

Study of localized levels in proflavine complexes with nucleic acid bases

D SARKAR and T N MISRA

Department of Spectroscopy, Indian Association for the Cultivation of Science, Calcutta 700032, India

MS received 23 January 1989; revised 5 June 1989

Abstract. The semiconduction activation energies of the nucleic acid bases adenine, guanine, thymine and uracil complexes with proflavine dye at various dye concentrations are measured in both the ohmic and the space-charge-limited (SCL) regions. The complexes are found to be nonextrinsic at high dye concentration but approach the extrinsic situation as the dye concentration decreases. From the SCL data analysis various transport parameters are evaluated.

Keywords. Localized levels; dye–nucleic acid base complexes; extrinsic and nonextrinsic semiconduction.

1. Introduction

The space-charge-limited currents (SCLC) method is a tempting alternative for the study of distribution of localized states in crystalline and amorphous semiconductors especially due to its simplicity and straightforwardness (Lampert and Mark 1970; Kao and Hwang 1981). In most organic and biological materials semiconduction is governed by the localized levels. We, therefore, thought it worthwhile to study the localized levels in nucleic acid base–proflavine dye complexes as these have significant biological importance in the context of dye–DNA interactions. Dye–DNA interactions are principally interactions between the bases and the dyes and the nature of the interaction depends on the dye concentration (Geacintov *et al* 1981; Buchanan *et al* 1978). In this paper we report the results of our investigation on semiconductive properties of nucleic acid bases adenine, guanine, thymine and uracil complexes with the proflavine dye.

2. Materials and methods

The nucleic acid bases used, adenine, guanine, thymine and uracil and proflavine dye were obtained from the Sigma Chemical Co., USA. The complexes of the bases and the dye were prepared by taking the respective base and the dye in required proportions, dissolving in water (ammonia water in case of guanine), evaporating carefully on a steam bath and finally drying under vacuum. Semiconductive measurements were carried out on the sample in a sandwich cell configuration between a stainless steel and a SnO₂-coated glass electrode separated by a 0.05 mm thick teflon

spacer. Voltages upto 50 V were applied from dry batteries, while for higher voltages a d.c. power supply (model 733 APLAB, India) was used. Currents were measured by an electrometer amplifier (Model EA 815, ECIL, India). Temperature measurements were made by a copper-constantan thermocouple and a panel meter (Model 100, HIL, India). After each voltage application sufficient time was allowed to ensure that true equilibrium was attained.

3. Results and discussion

In wide-band-gap solids, the mechanism of carrier injection from the electrodes is often responsible for electrical conduction. At lower voltages, however, injected carriers are smaller in number than thermally generated ones and one gets ohmic conduction. The current density (J) expression in the ohmic regime is

$$J = n_c e \mu_0 V / L, \quad (1)$$

where n_c is free carrier density, e is elemental charge, μ_0 is microscopic mobility, V the applied voltage and L the electrode spacing. Conduction at higher voltages involves the presence of space charge due to large injected carrier density. According to the SCLC theory, the most general expression for the steady state current density is (Stockmann 1981; Nespurek *et al* 1984)

$$\begin{aligned} J &= \mu_0 \epsilon \epsilon_0 \theta \left(\frac{m-1}{m} \right) \left(\frac{2m-1}{m} \right)^2 (1+B) \frac{V^2}{L^3} \\ &= e \mu_0 n_c \left[\frac{\epsilon \epsilon_0}{e(n_c + n_t)} \left(\frac{m-1}{m} \right) (1+B) \right]^{m-1} \left(\frac{2m-1}{m} \right)^m \frac{V^m}{L^{2m-1}}, \end{aligned} \quad (2)$$

where n_t is the density of trapped carriers, ϵ the dielectric constant, ϵ_0 the free space permittivity, $m = [d(\ln J)/d(\ln V)]$ is the slope of $J - V$ in the log-log plot and

$$\begin{aligned} B &= - [dm/d(\ln V)] / \{m(m-1)(2m-1)\}, \text{ for } m = 2, \text{ one attains} \\ J_{\text{SCL}} &= (9/8) \mu_0 \theta \epsilon \epsilon_0 V^2 / L^3, \end{aligned} \quad (3)$$

where $\theta = n_c / (n_c + n_t) = (N_c / N_t) \exp(-E_t/kT)$ is the fraction of total free carriers, N_t being the effective density of trapping sites at energy E_t below the conduction band edge. From (1) and (3) one gets the transition voltage from ohmic to SCL regime as

$$V_t = (8/9) e n_c L^2 / (\epsilon \epsilon_0 \theta). \quad (4)$$

Evidently V_t has a thermal activation energy equal to the difference in the activation energies in the ohmic and the SCL regimes contained in n_c and θ respectively. Thus V_t should be temperature-dependent unless the sample is extrinsic.

In terms of ohmic relaxation time $\tau = \epsilon / \sigma_0$, σ_0 being the dark conductivity,

$$V_t = (8/9) L^2 / \mu_0 \tau \epsilon_0 = (8/9) L^2 \sigma_0 / \mu_0 \epsilon \epsilon_0. \quad (5)$$

In figure 1 we show the $I - V$ plots for adenine-proflavine and guanine-proflavine complexes with a proflavine to guanine ratio of 0.5 (mol mol⁻¹) at four different

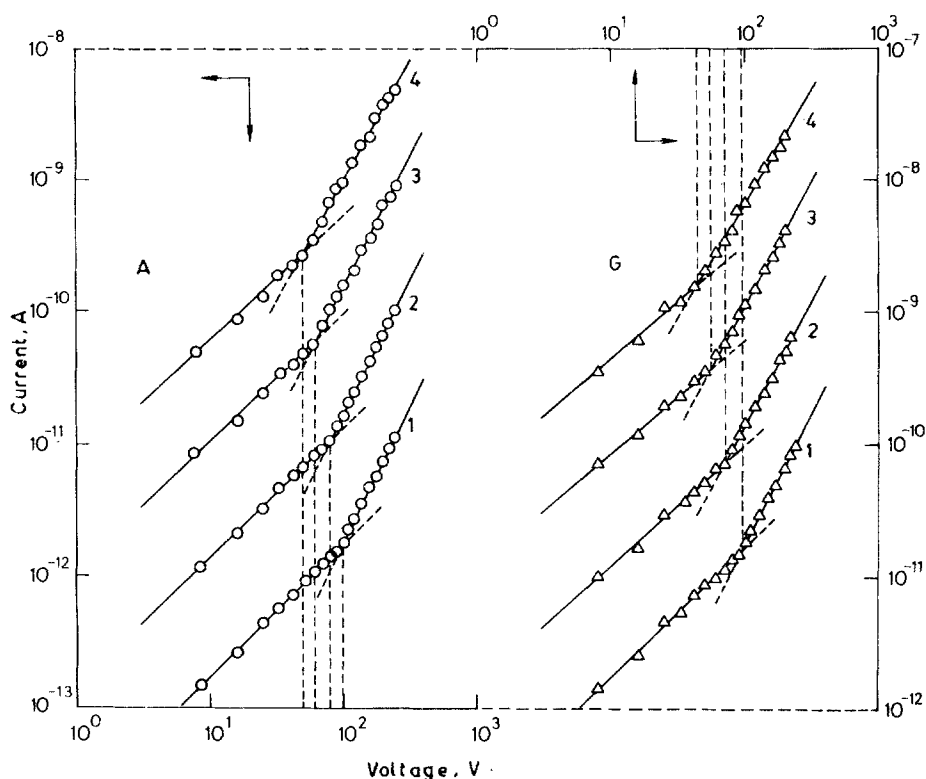


Figure 1. I - V plots for proflavine complexes with adenine (A) and guanine (G) with a dye/base ratio of 0.5 at (1) 303, (2) 323, (3) 343, and (4) 363 K.

temperatures 303, 323, 343 and 363 K. The I - V 's are ohmic at lower fields followed by a space-charge-limited square law behaviour at higher fields. The transition voltage V_t is found to change with temperature.

