Space charge limited currents in chlorazole black E dye

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Abstract. Space-charge-limited-currents have been studied in Chlorazole Black E (CBE) dye to understand the current-voltage relationship and the nature and distribution of traps present in the dye. Three distinct regions of voltage-current characteristics have been observed probably for the first time. The results have been discussed on the basis of carrier injection theory. There are non-uniformly distributed deep as well as shallow traps.

Keywords. Space-charge-limited-current; traps; carrier injection; chlorazole black E dye.

1. Introduction

Photovoltaic studies on merocyanine dyes (Morel *et al* 1983; Morel *et al* 1978) have generated a lot of interest in the studies of electrical properties of organic dyes. Sharma (1985) collected the various organic solar cells studied so far along with their efficiencies, open-circuit voltages, fill factors and stabilities. These cells use a polycrystalline thin film. Though a lot of work has been done on organic dye solar cells (Kudo and Moriizumi 1981; Chamberlain *et al* 1981; Kudo *et al* 1981; Yoshimura *et al* 1981; Chamberlain *et al* 1982; Skotheim *et al* 1982; Chauhan *et al* 1983; Sharma *et al* 1983; Loutfy *et al* 1983; Sharma 1985), very little attention has so far been paid towards studying other electrical properties of the dyes. An important parameter controlling the photovoltages in thin film solar cells and the electrical conductivity of solids is the nature of the traps. In most organic molecular crystals the trap distribution is Gaussian (Silinsh 1970; Silinsh *et al* 1974; Nespurek and Silinsh 1976; Silinsh *et al* 1978). However other types of distribution cannot be ruled out. The nature of the traps is reflected in the current-voltage relationship. A study of space-charge-limited-current (SCLC) is considered a good probe into the nature and distribution of traps. We have therefore studied the current-voltage characteristics of CBE dye. Since thin films of dyes in solar cells are polycrystalline our interest lies in the study of polycrystalline samples. Therefore powder compacts of unpurified as well as purified material were used for the present studies. The results have been used to understand the nature of the traps and their distribution in the dye.

2. Experimental

The CBE dye obtained from Sigma Chemical Company, USA was only 50% pure. Since the presence of impurities in organic dyes is a major impediment in the investigation of their electrical properties, the dye was subjected to further purification by chemical precipitation, column chromatography and sublimation techniques. For chemical precipitation, a saturated solution of CBE dye was prepared in triple distilled dimethyl formamide and filtered to remove the insoluble

impurities. The pure dye was precipitated out by adding chloroform to the filtrate. This process, repeated three times, gave a high purity material but the yield was low. For chromatographic purification, the dye purified by chemical technique, was dissolved in a mixture of propanol, acetone, triple distilled water and acetic acid in 5:5:3:1 ratio. Finally the dye was sublimed under a vacuum of 10^{-6} torr. Unfortunately the dye could not be put to zone refining. But the purity of the dye was estimated to be better than 99.99%. For space-charge-limited-current studies thin pellets were prepared in a evacuable die (Pyel Unicam). The pressure applied to the die, having $\frac{1}{2}$ inch diameter was 10 tons. In some preliminary studies it was found that the conductivity of the CBE dye pellet became constant at a pelletising pressure of 10 tons and more. It was also noted that the pelletising pressure does not effect the I-V characteristics at these pressures. The thickness of the samples prepared ranged between 0.09 mm and 0.16 mm. The measuring set-up consisted of a conductivity cell (Chauhan *et al* 1983), a regulated power supply and an electrometer (Keithley 610C). The measurement of current as a function of applied field was taken in dark at room temperature ($\sim 300^\circ\text{K}$). The samples were cycled six times with electric field and all the measurements were taken under steady state conditions. No hysteresis was observed on increasing and decreasing the field. Also no aging effect was observed on I-V curves.

3. Results and discussion

Figure 1 shows the current-voltage characteristics of unpurified and purified samples. The applied electric field was cycled between 300 volts/cm and 12000 volts/cm. As

Figure 1. Log J -log E plot for chlorazole black E dye.

can be seen the current-voltage curve, for unpurified sample, follows a straight line on a log-log plot, having a slope of 1.5 yielding $J \propto E^{3/2}$. For purified sample the current-voltage curve on log-log plot can be divided into three distinct straight lines marked A, B and C. Straight line A extends upto $E = 1800$ volts/cm and has a slope of 0.96 (≈ 1) indicating an ohmic behaviour. Line B has a slope of 3.4. It starts from $E = 1800$ volts/cm and extends upto $E = 4500$ volts/cm. The third region starts from $E = 4500$ volts/cm and extends upto 12000 volts/cm.

It is reported (Lyons and Gutmann 1967; Kao and Hwang 1981) that in trap-free solids and in solids having only the shallow traps the injected currents follow an E^2 law after the ohmic region. But when there are shallow as well as deep traps and the distribution of the traps is nonuniform, the current varies as E^n where $n > 2$. This is the situation presently observed for the region marked B. In case there are shallow as well as deep traps and the trap distribution is uniform the injected current varies exponentially with the applied field. Further it has also been reported (Silinsh 1970) that the constancy of slope in the $\log J$ vs $\log E$ curve in the superlinear region of the current-voltage characteristic (region B) with $n > 2$ within a wide range of field intensity values is an absolutely indispensable condition for the validity of the exponential distribution of traps. In the region C the injected current follows an E^2 law. This suggests that at this stage all the traps are filled and the injection is in the conduction band only. In this situation the injected currents follow the Child-Langmuir law, a situation consistent with our observation in region C. So far there is no other study on the traps in chlorazole black E dye which we can use to cross-check our conclusions.

Further studies on the CBE dye are in progress and will be reported elsewhere.

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References

- Chamberlain G A 1982 *J. Appl. Phys.* **53** 9
- Chamberlain G A, Cooney P J and Dennison S 1981 *Nature (London)* **289** 45
- Chauhan J P S, Rai R C, Tripathi A K and Mathur S C 1983 *J. Mater. Sc. Lett.* **2** 149
- Kao K C and Hwang W E 1981 *Electrical transport in solids* (New York: Pergamon Press) pp 145
- Kudo K and Moriizumi T 1981 *Jpn. J. Appl. Phys.* **20** L553
- Kudo K, Shinohara T, Moriizumi T, Iriyama K and Sugi M 1981 *Jpn. J. Appl. Phys.* **20** 135
- Loutfy R O, Shing Y H and Murti D K 1983 *Solar Cells* **5** 331
- Lyons L E and Gutmann F 1967 *Organic semiconductors* (New York: John Wiley) pp. 558
- Morel D L, Ghosh A K, Feng T, Stogryn E L, Purwin P E, Shaw R F and Fishman C 1978 *Appl. Phys. Lett.* **328** 495
- Morel D L, Stogryn E L, Ghosh A K, Feng T, Purwin P E, Shaw R F and Fishman C 1983 *J. Phys. Chem.* **88** 923
- Nespurek S and Silinsh E A 1976 *Phys. Status Solidi* **A34** 747
- Sharma G D 1985 *Photovoltaic studies on some organic dyes*, Ph.D thesis, Department of Physics, Indian Institute of Technology, New Delhi
- Sharma G D, Tripathi A K, Mathur S C and Dube D C 1983 *J. Mater. Sc. Lett.* **2** 433
- Silinsh E A 1970 *Phys. Status Solidi* **A3** 817

Silinsh E A, Jurgis A, Gailis A K and Taure L F 1974 Electrical properties of organic solids, Summer School, Karpacz, Wroclaw, p. 40

Silinsh E A, Muzikante I J and Taure L F 1978 Electrical and related properties of organic solids, Paper of Int. Conf., Karpacz, Poland, p. 71

Skotheim T, Yang J M, Otvos J and Klein M P 1982 *J. Chem. Phys.* **77** 6144

Yoshimura T, Kiyota K, Ueda H and Tanaka M 1981 *Jpn. J. Appl. Phys.* **20** 1671