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Electrical conduction in vacuum deposited polyvinyl fluoride (PVF) films

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I-V characteristics of vacuum deposited polyvinyl fluoride (PVF) films have been investigated as a function of temperature in the range of 303 K to 403 K and as a function of thickness in the range of 2500 Å to 10000 Å, respectively. The I-V curves of these films show two distinct regions of conduction, viz., ohmic region at low-fields with slope ∼1 and non-ohmic region at high-fields with slope ∼2. Space charge limited conduction (SCLC) has been suggested as the dominant mechanism of conduction at high-fields.

1. Introduction

Polymers in their solution grown films forms find wide applications as electrical and electronic materials [1–6]. However, the recent trends [7–10] in these materials have been in investigating their electrical and dielectric properties in vacuum deposited film forms. It is because the later films are free from undesirable solvents traces, impurities, additives etc. Further these films are more uniform and reproducible as they are grown in vacuum. Keeping this in view we have studied the mechanism of high-field conduction for the first time in vacuum deposited polyvinyl fluoride (PVF) films. Large space charge effects have been observed in these films. These important investigations would prove useful for applications of PVF in general and as interface layer material in specific areas such as electrophotography and optoelectronics. These interesting results are discussed in this paper.

2. Experimental

PVF was obtained from Polysciences Inc., USA and its thin films (about 2500 Å to 10000 Å) were vacuum deposited [8] on thoroughly cleaned glass slides in a chamber at a pressure of about 10^{-5} torr using the conventional vacuum evaporation technique. To achieve better adherence of these films to the substrate they were annealed in air at a temperature of about 383 K for 2 h. The thickness of the film was measured using the gravimetric method. A copper wire of 0.058 cm thickness was put on the top of these films. Silver electrodes were then vacuum deposited on top of these PVF films. These resulted in a sample having surface geometry with polymer film width between the electrodes being ∼0.058 cm. These samples were then used for dc conductivity measurements. The current-voltage (I-V) measurements were performed at different thicknesses in the range 2500 Å to 10000 Å and at different temperatures in the range from 303 K to 403 K, respectively. These measurements were carried out using a Keithley 610C electrometer and Aplab high voltage dc power supply.

3. Results and discussion

Fig. 1 shows the I-V characteristics on a log-log scale for the PVF films (thickness ∼5000 Å) at different temperatures. Curves 1 to 5 in Fig. 1 correspond to the temperatures 303, 325, 340, 375 and 403 K, respectively. It is seen from these I-V curves that there are distinctly two regions of conduction, viz., the low-field ohmic region with I-V slope ∼1 and the high-field non-ohmic region with I-V slope ∼2. It is further seen from these curves that the slope of high-field conduction region decreases slightly with the increase in the temperature. The activation energies of the charge carriers responsible for above conduction have been evaluated by usual Arrhenius type log I versus $1/T$ plots (using the data from Fig. 1) at various voltages ranging from 50 V to 1500 V. These plots are shown in Fig. 2. The activation energy (U) obtained from the slope of these curves have been found to be ∼0.58 eV.

Fig. 3 shows the I-V characteristics on a log-log scale for PVF films at a constant temperature of about 303 K but for different thicknesses. Curves 1 to 4 correspond to thicknesses of 2500, 5000, 7500 and 10000 Å, respectively. The curves in Fig. 3 also show the same two distinct regions of conduction as explained above, viz., low-field ohmic conduction with slope ∼1 and high-field non-ohmic conduction with slope ∼2. It is further seen from these curves that the transition voltage (V_{tran}) which separates the two regions of conduction depends on the thickness (d) of PVF films. In fact the V_{tran} shifts to higher voltage with the increase in d of the films.