Roberts and Schmidlin (1969) have shown that measurement of thermal activation energies for both ohmic and SCL conduction over a broad temperature range enables the deduction of localized levels in semi-insulators. In wide-band-gap materials conduction is governed by some localized dominant levels situated in the band gap and at each temperature there is only one such level for a carrier. In narrow-band-gap materials dominant levels tend to be the transport bands. The concentration and location of these dominant levels completely determine the Fermi level. If the excess donor concentration is small in comparison to the concentration of electrons in the dominant electron level, the Fermi energy is located in between the two dominant levels in such a way as to make the concentration of electrons and holes equal in their respective dominant levels. This is what is called the nonextrinsic situation. Thus, the activation energy for electrical conduction must generally involve some combination of the energy required to raise carriers from their dominant levels to their corresponding transport bands and to create carriers in the dominant levels if they are not already supplied by some other means (impurities or injection). The activation energies for ohmic and SCL regions are contained in n_c and θ respectively,

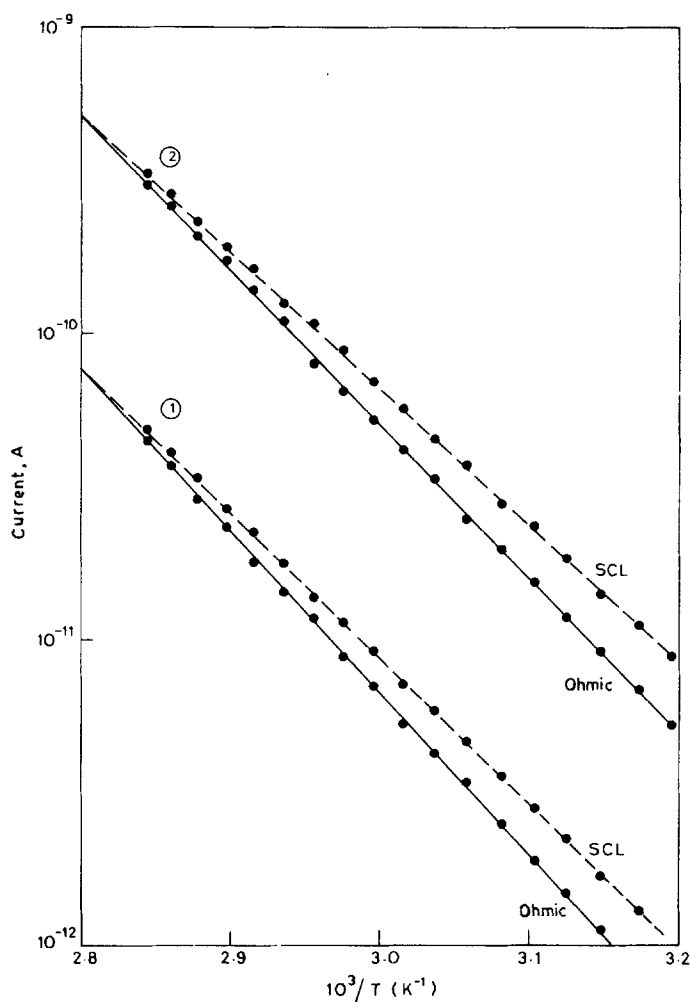


Figure 2. I vs $1/T$ plots for adenine (1) and guanine (2) with proflavine (0.5). SCL currents being normalized at $T^{-1} = 2.8 \times 10^{-3} \text{ K}^{-1}$.

which, for the nonextrinsic case, are given as

$$n_c = N_c(N_q/N_m)^{1/2} \exp \left[- \left\{ (E_c - E_m) + \frac{1}{2}(E_m - E_q) \right\} / kT \right], \quad (6)$$

and

$$\theta = (N_c/N_m) \exp \left[-(E_c - E_m)/kT \right], \quad (7)$$

where N_q , N_m are the effective number of dominant holes and electron states, respectively, and E_c , E_m and E_q are energies characterizing the conduction, dominant electron and dominant hole states, respectively.

In figure 2 we have shown I vs $1/T$ plots for adenine and guanine complexes with a dye/base ratio of 0.5 at the ohmic and the SCL regions. The two regimes have different activation energies suggesting the complexes to be nonextrinsic. Similar results are obtained for other base-dye complexes and also for the complexes of other

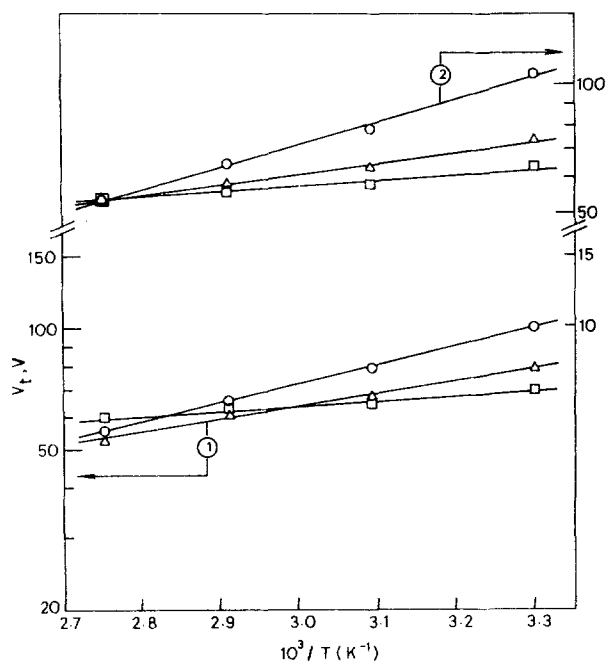


Figure 3. V_t vs $1/T$ plots for (1) adenine and (2) guanine complexes with proflavine dye at dye:base ratios of 0.50 (—○—), 0.10 (—△—) and 0.05 (—□—).

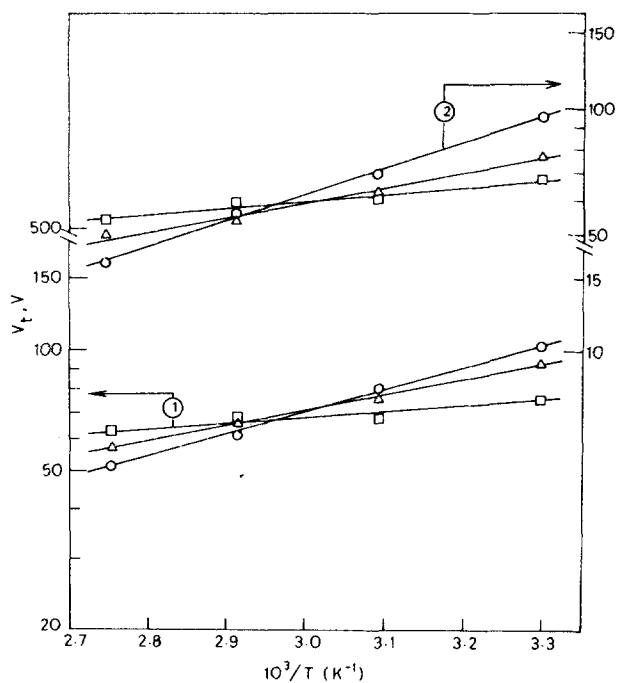


Figure 4. V_t vs $1/T$ plots for (1) uracil and (2) thymine complexes with proflavine dye at dye: base ratios of 0.50 (—○—), 0.10 (—△—) and 0.05 (—□—).

dye/base ratios (0.1 and 0.05). However the difference in the activation energies for ohmic and SCL conduction decreases with dye concentration and the difference is almost equal to the experimental error margin (± 0.015 eV) for the complexes with

Table 1. Various transport parameters in adenine (A), guanine (G), uracil (U) and thymine (T) complexes with proflavine (PF) dye of different dye concentrations.

Complexes	μ_e from (3) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ($\times 10^{-10}$)	μ_e from (4) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ($\times 10^{-10}$)	N_0/l ($\times 10^{12}$)	σ_0 (expt.) ($\Omega^{-1} \text{cm}^{-1}$) ($\times 10^{-16}$)	σ_0 from (5) ($\Omega^{-1} \text{cm}^{-1}$) ($\times 10^{-16}$)
<i>A:PF</i>					
1:0.5	2.79	2.69	9.71	2.69	2.93
1:0.1	1.98	1.90	8.76	2.00	2.03
1:0.05	1.56	1.70	7.14	1.61	1.41
<i>G:PF</i>					
1:0.5	25.0	27.2	9.14	29.8	28.6
1:0.1	25.7	24.8	7.33	21.8	22.2
1:0.05	14.2	13.3	6.38	10.5	10.8
<i>U:PF</i>					
1:0.5	3.79	3.68	9.52	4.20	4.25
1:0.1	4.04	4.23	7.52	3.82	3.72
1:0.05	2.20	2.10	6.66	1.68	1.72
<i>T:PF</i>					
1:0.5	3.05	2.67	10.0	3.20	3.42
1:0.1	2.06	1.93	6.95	1.61	1.66
1:0.05	1.47	1.33	6.00	0.93	1.00

Table 2. Experimental activation energies in ohmic and space-charge-limited region in adenine (A), guanine (G), uracil (U) and thymine (T) complexes with proflavine (PF) dye of different dye concentrations.

Complexes	E (eV)	E_{SCL} (eV)	$E - E_{\text{SCL}}$ (eV)	Activation energy of V_i (eV)	$E_c - E_m$ (eV)	$E_c - E_q$ (eV)
<i>A:PF</i>						
1:0.50	1.035	0.935	0.100	0.105	0.935	1.135
1:0.10	0.950	0.880	0.070	0.075	0.880	1.020
1:0.05	0.850	0.825	0.025	0.030	0.825	0.875
<i>G:PF</i>						
1:0.50	0.990	0.875	0.115	0.130	0.875	1.105
1:0.10	0.760	0.680	0.080	0.085	0.680	0.840
1:0.05	0.650	0.620	0.030	0.035	0.620	0.680
<i>U:PF</i>						
1:0.50	1.050	0.950	0.100	0.100	0.950	1.150
1:0.10	0.950	0.900	0.050	0.060	0.900	1.000
1:0.05	0.875	0.850	0.025	0.025	0.850	0.900
<i>T:PF</i>						
1:0.50	1.075	0.960	0.115	0.110	0.960	1.190
1:0.10	0.960	0.905	0.055	0.050	0.905	1.015
1:0.05	0.900	0.875	0.025	0.030	0.875	0.925

dye contents of 0.05 mol. This fact is also confirmed by the V_f vs $1/T$ plots shown in figures 3 and 4.

Equations (1)–(5) can be used to evaluate the transport parameters. These are summarised in table 1. In table 2 we summarise the experimental results showing the activation energies in the ohmic and the SCL regions and evaluate various dominant levels using (6) and (7).

Nucleic acid bases adenine, guanine, thymine and uracil in the pure state are *n*-type intrinsic semiconductors and the dominant electron level has enough charge carriers (supplied by impurities or by electrode injection) to participate in conduction. On addition of proflavine dye which is a *p*-type material, some of these charge carriers are immobilized by the recombination process. This lowers the Fermi level between the dominant electron and the hole levels and the material becomes nonextrinsic. The activation energy is now the energy required to create carriers in the dominant electron level by activation from the dominant electron level to the transport band. This also increases the cross-over voltage with increase in dye concentration.

References

- Buchanan J D, Power D M, Philips G O and Davis J V 1978 *Int. J. Radiat. Biol.* **33** 551
Geacintov M E, Waldmeyer J, Kuzmin V A and Kolubatev T 1981 *J. Phys. Chem.* **85** 3608
Kao K C and Hwang W 1981 *Electrical transport in solids* (Oxford: Pergamon)
Lampert M A and Mark P 1970 *Current injection in solids* (New York: Academic Press)
Nespurek S, Zmeskal O and Schauer F 1984 *Phys. Status Solidi* **A85** 619
Roberts G G and Schmidlin F W 1969 *Phys. Rev.* **180** 785
Stockmann F 1981 *Phys. Status Solidi* **A64** 475