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A study of electrical conduction in solution grown doped ethyl cellulose films

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Abstract : A detailed study of electrical conduction in solution grown ferrocen doped ethyl cellulose (EC) films has been made at different fields between (3.0-6.5) $\times 10^4$ volts/cm as a function of temperature in the range 333–383 K at a constant thickness of about 20 microns in the M-I-M sandwich configuration. The role of dopant molecular concentration in the polymer matrix and modification in the conduction characteristics and certain transient effects such as a large burst of current immediately after the application of voltage have been observed. The results show two distinct regions corresponding to different types of conduction; region I at low or moderate fields with a slope ≈ 1 and high field region with a slope ≈ 2 where the conduction current were found to be space charge limited. The current–voltage (*I-V*) characteristics of different samples for the quantitative information about the transport parameters are analysed. At lower fields, Ohm's law is seen to be followed, while at higher fields the Richardson mechanism alongwith space-charge limited (SCL) conduction is the controlling transport mechanism. The increase in current, with ferrocen doping has been attributed, to the formation of charge transfer complexes.

Keywords : Electrical conduction, polymer film, Richardson-Schottky mechanism; space charge limited current; charge transfer complex.

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1. Introduction

In recent years, there has been considerable interest in the study of metal-polymer-metal structures for their possible use in microelectronics. Polymers are a group of materials that typically have very high electrical resistivity and dielectric strength. The conduction mechanism in them is mainly characterized by the transport parameters such as charge carrier density and the charge carrier mobility. For materials exhibiting non-ohmic behaviour, *I-V*

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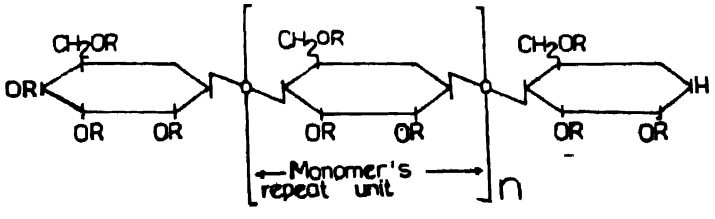
measurements constitute one of the accurate and direct methods of determining the carrier density and the carrier mobility. The carrier mobility may be increased by impregnating them with suitable impurity. This effect has been attributed to the formation of charge transfer complexes. These complexes effectively reduce the trapping of charge carriers and make more carriers available for conduction, thereby enhancing the charge carrier drift in polymers [1-4].

Considerable attention has been devoted to the problems of the change in the electrical conduction in polymers due to intentional doping with low molecular weight compounds. Depending on their chemical structure and the way in which they react with the macromolecular matrix, doping substances decrease the resistivity of the polymer to different degrees [5,6]. The purpose of the present work was to carry out a careful investigation on the steady state conduction, in ferrocen doped EC films, both at low or moderate and at high fields to understand the role of dopant molecules when added in varying concentrations to a polymer matrix in modifying its conduction characteristics. The study is also aimed to find out the possibility of the existence and nature of distribution of traps and to know how impurity affects electrical parameters like carrier mobility, activation energy etc.

2. Experimental details

The work reported in this paper has been carried out on ferrocen doped ethyl cellulose (EC) films.

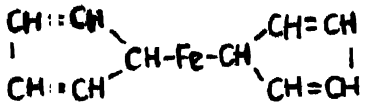
EC is a weakly polar polymer. The slight polar nature of the polymer is due to the difference in electronegativity of the main chain bond C–O–C and its side groups. The electronegativity of the main chain bond arises from the difference in the electronegativity of C and O atoms; however, the electronegativity of side groups arises from the difference in electronegativity of H_2C–C_2H_5 and C–O–C_2H_5 bonds in side chains. The reported glass transition temperature (T_g), the softening and melting temperatures, for *Ec*, lies between 408–418 K and 438-448 K respectively [7]. It's structural formula is



where $R = C_2H_5$

Ferrocen is π -bonded, orange coloured, non-polar; crystalline solid. It is a cyclopentadine complex having molecular formula $C_{10}H_{10}Fe$ in which an iron atom is sandwiched [8] between two cyclo-pentadine anions. There are eighteen valence electrons (in addition to single C–H bonds and C–C bonds of two rings) that is the pair for each of the nine orbitals of iron atom. These nine pairs of electrons may be distributed on ten C–C and

ten Fe–C bond position with use of only stable orbitals of atoms. The Fe–C bonds have a small amount 12% of ionic character. It's structure is



Films of ferrocen doped ethyl cellulose (EC) were prepared by dissolving EC (2.1 g) and ferrocen in a common solvent chloroform (30 cc) at 303 K for 10 min. The doping concentration was changed by varying the amount of ferrocen (*i.e.* 40, 80, 120 and 175 mg) added to the polymer matrix in weight quantities. The films were dried in a vacuum. Thickness of the sample was determined by measurement of their capacitances at 15 kHz, using a dielectric constant $\epsilon = 3$ (for EC). Thickness of the sample was of the order of approximately 20 microns throughout the study except in the case of thickness variation. Samples of different thicknesses were obtained by changing the concentration of the polymer solution. Vacuum deposited electrodes (Al, Ag, Cu and Au) were used during this investigation. The geometry of the sandwich configuration of the electrodes, the method of field/temperature variation and thickness measurements were the same as reported earlier [4,9]. The current was recorded with a Keithley 600 B electrometer at a rate of 4 K per min. The voltage has been applied from a high-voltage unit (EC-HV 4800 D). The temperature and field range was limited, because beyond these, films show breakdown.

3. Results and discussion

Figure 1 represents the *I-V* curves for ferrocen (40 mg) doped EC samples at different temperatures (333, 343, 353, 363, 373 and 383 K). The effect of higher concentrations of ferrocen (*i.e.* 80, 120, 175 mg) on *I-V* characteristics of polymer matrix (at a fixed temperature 353 K) have also been placed in the same figure. The ferrocen (40 mg) doped EC samples have only been studied. These curves exhibit almost similar nature for all temperatures from 333 to 383 K and show two distinct parts; one at lower field $(3.0\text{-}4.5)\times 10^4$ volts/cm and the other at higher field region ($> 4.5 \times 10^4$ volts/cm). Doping with higher amount of ferrocen (*i.e.* 80, 120 and 175 mg, by weight ratio) increases the current.

The *I-V* characteristics of ferrocen doped EC films at a fixed temperature (353 K) but for different thicknesses of the films (ranging from 5 to 35 μm) are shown in Figure 2. Thinnest film (≈5 μm) exhibits more current than thick films.

The Schottky plots (Figure 3) of ferrocen doped EC samples show the variation of current with field in the form of log I versus $\sqrt{E}$. Figure 3 also gives log I vs $\sqrt{E}$ plots for ferrocen doped EC films with dissimilar electrode combinations (*i.e.* Al–Cu, Al–Ag and Al–Au) all taken at 353 K. The lower electrode was Al for all samples. The magnitude of the current was found to be higher in dissimilar electrode combinations (Al–Cu, Al–Ag and Al–Au) than similar electrode (Al–Al) system.

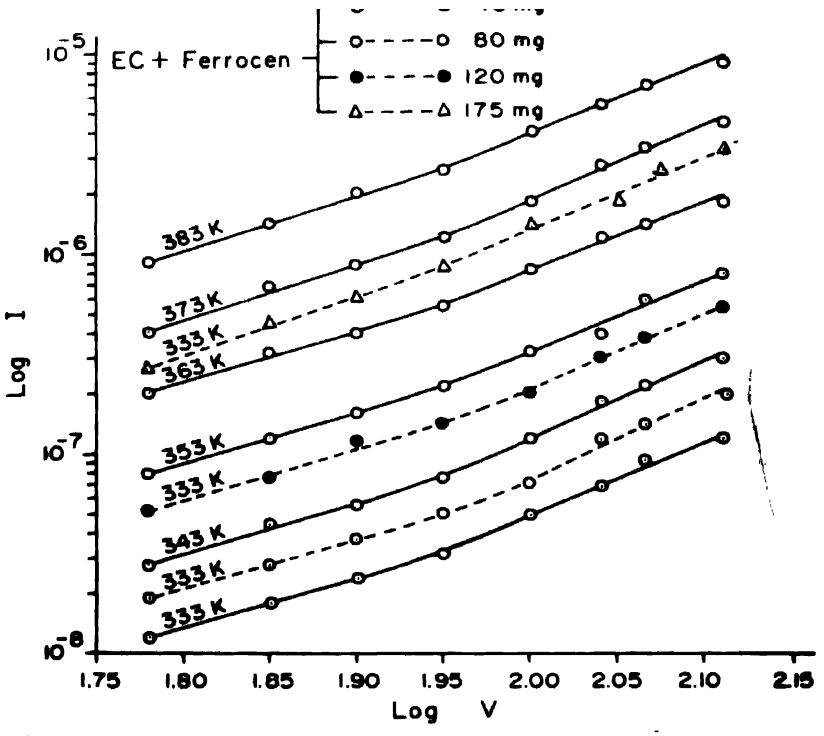


Figure 1. log *I versus* log *V* plots for EC and ferrocen (40, 80, 120 and 175 mg, by weight ratio) films.

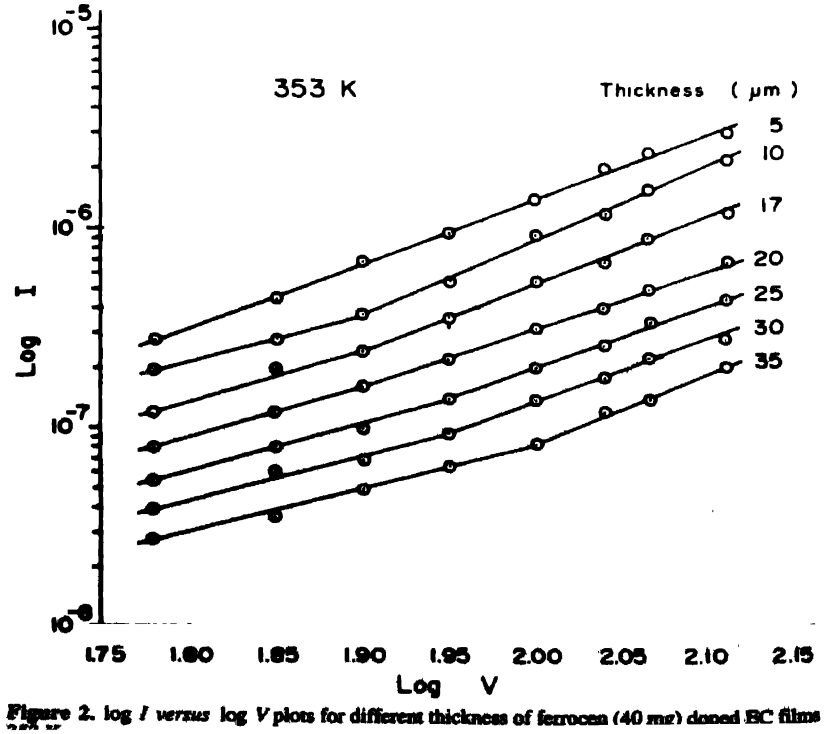


Figure 2. log *I versus* log *V* plots for different thickness of ferrocen (40 mg) doped EC films at

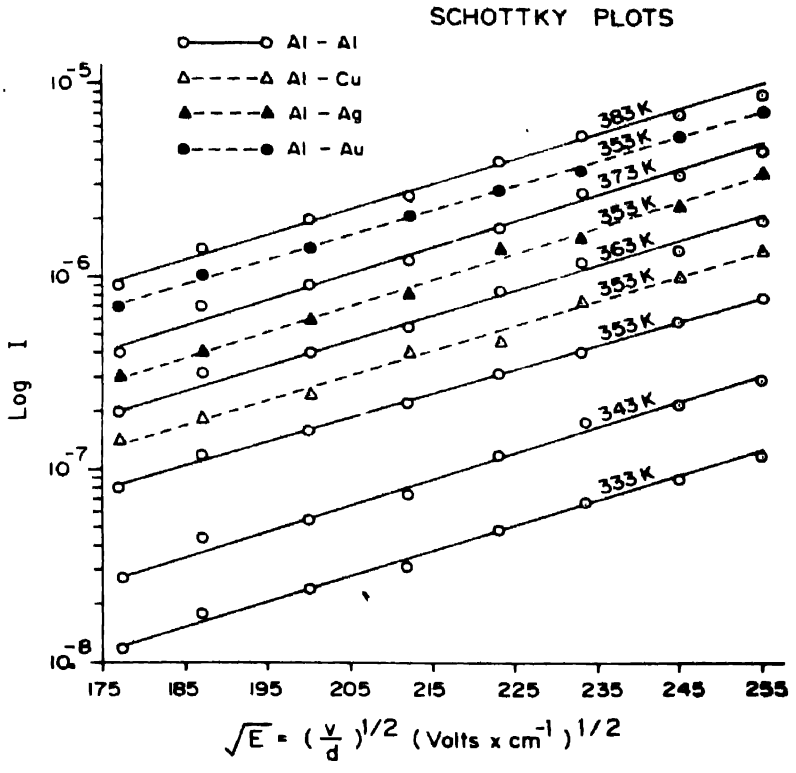


Figure 3. log *I versus* $\sqrt{E}$ plots (Schottky plots—similar and dissimilar electrode systems) for ferrocen doped EC films.

Variation in current with temperature at different fields (log *I versus* $10^3/T$) is shown in Figure 4. Their slopes give the corresponding values of activation energy (P). The value of P with square root of applied field has been traced in Figure 5.

Figure 1 shows the *I-V* characteristics at various temperatures on semi log scale for approximately 20 μm thick film. It is observed from these curves that for temperatures > 333 K, two regions of conduction *i.e.* ohmic conduction with slope (m value) of curve ≈1 at lower fields (< 4.5×10^4 volts/cm) and a non-ohmic conduction with slope ≈ 2 at higher fields (> 4.5×10^4 volts/cm) are observed. The effect of temperature on *I-V* characteristics may be explained as follows : with the increase of temperature, the probability of thermal ionization of the trapping centres increases, thus causing a shift in the quasi Fermi level which gives rise to a lowering of the barrier across which the electrons have to be transported and the conduction becomes more or less ohmic. The ohmic behaviour can be understood on the basis of the reasonable assumption that at lower fields, the injection of carriers from the contacts is less and the initial current is governed by the intrinsic free carriers in the material. The current will be ohmic until the injected free carrier density becomes comparable with the thermally created carrier density. However, at sufficiently higher fields the current is

dominated by space-charge-limited conduction (SCLC) and the conduction is mainly due to injected space charge.

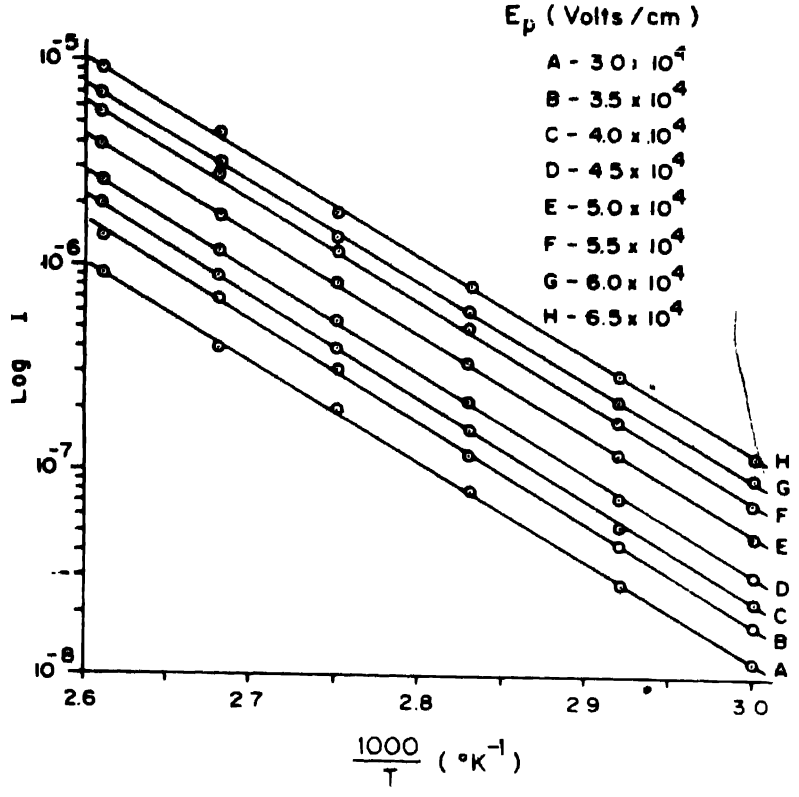


Figure 4. log I *versus* $10^3/T$ plots at different fields for ferrocen doped EC films.

Cellulose derivatives are prominent species among high polymers containing a lot of structural disorders and impurities within them. The value of slope coefficient ($m > 2$) of characteristics are typical for the continuous trap level distribution in the band gap of semi insulating EC. The defects and impurities can govern the conduction mechanism and also act as trapping centres and get populated by injected charge carriers from the electrodes. Charge carriers from these localized levels are thermally excited to their respective bands causing thermally activated ohmic conduction. Depending upon the population of these levels and their respective band the conduction may change from ohmic to Schottky-emission [4,6].

Thin polymer films are known to be a mixture of amorphous and crystalline regions. The conductivity behaviour of such films may be dominated by properties of amorphous regions. Presence of amorphous regions give rise to localized states. Since there are many localized states, the release or excitation of the carriers in these states dominates the conduction process. Consequently doping should not affect the conductivity too much unless the dopants are present in sufficient quantity to markedly affect the position of Fermi level. The molecules of dopants enter either in the amorphous regions of the polymer or at the

disordered regions like chain folds. If they are present in low concentration they will give rise to additional molecular sites for trapping of charge carriers. Such localized sites formed by

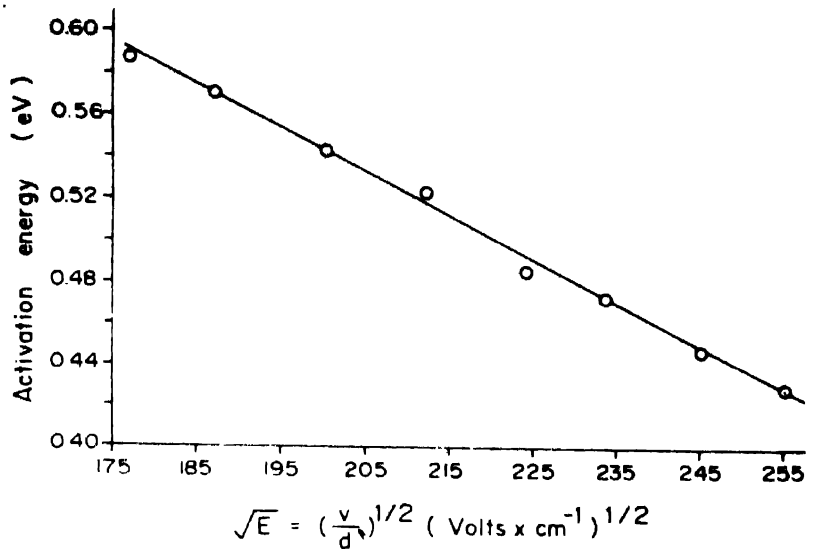


Figure 5. Activation energy *versus* square root of field for ferrocen doped EC films.

dopant molecules can be defined in molecular terms using the difference in ionization potentials as an indication of trap depth. As the dopant concentration is increased the dopant molecules start bridging the gap separating the two localized states and lowering the potential barrier between them, thereby facilitating the transfer of charge carrier in between two localized states [1].

Introduction of ferrocen in EC may give rise to extrinsic generation of carriers and traps. The order of current for pure EC [6] was 10^{-10} A, while that for doped samples (in the present case) it is 10^{-7} A. The fall of the current from initial value to a steady value is of a higher value for doped EC as compared to pure EC. These observations suggest that ferrocen introduces donor levels which get localized, giving rise to extrinsic charge carriers and charge traps. If the insulator contains a large number of donor levels, there are many free carriers available in the insulator conduction band and it presents a high conductivity as compared to contacts where depletion regions exist. Current increases as the concentration of ferrocen increased (Figure 1). Increase in ferrocen concentration in the polymer matrix increases the anisotropy which may be responsible for the creation of new trapping sites [10]. Due to active π-bond it allows nuclear substitutional reactions [11], which may result in the formation of charge transfer complexes. This agree with the earlier findings [12]. The possibility of some crystallites embeded with amorphous phase cannot be ruled out, hence, it is reasonable to suppose that molecules of ferrocen may occupy the interstitial sites between the polymer chains of amorphous phase and link them with some type of bonds due to charge transfer processes between ferrocen and ethoxy group of EC. It is also not improbable that these

ethoxy groups may be linked by ferrocen molecules to such extent that they may not further take part in reorientational processes [6]. The other possible role of ferrocen impregnation with EC may be, to develop excess charges in the polymer matrix. The current of whole system is enhanced due to either increase in carrier concentration or their mobility or both.

The high-field electronic conduction mechanisms commonly discussed for various polymer films are space-charge limited conduction (SCLC), Richardson-Schottky (RS), Poole-Frenkel (PF) emission and tunneling of carriers into or via traps. In order to establish the dominant mode of conduction in a particular material, one has to look into the detailed analysis of I-V data of the material in terms of the theoretical considerations available for different types of processes. The Schottky emission is analogous to thermionic emission as it involves charge emission from metal with difference that the barrier height is lowered by the reduction in the metal insulator work function due to applied electric field. The P-F mechanism is applied to the thermal excitation of electrons from traps into the conduction band of the insulator. The restoring force in R-S and P-F effects is due to Coulomb interaction between the escaping electron and positive charge, they differ in that the positive image charge is fixed for P-F barriers, but mobile with Schottky emission. An increase in electric field reduces the Coulombic potential of trapped charge carriers in its direction and increases the possibility of the thermal excitation of charge carriers into the conduction band of the insulator giving rise to non-ohmic characteristics.

The classical Richardson-Schottky emission is usually expressed in the form

$$J = AT^2 \exp\left\{-\frac{X_{RS}}{kT}\right\} \exp\left\{\beta_{RS} V^{1/2}\right\} \tag{1}$$

with

$$\beta_{RS} = \left(\frac{e}{kT}\right)\left(\frac{e}{4\pi\varepsilon\varepsilon_0 d}\right)^{1/2}, \tag{2}$$

where J is the current density, A is a constant, T is the temperature, e is the electronic charge, V is the voltage, X is the Schottky (electrode) barrier, k is the Boltzmann's constant, d is the film thickness, ε is the dielectric constant and ε_0 is the permittivity of free space. However, in the case of a low-mobility material, the diffusion-limited Richardson-Schottky effect must be considered

$$J = \left(\frac{\sigma V}{d}\right) \exp\left\{-\frac{X_{RS}}{kT}\right\} \exp\left\{\beta_{RS} V^{1/2}\right\}, \tag{3}$$

where σ is a constant.

A similar equation describes the bulk limited Poole-Frenkel effect

$$J = \left(\frac{\sigma V}{d}\right) \exp\left\{-\frac{X_{PF}}{kT}\right\} \exp\left\{\beta_{PF} V^{1/2}\right\}, \tag{4}$$

where X_{PF} is now the barrier associated with the promotion of an electron from a donor level to the conduction state, or, alternately, the promotion of an electron from a valence state to an acceptor level and $\beta_{PF} = 2\beta_{RS}$ in the simple model usually considered.

To determine the actual conduction mechanism the value of β, at different temperatures deduced from the plots of log I vs $\sqrt{E}$ (Figure 3) are compared with that of the theoretical values are listed in Table 1. The values of β_{exp} are nearer with those of β_{RS} rather than with those of β_{PF} suggesting thereby the RS mechanism to be the dominant mode of conduction, though the evidence may not be conclusive.

Table 1. Theoretical and experimental values of β, N_c/N_t, activation energy and trap depth at different temperatures for ferrocen doped ethyl cellulose films

Temperature (K)	β_{RS} ($..\times 10^{-2}$)	β_{PF} ($..\times 10^{-2}$)	β_{exp} ($\times 10^{-2}$)	N_c/N_t ($\times 10^{-2}$)	Activation energy (eV)	Trap depth ($.\times 10^{-2}$) eV	θ
333	4 998	9.976	6 193	6 945	0 589	15 98	
343	4 376	8 752	6 011	7 993	0 57	15 88	
353	4.086	8.172	5 981	8 112	0 542	16 13	4.94
363	3 891	7 782	5 473	8 459	0 524	15 37	$\times 10^{-6}$
373	3 712	7 424	5 101	8 781	0.484	14 98	
383	3 411	6 822	5 017	8 995	0 474	15 88	

It is difficult to draw a difinite conclusion from the coincidence of β-values alone. It may not be a satisfactory evidence for deciding the conduction mechanism. There are number of shortcomings in Schottky emission theory and suffers from large deviation in its constant which may not give rise to agreement between theoretical and experimental results. Similarly P-F approach maintains the R-S formalism considering the barriers due to traps. If one takes an asymmetric MIM structure with two electrodes of different work functions the current in the case of Schottky effect will be asymmetrical when polarities are reversed. But it remains practically unchanged in the case of the P-F effect, since it does not depend on potential barrier at the interfaces.The proper way of distinguishing between the P-F and Schottky mechanisms was suggested by Jonscher and Ansari [13]. Thus, the effect of nature of electrode materials of different work functions on the I-V characteristics has to be considered for deciding conduction mechanism.

Figure 3 exhibits the I-V characteristics of doped EC films at 353 K for electrode metals aluminium, copper, silver and gold having work function 3.38, 4.46, 4.31 and 4.46 respectively. The current through the sample (at a particular temperature) differs when the upper electrode aluminium is replaced by silver, copper or gold electrode. The magnitude of the current was found to be higher in dissimilar electrode (Al–Ag, Al–Cu or Al–Au) than similar electrode (Al–Al) combinations. This shows the effect of the materials of electrodes on

the current of the sample sandwiched between them. The values of current seem to be controlled by the effective work function for metal–insulator–metal interfaces. The difference between the work function of metal (1) and metal (2) will control the magnitude of current but for similar electrode (Al–Al) system, the characteristics of the polymer may prevail as the net contribution of current injected from electrode would then be zero [14]. Different lines were obtained for Al–Al, Al–Cu, Al–Ag and Al–Au combinations. When current is plotted against $10^3/T$, the result is a straight line. Such plot at various fields (ranging from 3.0–6.5 × 10^4 volts/cm) are shown in Figure 4. This observation is consistent with the proposed RS mechanism and suggests that in the low or moderate field region the conduction in doped EC films is governed by the RS effect in which the carriers are injected over the field-dependent polymer-electrode interfacial barrier.

In high field conduction region *i.e.* region II, the *I-V* characteristics have a slope of about 2, and it is suggested that the region is governed by space-charge limited (SCL) currents. This is because, when the *I-V* data are analyzed with the mathematical details available for SCL currents, a perfect correspondence between experimental and theory is observed

Injection of charge carriers into the bulk of the material is found to give rise to a current flow, which is limited by space charge effects. It can be shown that in a trap-free solid, the SCL currents I_0 is given by

$$I_0 = \frac{10^{-13} \mu \varepsilon A V^2}{d^3}, \tag{5}$$

where μ is the mobility of the carriers; ε is the relative dielectric constant of the material; A the area of the sample; d the thickness of the sample; and V is the applied voltage. If only shallow traps are present, only a fraction of the carriers injected from the contact will be free, the remainder will be immobile within the traps. The ratio of the free carriers n to trapped n_t is constant and independent of the applied voltage. In this range the current I_t is given by

$$I_t = \theta I_0 \tag{6}$$

$$\theta = \frac{n}{n_t} = \frac{N_c}{N_t} \cdot \exp\left(\frac{E_t}{k_t}\right), \tag{7}$$

where N_c is the effective density of states in the valence band, N_t represents the concentration of shallow trapping levels which are all assumed to have equal energy so that they are situated at E_t eV above the top of the valence band.

Space charge limited current sets in at that voltage V_t for which the intrinsic current equals the SCL current. Thus,

$$n_0 e \mu \left(\frac{V_t}{d}\right) = \frac{10^{-13} \mu \varepsilon \theta V_t^2}{d^3}$$

$$= 10^{13} n_0 e d^2 (\varepsilon\theta)^{-1}, \tag{8}$$

where n_0 is the concentration of free carriers before injection. Thus, the voltage at which the deviation from ohmic behaviour is observed is a measure of the density of the normal-volume-generated carriers.

The theoretical trap-free SCL currents I_0 at a given applied voltage can be calculated from eq. (1) using the following values for the parameters $d = 20\times10^{-6}$ m, $A = 1.33\times10^{-4}$ m^2, $\varepsilon = 3$, $\mu = 2\times10^{-14}$. According to eq. (6), the ratio of experimentally observed current I_t at a given applied voltage to the theoretical trap-free SCL current I_t at the same voltage then equals θ. Values of θ have been calculated for different voltages. The mean value of θ amounts to 4.94×10^{-6}. Such a low value of θ supports the large effect of shallow traps on the SCL currents in ferrocen doped EC films.

With in the quadratic region, the current-density is given by

$$I_t = 10^{-13}\left(\frac{\mu\varepsilon V^2}{d^3}\right)\frac{N_c}{N_t}\cdot\exp\left(\frac{E_t}{Kt}\right). \tag{9}$$

From eq. (9), it is evident that if one plots log I_t against $1/T$ the slope of the straight line thus obtained equals $(-E_t / k)$, while the intercept for the limit of $1/T \rightarrow 0$ equals to 10^{-13} $(\mu\varepsilon V^2/d^3)$ (N_c/N_t) from which (N_c/N_t) can be calculated.

The slope of log I versus $10^3/T$ at different fields (Figure 4) is seen to be approximately the same indicating that single type of trapping levels, all of equal energy, are operating. The trap depth E_t, at different fields are evaluated from the slope of these curves. The mean value of trap depth is found to be 15.4×10^{-2} eV Values of N_c/N_t at different fields are obtained by extrapolating each of the lines to $1/T = 0$.

The SCL currents may also determine the transient behaviour such as a large burst of current immediately after the application of voltage followed by a steady decline in current on standing. In the present case large currents obtained just after the application of voltage subsided to much smaller steady values after a certain length of time. The possible application of voltage causes a cloud of carriers, that is, a space charge, to be injected, from the contact into the sample. This free charge give rise to a large burst of current. If the space charge remained untrapped, the peak value of the transient current would continue as a steady current.

In the present case the slope of I-V curves are seen not to exceed the value 2. Usually a slope of 2 indicates shallow trapping, but this does not seem to exclude the possibility of deep traps in the present case. The attribution of the currents in high field region to SCL conduction is further supported by the following observations (i) EC being an amorphous material, would provide a large number of trapping centres and trapping of charge carriers in these trapping sites would result in the build-up of a space charge, (ii) the build-up of a space charge is also confirmed by our earlier thermally stimulated discharge current study [12,15].

4. Conclusion

It is concluded from the study that in ferrocen doped EC films (i) at lower values of fields, ohmic conduction prevails; (ii) while at high fields, space charge limited current is the associating factor for the conduction and (iii) for ferrocen doped EC films a two-fold mechanism explains the high field conduction. Besides carriers injected from electrodes, Richardson-Schottky emission is the dominant process responsible for the transport of charge carriers. The enhancement in current due to ferrocen doping has been attributed to the formation of charge transfer complexes.

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