To understand the mechanism of high-field conduction in vacuum deposited PVF films, the above I-V-T

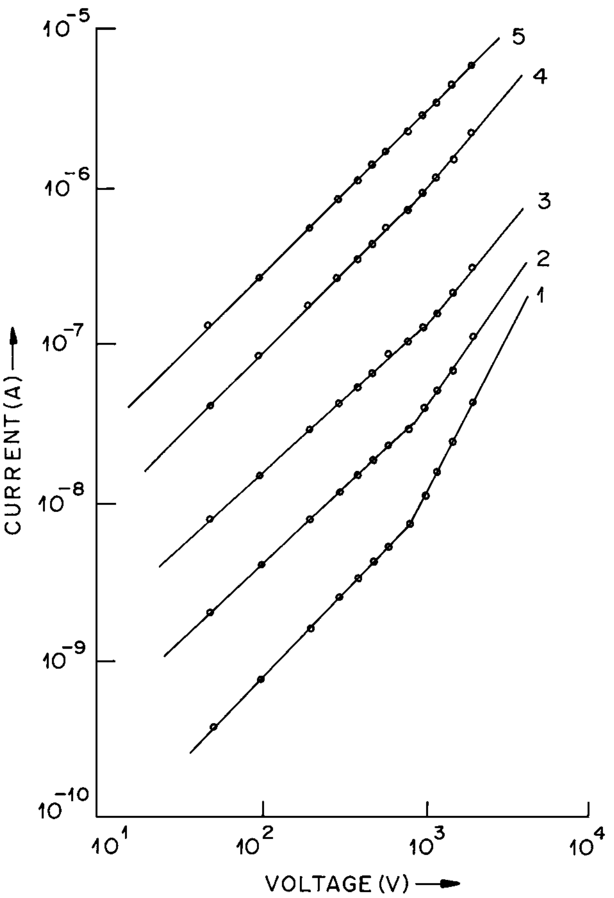

Figure 1 I-V characteristics on a log-log scale of vacuum deposited PVF films of thickness ~5000 Å for different temperatures. Curves 1 to 5 correspond to temperatures of 303, 325, 340, 375 and 403 K, respectively.

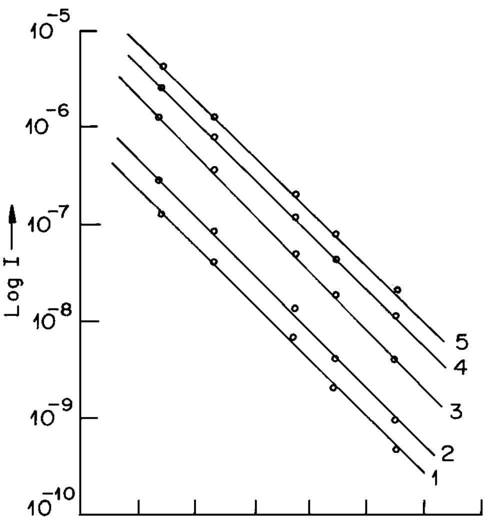

Figure 2 Log I versus $1/T$ plots of vacuum deposited PVF films of thickness ~5000 Å at different voltages. Curves 1 to 5 correspond to voltages 50, 100, 500, 1000 and 1500 V, respectively.

(Fig. 1) and I-V-d (Fig. 3) data has been analysed in terms of various mechanisms known [11, 12] to govern the high-field conduction region. It includes the Poole-Frenkel (PF) effect, Richardson-Schottky (RS) effect, space charge limited conduction (SCLC), etc. As regard PF and RS mechanism, the current density (I) is

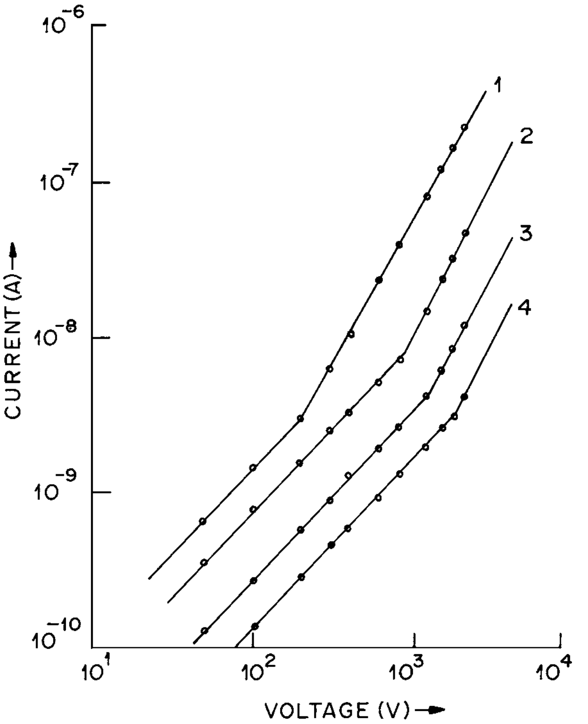

Figure 3 I-V characteristics on a log-log scale of vacuum deposited PVF films at 303 K for different thicknesses. Curves 1 to 4 correspond to 2500, 5000, 7500 and 10000 Å, respectively.

known [11, 12] to obey the following expression:

$$I = AT^{2}\exp(-\Phi/kT)\exp\left(\beta_{\mathrm{RS}}V^{1/2}\big/kTd^{1/2}\right) \qquad (1)$$

where A is the Richardson's constant, T the temperature, ϕ the work function, k the Boltzman constant, V the voltage, d the thickness of the film and β_{RS} a constant whose value can be calculated by:

$$\beta_{\mathrm{RS}} = (e^{3}/4\pi\epsilon\epsilon_{0})^{1/2} \qquad (2a)$$

and

$$\beta_{\mathrm{PF}} = 2\beta_{\mathrm{RS}} \qquad (2b)$$

where e is the electronic charge, ϵ the high frequency dielectric constant of the material and ϵ_0 the permittivity of free-space.

To see whether our above experimental data fits into the PF and RS Equation 1 a semilog plots of log I versus $V^{1/2}$ were made (using the data of Fig. 1) for all the above temperatures and these plots are shown in Fig. 4. The linearity obtained in these plots indicates that perhaps the high-field region in PVF films is governed either by the RS mechanism or by the PF mechanism. To verify it the values of β_{RS} or β_{PF} were obtained from these experimental plots. Also their values were obtained theoretically using the Equations 2a and b. The value of the dielectric constant (ϵ) used in these calculations is ~7 which is the high frequency dielectric constant of PVF at 1 MHz [13]. Large discrepancy were found in the experimental and theoretical values of β and hence the possibility of either RS or PF governing the high-field conduction in vacuum deposited PVF was ruled out.

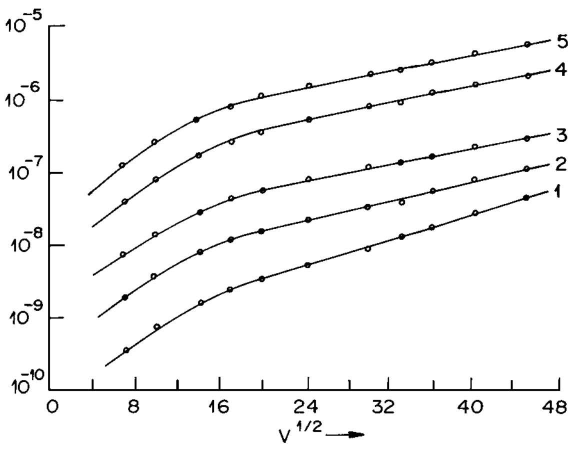

Figure 4 Log I versus $V^{1/2}$ plots using the data of Fig. 1.

Alternatively the I-V-T and I-V-d data was analysed in terms of the possibility of space charge limited conduction (SCLC). In fact, for the currents to be limited by SCLC, it is known [12, 14] that the current density (I) and transition voltage (V_{tran}) in this case obey the following equations:

$$I = (9/8)\mu_e \epsilon V^2/d^3 \tag{3}$$

and

$$V_{\text{tran}} = (8/9)en_t d^2/\epsilon \tag{4}$$

where μ_e is the effective drift mobility of charge carriers in the presence of shallow traps, ϵ the high frequency dielectric constant of the material, V the applied voltage, V_{tran} the transition voltage separating the two regions of conduction, d the thickness of the film and e the electronic charge and θ the ratio of the free carrier density (n_0) to the trapped carrier density (n_t) i.e., $\theta = n_0/n_t$.

It is seen from the Equation 3 and 4 that the currents to be governed by SCLC, (i) I in the high-field region should be proportional to V^2 and d^{-3} and (ii) V_{tran} should be proportional to d^2. To verify this a log-log plots of V_{tran} versus d and I versus d in the high-field region (∼17 kV/cm) have been made and these are shown in Figs 5 and 6, respectively. Fig. 5 gives the slope ∼2 and Fig. 6a slope ∼−3. Therefore, it is seen from these figures that I and V_{tran} obey the SCLC expected behaviour, i.e., $I \propto V^2$; $I \propto d^{-3}$ and $V_{\text{tran}} \propto d^2$. Hence in view of these observations SCLC mechanism has been suggested as the dominated mechanism of conduction in vacuum deposited PVF films at high fields. Further from the value of U as calculated earlier it is suggested that the charge carriers responsible for this conduction lie at an energy level of ∼0.58 eV at all fields. Such an observation suggests that perhaps the energy level of traps to which the charge carriers are injected from the electrodes does not vary with the applied field and the contact remains injecting all the time which is the prerequisite [12] for observing the space charge limited currents.

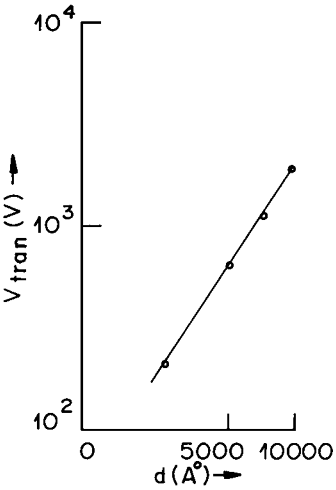

Figure 5 Log-log plots of V_{tran} versus d using the data of Fig. 3.

TABLE I Value of the trapped carrier density (n_t) and the drift mobility (μ_e) calculated for different thicknesses as per SCLC equations

S. No.	Thickness of films (d) (Å)	V_{tran} (Volts)	$n_t \times 10^{19}$ (cm^{-3})	$\mu_e \times 10^{-23}$ (cm^2/V-s)
1	2500	220	1.71	1.34
2	5000	700	1.36	2.03
3	7500	1200	1.03	1.79
4	10000	1800	0.88	1.54

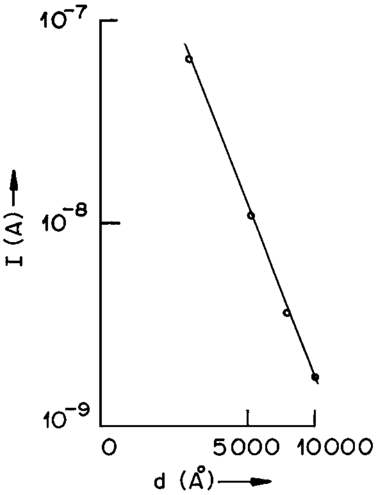

Figure 6 Log-log plots of I versus d using the data of Fig. 3.

Further, using the Equations 3 and 4, the values of n_t and μ_e have been calculated for different thicknesses and are listed in Table I. It is seen from Table I that the average values of n_t and μ_e have been found to be ∼1.25 ×, 10^{19} cm^{-3} and ∼1.68 × 10^{-23} cm^2/V-s, respectively. These values show a large trap carrier density and a very low effective drift mobility of charge carriers in PVF films. This indeed indicates a large effect of trapping mechanism during conduction. In fact the order of mobility in the absence of traps (μ) in polymers has been reported [15] to be ∼10^{-5} cm^2/V-s; therefore using the average value of μ_e, one finds the value of θ as low as ∼10^{-18} indicating thereby a huge trapping effect of charge carriers during conduction because in case of a normal shallow trapping the value of θ have been reported [12, 14] to be ∼10^{-7} in inorganic films. Thus, such a low value of θ further supports the dominance of suggested SCLC mechanism at high-fields in vacuum deposited PVF films.

4. Conclusions

(i) The I-V characteristics of vacuum deposited PVF films consist of two regions of conduction, viz., low-field ohmic region with slope ~ 1 and the high-field non-ohmic region with slope ~ 2 and separated by a transition voltage (V_{tran}).

(ii) The activation energy (U) of the charge carriers responsible for conduction has been found to be ~ 0.58 eV.

(iii) The high-field non-ohmic behaviour of vacuum deposited PVF films has been attributed to the space charge limited conduction (SCLC) mechanism.

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