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Electronic properties of polyindole and polycarbazole Schottky diodes

P. Syed Abthagir, R. Saraswathi *

Department of Materials Science, Madurai Kamaraj University, Madurai-625 021, Tamil Nadu, India

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Abstract

Indole, indole-5-carboxylic acid, carbazole and *N*-vinylcarbazole have been polymerized electrochemically on indium tin-oxide substrates. The four polymers have been used for the construction of Schottky barriers with Al, In, Sb and Sn metals. The dark current–voltage and capacitance–voltage characteristics of the diodes have been studied to derive information on junction parameters. All the junctions showed rectification, but the estimated values of saturation current and ideality factor are high.

Keywords: Polyindole; Polyindole-5-carboxylic acid; Polycarbazole; Poly(*N*-vinyl carbazole); Band gap energy; Schottky diode; Junction properties

1. Introduction

Organic electronics has the potential to create a new range of devices and applications. For more than a decade now, organic thin film transistors based on conjugated polymers have been envisioned as a viable alternative to more traditional, main stream transistor based on inorganic materials [1–3]. The absorption of light energy in the thin organic layer can be converted into electrical, chemical and thermal energy, leading to some interesting applications such as solar cells, non-linear optical devices, luminescence devices and energy conversion and storage devices [4–6]. Hence basic research is necessary on the use of these organic semiconducting polymers as active element for these devices. Research into polymeric photovoltaics is at a very early stage. Conjugated polymers can exhibit electron–hole conduction similar to conventional semiconductors, an effect that is enhanced by chemical doping [7]. Electrical currents are produced by separating the electron–hole

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* Corresponding author. Tel.: +91 452 2458247; fax: +91 452 2459181.

E-mail address: saraswathir@yahoo.com (R. Saraswathi).

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pairs. This is done by forming interfaces between materials having different ionization potentials and electron affinities. Interfaces are created by superimposing layers of metals, inorganic oxides, and polymers, or by creating interpenetrating polymer networks. Although the best photovoltaic polymers produced so far are less efficient than their silicon counterparts, they produce much higher open-circuit voltages [8–10]. Schottky devices have been made from conjugated polymers including polyacetylene, polypyrrole, polythiophene, poly(*p*-phenylenevinylene), polyaniline and poly(*N*-methylaniline) [11–19] by several researchers.

In this work, the electrical properties of polyindole and polycarbazole-based Schottky barriers have been studied in order to improve the performance of the devices. The dark current–voltage characteristics will give information on the quality of the ohmic contact, the rectifying diode behaviour, the leakage current, and the series resistance that influence the efficiency of the photovoltaic cells. The dark capacitance–voltage measurements will give information about the contact potential and the space charge layer width of the junction, which play a crucial role in the photovoltaic devices [20].

The chemical and electrochemical synthesis of polyindole have been discussed in detail by Billaud and coworkers [21–25]. The doped polyindole was obtained in the form of an air stable conducting polymer, green in colour. Polyindole-5-carboxylic acid is an interesting conducting polymer because depending on the pH of the solution it can be self-doped [26]. Bartlett and Farrington developed a micro pH sensor based on this polymer [27]. The polymer showed good stability and rapid response to changes in solution pH. Also the films could be stored dry and reused. Koleli et al. [28] reported the properties of the Schottky barrier formed on a polyindole-*n*-GaAs interface.

Polycarbazole is a material with possible applications in sensors [29], rechargeable batteries [30], photocorrosion inhibition [31], electrocatalysis [32], electrochromic displays [33] and electronic devices [34–36]. The polycarbazole-based electrochemical transistor was reported to be superior to other conducting polymer transistors [37]. A *n*-$MoSe_2$ photoanode was stabilized in an acid chloride solution by grafting it with polycarbazole. The grafted electrode was useful for applications in photovoltaic power sources [38]. Recently poly(*N*-vinylcarbazole) has attracted attention in applications related to organic light-emitting diodes [39–41]. Devices in which the emitting layer is formed by poly(*N*-vinylcarbazole) blended with other polymeric systems have shown remarkable increase in luminance efficiency, as compared to those in which poly(*N*-vinylcarbazole) was not incorporated. Very recently, there have been some interesting reports concerning the design and the testing of Alq_3/poly(*N*-vinylcarbazole) light-emitting diodes [42,43]. Poly(*N*-vinylcarbazole) served as a hole-transport layer, and Alq_3 played the role of an emitting layer [44].

2. Experimental

Indole (SRL) and carbazole (Merck), were recrystallized from methanol. Indole-5-carboxylic acid (Acros) and *N*-vinylcarbazole (Aldrich) were used as received. The electrochemical deposition of the polymers and current–voltage (*J*–*V*) measurements were carried out using a EG&G PAR, Model 263A potentiostat/galvanostat. Depositions of Al, In, Sb and Sn ($0.2\,cm^2$) were done by vacuum evaporation technique under $\sim 10^{-6}$ Torr with 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&G PAR, Model 6310). The energy band gap was calculated from the absorbance data recorded by using a UV-visible spectrophotometer (Jasco Model 7800). The doping level of the polymers has been estimated using an elemental analyzer (Perkin Elmer 240).

3. Results and discussion

3.1. Electrodeposition of polymer films

Polyindole films were prepared from an aqueous-methanolic solution (1:3) containing $0.3\,mol\,dm^{-3}$

Table 1
Synthesis and conductivity data

No.	Synthesis conditions used for polymer preparation	Film thickness (μm)	Room temperature conductivity ($S\,cm^{-1}$)	Doping level (%)	Energy band gap E_g (eV)
1	0.3 M indole, 5 M HBF_4, 0.6 V vs Ag, $AgCl/Cl^-_{(saturated)}$	4	1.0×10^{-2}	20	2.35
2	20 mM indole-5-carboxylic acid, 0.1 M $LiClO_4$ in CH_3CN, 1.2 V vs Ag	5	6.5×10^{-3}	Self-doped	2.4
3	5 mM carbazole in 75 vol.% of CH_3OH, 25 vol.% 5 M $HClO_4$ in H_2O, 1.05 V vs Ag, $AgCl/Cl^-_{(saturated)}$	2	5.0×10^{-4}	45	2.65
4	5 mM *N*-vinylcarbazole, 75 vol.% of CH_3OH, 25 vol.% 5 M $HClO_4$ in H_2O, 1.2 V vs Ag, $AgCl/Cl^-_{(saturated)}$	2	5.9×10^{-6}	50	3.2

indole and 5 mol dm^{-3} HBF_4, by applying a polymerization potential of 0.6 V vs Ag, $AgCl/Cl^-$ (satd). Polyindole-5-carboxylic acid film was electrodeposited from acetonitrile containing 2×10^{-2} mol dm^{-3} monomer and 0.1 mol dm^{-3} $LiClO_4$, under a constant potential of 1.2 V vs Ag. Polycarbazole and poly(*N*-vinylcarbazole) were obtained by electropolymerization from aqueous-methanolic solution containing 5×10^{-3} mol dm^{-3} monomer and 5 mol dm^{-3} HBF_4. The films were deposited potentiostatically by applying 1.05 V for polycarbazole and 1.2 V vs Ag, $AgCl/Cl^-$ (satd) for poly(*N*-vinylcarbazole). One set of additional experiments has been carried out with poly(*N*-vinylcarbazole) synthesized from acetonitrile containing 0.1 mol dm^{-3} $LiClO_4$ at a potential of 1.2 V vs Ag. The thickness of the polymer films were calculated from the electrochemical charge passed during deposition and are given in Table 1. Elemental analysis of the powder samples of polymers resulted in the estimation of the doping levels as 20% for polyindole, 45% for polycarbazole and about 50% for poly(*N*-vinylcarbazole). Polyindole-5-carboxylicacid is a self-doped polymer [26]. The conductivity of the polymers are given in Table 1.

3.2. Estimation of energy gap

The band gap of the polymers are evaluated from the absorbance spectra of the polymers coated on an optically transparent indium tin oxide (ITO) substrate (Fig. 1). The substrate absorbance, if any, was corrected by introducing an uncoated substrate of the same size as the reference. The band gap of the polymer is estimated using the relation [45]

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

where α is the absorption constant, 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 direct energy band gap respectively. Hence a straight line graph can be plotted between α^2 and $h\nu$. The intercept to the $h\nu$ axis gives the direct energy band gap of the semiconducting polymer (Fig. 1). It may be noted that the E_g estimated from the plots are lower than the optical band gap (E_g^{opt}) values obtained from the absorption maxima (Table 1). This can be attributed to the random distribution of the dopant ions in the semiconducting polymer [46,47]. The randomness of the ionized impurities causes fluctuations in the local potential which is particularly more pronounced in a heavily doped semiconductor resulting in the tailing of the valence and conduction bands into the energy gap.

3.3. Junction properties

Fig. 2 shows a schematic representation of the ITO/polymer/metal (Al, In, Sb and Sn) diode constructed in the sandwich configuration. The current–voltage (*J*–*V*) characteristics of the metal–polymer diodes can be discussed in the light of Schottky emission [48,49]. The details about the theoretical treatment of Schottky emission has been already given elsewhere [18]. In brief, the Schottky effect involves the emission of the

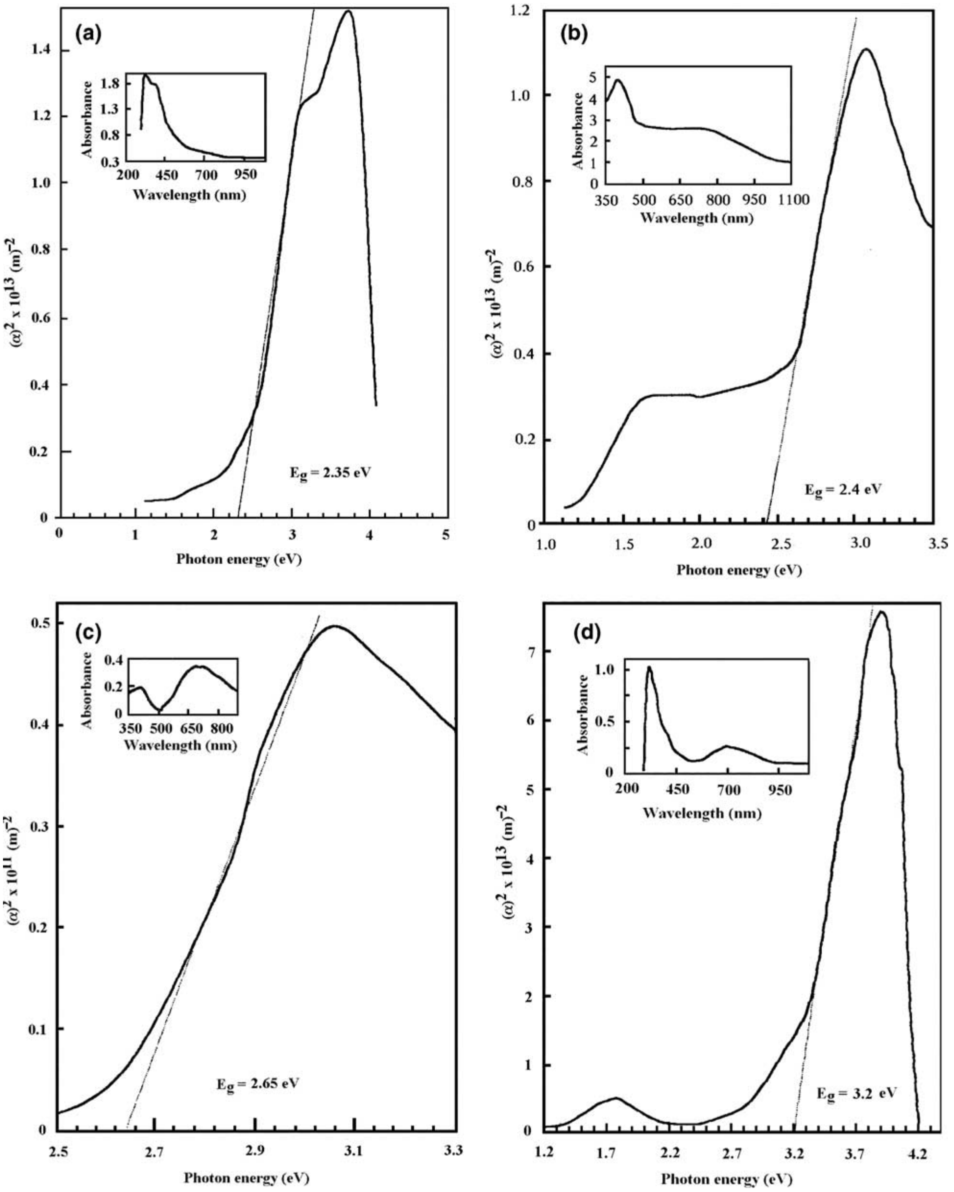

Fig. 1. The evaluation of band gap of (a) polyindole-perchlorate, (b) polyindole-5-carboxylic acid, (c) polycabazole-perchlorate and (d) poly(*N*-vinylcarbazole)-perchlorate. Inset: Optical absorption spectrum of film (a), (b), (c) and (d) coated on ITO substrate respectively.

electrons by thermal activation from the metal electrode into the conduction band of the polymer over a potential barrier between the metal–polymer interface. Accordingly, the current–voltage relationship for the Schottky barrier is given by the Shockley equation as

$$J = J_0 \exp(eV/nkT) \qquad (2)$$

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

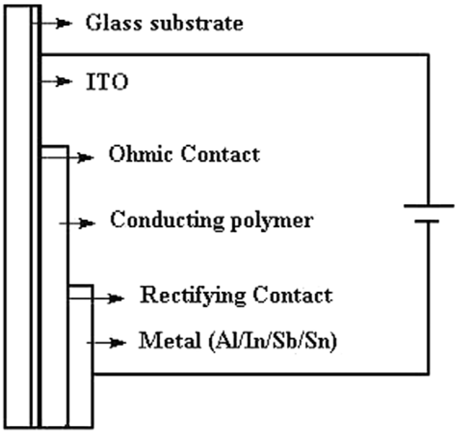

Fig. 2. Schematic representation of sandwich configuration of ITO/p-type conducting polymers/metal diode.

n the ideality factor of the diode (for an ideal diode $n = 1$). According to Eq. (2), as $eV/kT \gg 1$, $\ln J$ vs 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 vs V. From J_0, the barrier height ