

# Rectifying properties of poly(N-methylaniline)

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The electrical properties of various metal (Al/In/Sb/Sn)/poly(N-methylaniline)/gold Schottky diodes are described. The temperature-dependent dark current ( $J$ )–voltage ( $V$ ) characteristics indicate that the junctions formed with Al/In possess better rectifying properties with Schottky emission. In the case of junctions formed with Sb/Sn, Poole–Frenkel emission appears to be the dominant mechanism. The junction parameters of ideality factor, reverse saturation current, and barrier potential have been evaluated and compared with the reported values for Schottky barriers based on polyaniline and a few of its substituted derivatives. The capacitance ( $C$ )–voltage ( $V$ ) data obtained at different frequencies have been used to evaluate the carrier concentration, mobility, depletion width, contact potential, and work function of the polymer.

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## 1. Introduction

Semiconducting organic conjugated polymers can be used as active materials in the fabrication of junction devices [1–3]. In particular, electrical properties of heterojunctions and Schottky barriers devised with thin films of polyacetylene, polythiophene, polyparaphenylene, polypyrrole, and polyaniline have been reported [4–10]. Of these polymers, polyaniline has attracted considerable attention because of its good environmental stability [11]. The effect of doping on rectification and photovoltaic characteristics was reported by Chen and Fang [12]. The method of film preparation was shown to have a definite effect on the device parameters [13, 14]. Recently, the Al/polyaniline junction has been shown to act as a sensor for the detection of methane gas [15].

Poly(N-methylaniline), a substituted polyaniline is known to possess better stability to oxidation than polyaniline [16, 17]. We have recently characterized poly(N-methylaniline) and its sulfonated analog as cathode-active materials in rechargeable batteries [18]. To our knowledge, no other application of this polymer has been reported yet. In this paper, we report the junction characteristics between p-type (anion-doped) poly(N-methylaniline) and some metals. The results are compared with the reported literature data on polyaniline.

## 2. Experimental

N-methylaniline was purified by vacuum distillation. Poly(N-methylaniline) films with thickness of about 10  $\mu\text{m}$  were prepared by the cyclic voltammetry technique. The film thickness was evaluated from the coulombic charge passed for its preparation [19, 20]. The electrolyte solution consisted of 1 M monomer and 1 M HCl in water. The polymer film was deposited on a gold-

coated glass electrode by cycling for 100 times between 0 and 0.55 V versus SCE in a single compartment cell with platinum as the counter electrode (EG and G PAR, Model 263A Potentiostat/Galvanostat). After polymerization was completed, the films were rinsed in 1 M HCl and carefully dried and stored under vacuum. Depositions of Al, In, Sb, and Sn (0.2  $\text{cm}^2$ ) were done by a vacuum evaporation technique under  $\sim 1.3 \times 10^{-4}$  Pa using suitable masking. Conductive silver paint was used to take contact leads from the polymer and metal. Capacitance–voltage ( $C$ – $V$ ) measurements were made using an impedance analyzer (EG and G PAR, Model 6310). The energy band gap was calculated from the absorbance data recorded by using a UV-visible spectrophotometer (Jasco Model 7800). A liquid nitrogen cryostat equipped with a Pt-100 sensor and a PID temperature controller (Model DP-422, Scientific Solutions, Mumbai, India) was used to make low-temperature current–voltage measurements. The measurements above room temperature were taken by keeping the sample near a temperature sensor in a hot chamber that was electrically connected to a digital indicating temperature controller (thin-film heating unit maximum temperature 250 °C, Indian (Furnaces) Instruments, Chennai).

## 3. Results and discussion

The conductivity of the as-grown poly(N-methylaniline) at room temperature is about  $10^{-3}$   $\text{S cm}^{-1}$ . Fig. 1 shows a schematic representation of the Au/p-type poly(N-methylaniline)/metal (Al, In, Sb, and Sn) diode constructed in the sandwich configuration. Fig. 2 shows the absorbance spectrum of poly(N-methylaniline) coated on an optically transparent ITO substrate. The substrate absorption, if any, was corrected by introducing an

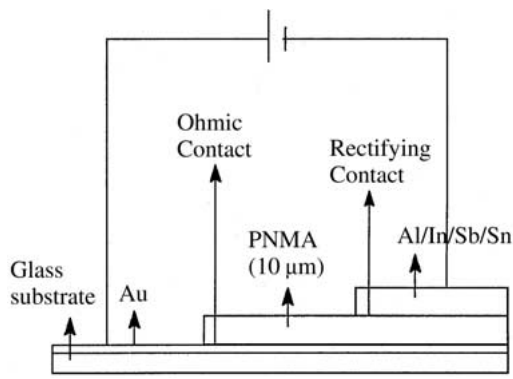


Figure 1 Schematic representation of sandwich configuration of Au/p-type poly(N-methylaniline)/metal (Al or In or Sb or Sn) diode.

uncoated substrate of the same size as the reference. The energy gap of the polymer is estimated using the relation [22],

$$\alpha = (2.303A)/d = m(h\nu - E_g)^{1/2} \quad (1)$$

where  $\alpha$  is the absorption coefficient,  $A$  is the absorbance, and  $d$  is the thickness of the polymer coating. The  $m$ ,  $h\nu$ , and  $E_g$  are an empirical constant, photon energy, and energy band gap. A plot of  $\alpha^2$  versus  $h\nu$  (inset in Fig. 2) gives a straight line, whose intercept on the energy axis is the energy band gap. The  $E_g$  value of poly(N-methylaniline) is estimated to be 3.2 eV. The parent polymer polyaniline has been reported to have  $E_g$  values ranging between 2.1 and 3.4 eV [8, 13].

Typical  $J$ - $V$  curves of the Schottky devices at room temperature in the dark are shown in Fig. 3. The forward bias corresponds to a negative voltage at the metal with respect to the polymer. The  $J$ - $V$  curves are asymmetric and non-linear. The forward current increases exponentially in the lower-voltage region and increases linearly in the higher-voltage region. These devices clearly exhibit rectifying behavior in the dark. At a forward

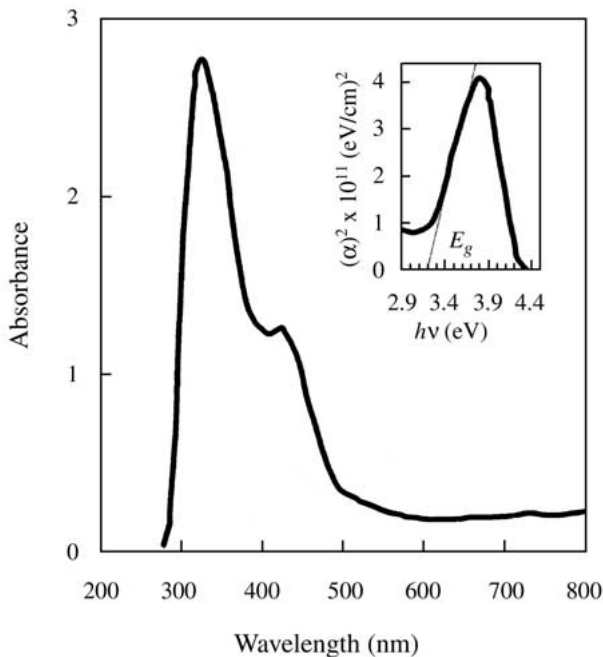


Figure 2 Optical absorption spectrum of doped poly(N-methylaniline) film coated on an indium-tin-oxide substrate. Inset: Curve used for the evaluation of band gap energy ( $E_g$ ) of poly(N-methylaniline).

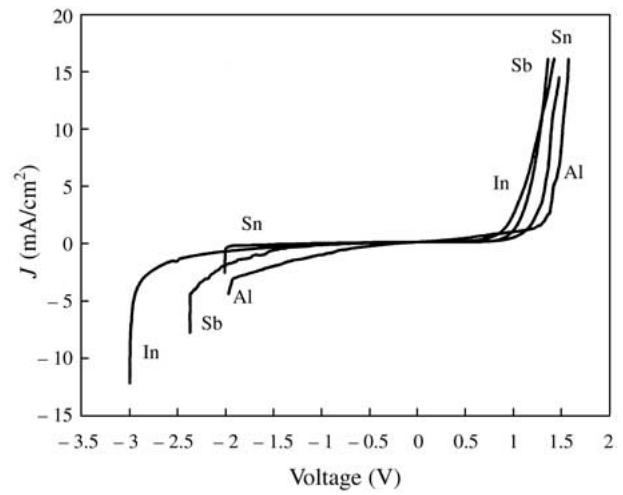


Figure 3 Dark current density versus applied voltage ( $J$ - $V$ ) for Au/poly(N-methylaniline)/metal.

bias voltage greater than 1.3 V, the current becomes linear, indicating that the device resistance is dominated by the bulk resistance of poly(N-methylaniline) in this voltage region.

The observed  $J$ - $V$  characteristics of the metal-polymer diodes can be discussed in the light of Schottky emission along with other phenomena such as Poole-Frenkel emission and space-charge limited current. The Schottky effect involves the emission of the electrons by thermal activation from the metal electrode into the conduction band of the polymer over a potential barrier between the metal/polymer interface [23]. The  $J$ - $V$  curve of Schottky barriers can be described by the standard thermionic emission theory for conduction across the junction [24]. Accordingly, the current-voltage relationship for the barrier is given by the Shockley equation as

$$J = J_0[\exp(eV/nkT) - 1] \quad (2)$$

where  $J$  is the current density per unit area,  $J_0$  the reverse saturation current density,  $e$  is the electronic charge,  $V$  the applied voltage,  $T$  the absolute temperature,  $k$  the Boltzmann constant, and  $n$  the ideality factor of the diode (for an ideal diode  $n = 1$ ). According to Equation 2, as  $eV/kT \gg 1$ ,  $\ln J$  versus  $V$  should be linear with an intercept corresponding to  $J_0$ . The ideality factor can be obtained from the slope of the logarithmic plot of  $J$  versus  $V$  (Fig. 4). From  $J_0$ , the barrier height  $\phi_b$ , can be deduced using the Richardson equation [23]

$$J_0 = A^*T^2 \exp[-e\phi_b/kT] \quad (3)$$

where  $A^*$  is the effective Richardson constant usually taken as  $120 \text{ A cm}^{-2} \text{ K}^{-2}$  [25]. The junction parameters including the ideality factor, barrier height, and reverse saturation current density for the metal/poly(N-methylaniline) diodes are tabulated along with the values reported by various authors for the polyaniline-based Schottky devices (Table I).

The Schottky effect is associated with the barrier at the surface of a metal and semiconductor, whereas the Poole-Frenkel effect is associated with the barriers in the bulk of a material. Donor and acceptor sites, and traps, as well as electrons in the valence band experience the Poole-Frenkel effect. The electrons are thermally

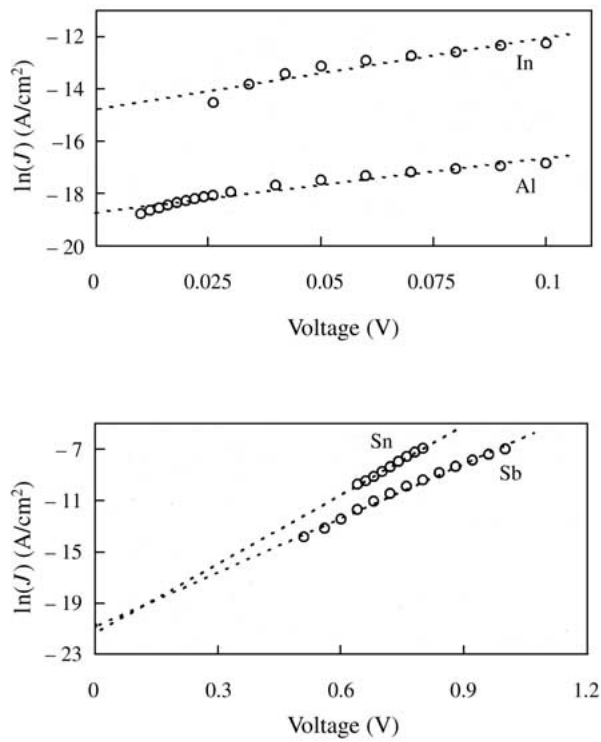


Figure 4  $\ln J$ - $V$  characteristics of the junctions for Au/poly(N-methylaniline)/metal.

emitted from the randomly-sited traps to the conduction band of the insulator by means of the lowering of the coulombic potential barrier by an external electric field [26]. The trap must be neutral when filled and positive when empty to establish the necessary coulomb potential [27, 28]. The current density for Poole-Frenkel emission can be expressed by the following equation:

$$J/V = (J/V)_0 \exp[\beta(V/d)^{1/2}/nkT] \quad (4)$$

where  $d$  is the thickness of the polymer coating and  $\beta = (e^3/\pi\epsilon\epsilon_0)^{1/2}$  in which  $\epsilon$  is the dielectric constant of the polymer and  $\epsilon_0$  is the free-space permittivity.

The space charge limited current (SCLC) is caused by the traps at the interfacial region between metal and polymer [29, 30]. The current is limited by the space charge when the density of free electrons injected into the polymer is larger than the number of acceptor levels resulting in bending of the bands in the opposite direction. The local field created by the space charge will drive the electrons back into the contact electrode. The entire current will be due to the diffusion of the carrier electrons. In other words, the current is limited by the large gradient of density of free carrier electrons. The expression for the current density in SCLC conduction mechanism [29] is given by

TABLE I Comparison of reported performance of metal/polyaniline junctions with the present work of metal/poly(N-methylaniline) junctions

No.	Polymer-film synthesis conditions	Device configuration	Ideality factor $n$	Barrier height $\phi_b$ (eV)	Reverse saturation current $J_0$ ( $\text{A cm}^{-2}$ )	Contact potential $V_c$ (V)	Carrier concentration $N_s$ ( $\text{cm}^{-3}$ )	Depletion width $D$ nm	Mobility $\mu$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	Ref.
1	Chemical oxidative polymerization of aniline in 1 M HCl with $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ oxidant in aqueous medium. Polyaniline was dissolved in N-methyl pyrrolidone (NMP) and film was cast onto ITO	Al/undoped polyaniline/ITO	1.95	1.03	$4 \times 10^{-11}$	0.90	$1.80 \times 10^{17}$	35.7	$1.74 \times 10^{-8}$	12
		Al/polyacrylic acid doped polyaniline/ITO	1.70	0.87	$5 \times 10^{-9}$	0.82	$1.40 \times 10^{18}$	16.0	$2.70 \times 10^{-5}$	
		Al/toluene-4-sulfonic acid doped polyaniline/ITO	1.30	0.78	$8 \times 10^{-7}$	0.72	$2.80 \times 10^{18}$	11.8	$4.68 \times 10^{-4}$	
2	Chemical oxidative polymerization of aniline in acidic medium, dissolved in NMP and film was prepared by coating onto $\text{SnO}_2$	Al/polyaniline/ $\text{SnO}_2$	1.98	0.48	—	—	—	—	—	33
3	Chemical oxidative polymerization in aqueous HCl with $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ oxidant	In/polyaniline	5.50	0.51	—	—	$1.00 \times 10^{17}$	—	—	34
		In/poly o-anisidine	9.65	0.49	—	—	$1.20 \times 10^{15}$	—	—	
		In/poly(aniline-co-o-anisidine)	4.41	0.49	—	—	$2.00 \times 10^{16}$	—	—	
4	Chemical oxidative polymerization of aniline in HCl with $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ oxidant in aqueous medium polyaniline film prepared by vacuum deposition onto ITO	ITO/polyaniline/In	1.60	0.56	—	—	—	—	—	13
		ITO/polyaniline/Sn	2.12	0.59	—	—	—	—	—	
		ITO/polyaniline/Pb	2.36	0.56	—	—	—	—	—	
		ITO/polyaniline/Al	1.20	0.55	—	—	—	—	—	
5	Chemical polymerization of o-toluidine in acidic medium with $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ oxidant	Platinum/poly(o-toluidine)/Al	1.56	—	$1.5 \times 10^{-5}$	7.60	$3.31 \times 10^{15}$	—	—	35
		Platinum/poly(o-toluidine)/Cu	3.32	—	$4.5 \times 10^{-5}$	3.60	$2.29 \times 10^{15}$	—	—	
6	Electrochemical synthesis 0.1 M aniline, 1 M aqueous HCl, at 25 °C by cyclic voltammetry (0.4–1.2 V) versus NHE, 100 $\text{mV s}^{-1}$	ITO/polyaniline/Al	4.20	0.76	—	0.65	$3.10 \times 10^{17}$	—	—	15
		—	3.70	0.80	—	—	—	—	—	
		—	3.20	0.83	—	—	—	—	—	
7	Electrochemical synthesis 1 M N-methylaniline, 1 M aqueous HCl by cyclic voltammetry method (0–0.55 V) versus SCE, 20 $\text{mV s}^{-1}$	Au/poly(N-methylaniline)/Al	1.83	0.89	$7.43 \times 10^{-9}$	0.84	$1.03 \times 10^{19}$	5.5	$6.02 \times 10^{-6}$	Present work
		Au/poly(N-methylaniline)/In	1.39	0.79	$3.85 \times 10^{-7}$	0.86	$5.19 \times 10^{18}$	7.9	$1.20 \times 10^{-5}$	
		Au/poly(N-methylaniline)/Sb	2.70	0.95	$9.10 \times 10^{-10}$	0.76	$5.19 \times 10^{18}$	7.4	$1.20 \times 10^{-5}$	
		Au/poly(N-methylaniline)/Sn	2.13	0.96	$4.91 \times 10^{-10}$	0.72	$1.73 \times 10^{14}$	—	$3.61 \times 10^{-1}$	

$$J = [(8\epsilon\epsilon_0\mu V^2)/(9d^3)] \sim V^2 \quad (5)$$

where  $\mu$  is the mobility of the carrier.

The variation of capacitance as a function of the reverse-bias voltage at different frequencies can provide information on carrier concentration, contact potential, and mobility of the carriers [31]. The capacitance of the metal/polymer junction can be expressed by the following equation:

$$C^{-2} = [2(V_c - V)]/(A^2\epsilon\epsilon_0N_s) \quad (6)$$

Here  $A$  is the area of the metal contact,  $N_s$  is the carrier concentration, and  $V$  is the applied voltage. The dielectric constant of the polymer,  $\epsilon$ , is assumed to be 3.4 [15, 32]. A plot of  $1/C^2$  against voltage should be linear for uniformly doped substrates. The intercept of the line with the voltage abscissa determines the built-in potential or contact potential  $V_c$  and the slope gives the carrier concentration  $N_s$ , which in turn can be related to carrier mobility ( $\mu$ ) and depletion width ( $D$ ) by the following equations:

$$\sigma = N_s e \mu \quad (7)$$

where  $\sigma$  is the electrical conductivity of the p-doped polymer,

$$D = [2\epsilon\epsilon_0(V_c + V)/(eN_s)]^{1/2} \quad (8)$$

The variation of capacitance for poly(N-methylaniline)-based diodes as a function of the reverse-bias voltage has been measured at different frequencies. Fig. 5 shows the representative linear plots of  $1/C^2$  versus reverse-bias voltage. The contact potentials, the calculated mobility and carrier concentration at 10 kHz are given in Table I.

The literature reports on the junction properties of metal–polyaniline barriers reveal that in most of the studies, the polymer has been synthesized as powder by the chemical oxidation of the monomer. The powder samples were either dissolved in N-methylpyrrolidinone to be cast as thin films [12, 33] or vacuum deposited on suitable substrates [13]. Except in one report [13], only one metal (either Al or In) has been used for junction formation. The results indicate that poly(o-anisidine) [34] and poly(o-toluidine) [35]-based junction devices gave higher ideality factor and saturation current and lower carrier concentration values compared to polyaniline. In the present study, poly(N-methylaniline) film has been directly deposited on Au substrate by electro-deposition and the junction properties with four different contact metals have been evaluated. The ideality factor is relatively small and the carrier concentration is higher by two orders of magnitude compared to polyaniline [12]. Among the four metals studied, Al/poly(N-methylaniline) and In/poly(N-methylaniline) junctions give better values for the ideality factor than Sb- and Sn-based devices. The carrier concentration is very much less for the Sn-based junction device and as a result the mobility and depletion width become large. The large depletion width does not favor the tunneling process. A carrier concentration of  $10^{18}$ – $10^{19}$   $\text{cm}^{-3}$  is necessary for the band-to-band tunneling [31]. Therefore, one cannot rule out the participation of other conduction mechanisms such as space-charge limited current (SCLC) and Poole–

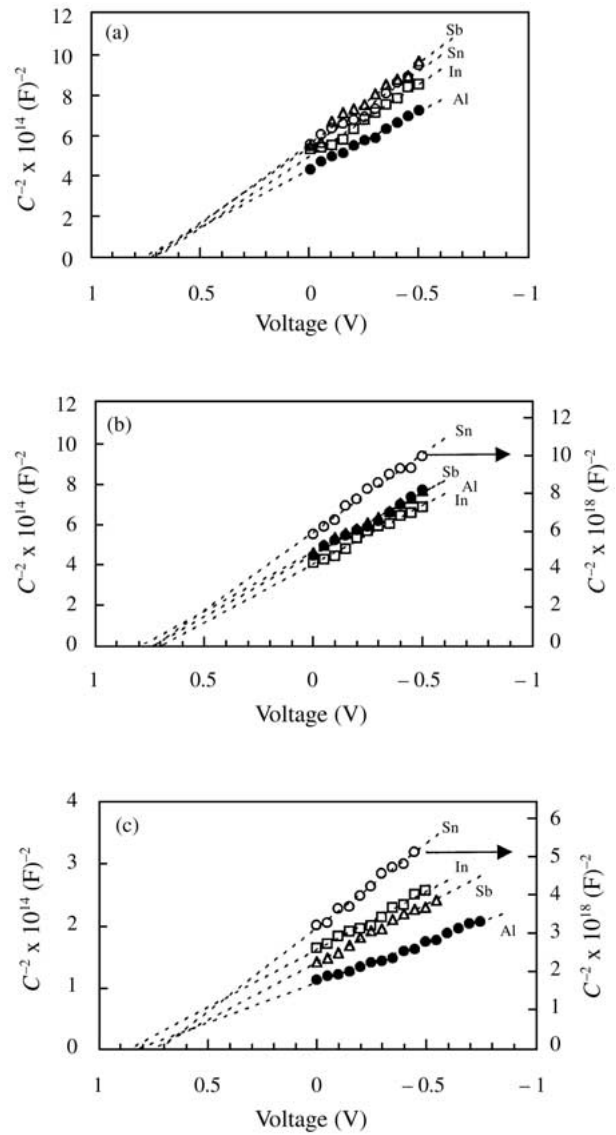


Figure 5 A plot of  $C^{-2}$  versus applied voltage for Au/poly(N-methylaniline)/metal at different frequencies (a) 100 Hz, (b) 1 kHz, and (c) 10 kHz.

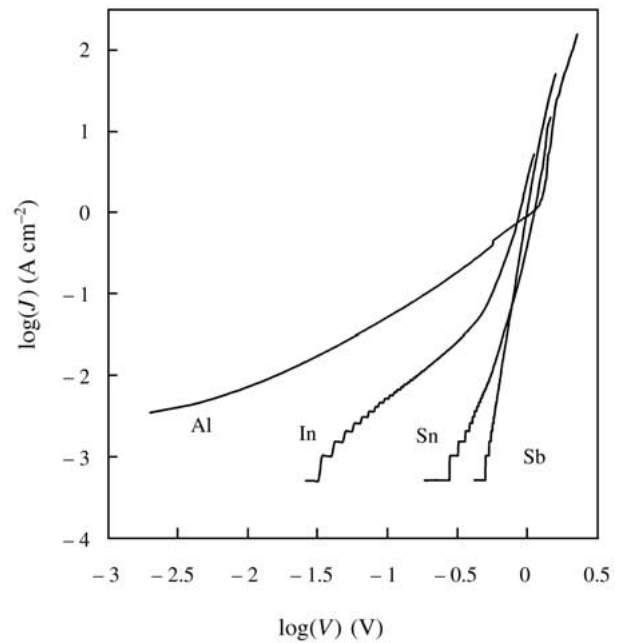


Figure 6 Relationship between  $\log(J)$  and  $\log(V)$  for Au/poly(N-methylaniline)/metal.

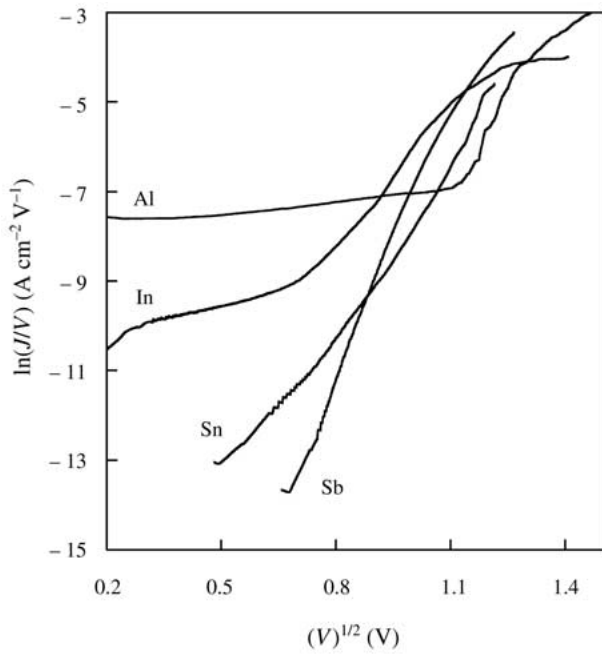


Figure 7 Relationship between  $\ln(J/V)$  and  $V^{1/2}$  for Au/poly(N-methylaniline)/metal.

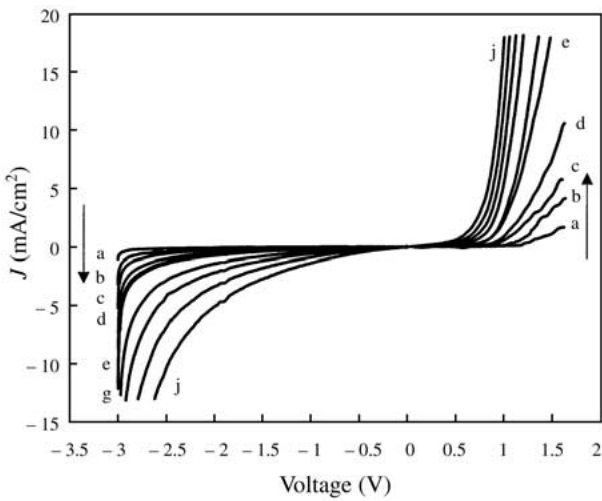


Figure 8 Dark current density versus applied voltage ( $J-V$ ) for Au/poly(N-methylaniline)/In diode at different temperatures: (a)  $-40^\circ\text{C}$ , (b)  $-20^\circ\text{C}$ , (c)  $-10^\circ\text{C}$ , (d)  $0^\circ\text{C}$ , (e)  $32^\circ\text{C}$ , (f)  $35^\circ\text{C}$ , (g)  $40^\circ\text{C}$ , (h)  $50^\circ\text{C}$ , (i)  $60^\circ\text{C}$ , and (j)  $70^\circ\text{C}$ .

Frenkel emission along with Schottky emission. When SCLC is dominant, one expects linearity on a plot of  $\log(J)$  versus  $\log(V)$  with a slope of 2 (Equation 5). A plot of  $\ln(J/V)$  versus  $V^{1/2}$  should give a straight line in the case of Poole–Frenkel emission (Equation 4). In the present case, the analysis of the  $J-V$  data for SCLC and Poole–Frenkel emission has been carried out (Figs. 6 and 7). Both the above plots do not give a straight line for the Al- and In-based junctions, thus ruling out the possibilities of SCLC and Poole–Frenkel emission mechanisms. Therefore it is inferred that Schottky emission is the major mechanism in these two devices. However, for Sn- and Sb-based junctions both plots show linearity. But the slope of  $\log(J)$  versus  $\log(V)$  plots are very much higher (9.6 for Sn and 5.5 for Sb) than the expected slope of 2 for SCLC mechanism. The straight

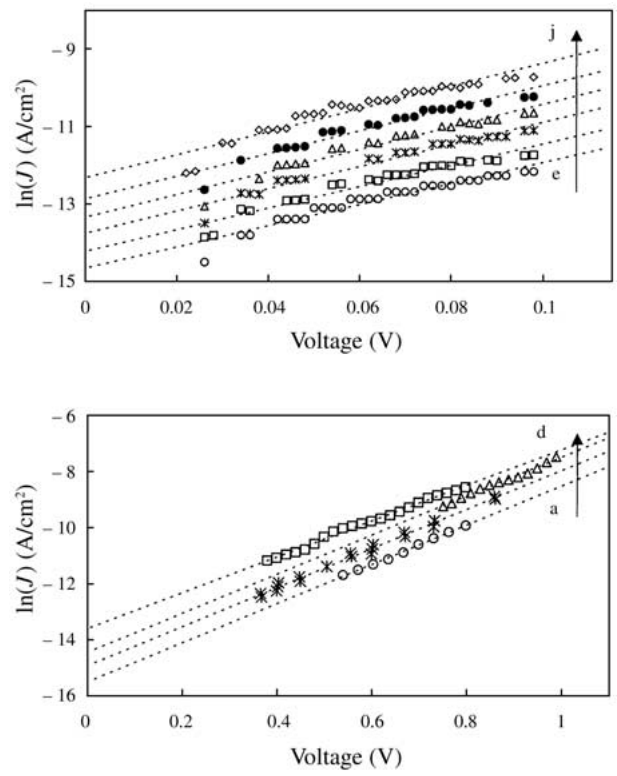


Figure 9  $\ln J-V$  characteristics of the junctions for Au/poly(N-methylaniline)/In diode at different temperatures: (a)  $-40^\circ\text{C}$ , (b)  $-20^\circ\text{C}$ , (c)  $-10^\circ\text{C}$ , (d)  $0^\circ\text{C}$ , (e)  $32^\circ\text{C}$ , (f)  $35^\circ\text{C}$ , (g)  $40^\circ\text{C}$ , (h)  $50^\circ\text{C}$ , (i)  $60^\circ\text{C}$ , and (j)  $70^\circ\text{C}$ .

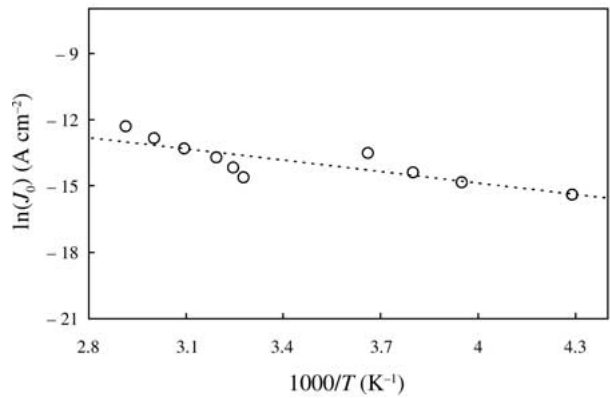


Figure 10 A plot of  $\ln(J_0)$  vs.  $1/T$  for Au/poly(N-methylaniline)/In diode.

lines in the  $\ln(J)$  versus  $V^{1/2}$  plots for the Sb- and Sn-based devices clearly indicate a Poole–Frenkel emission.

In order to further confirm that Schottky emission plays a dominant role in Au/poly(N-methylaniline)/In or Al, the  $J-V$  characteristics at different temperatures have been recorded (Fig. 8). The resulting data obey Equation 2. The forward current increases with increase in temperature at any applied voltage. The slopes of the  $\ln(J) - V$  plots (Fig. 9) are nearly constant with variation of temperature. A plot of  $\ln(J_0)$  versus  $1/T$  (Fig. 10) is a straight line. These results suggest that thermionic emission is the dominant mechanism of charge transport in poly(N-methylaniline) diode devices constructed with In/Al.

The work function of poly(N-methylaniline) can be obtained using [31]:

$$\phi_{sp} = qV_c + \phi_m \quad (9)$$

where  $\phi_{sp}$  and  $\phi_m$  are the work functions of the semiconducting poly(N-methylaniline) and metal, respectively. The contact potentials estimated from the C–V plots are given in Table I. Substituting the values of the work functions of the metals ( $\phi_{In} = 4.12$  eV,  $\phi_{Al} = 4.25$  eV,  $\phi_{Sb} = 4.05$  eV,  $\phi_{Sn} = 4.11$  eV) [29, 31] and the contact potentials, the work function of poly(N-methylaniline) is deduced to be  $4.9 \pm 0.1$  eV.

#### 4. Conclusions

Schottky diodes fabricated with the semiconducting poly(N-methylaniline) have shown unsymmetric, non-ohmic rectifying characteristics. The analysis of the  $J$ – $V$  data indicates that the junctions formed with Al/In possess better properties with Schottky emission as the major mechanism. However, in the case of junctions formed with Sb/Sn, the Poole–Frenkel effect appears to be dominant. The work function of the polymer is deduced to be about 4.9 eV.

#### Acknowledgment

P. Syed Abthagir gratefully acknowledges the Council of Scientific and Industrial Research, New Delhi for the award of a Senior Research Fellowship.

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Received 23 October 2002  
and accepted 15 May 2003