., et. al., (2007) Structural characterization and thermally stimulated discharge conductivity (TSDC) study in polymer thin films. Bull. Mater. Sci. 30, 163.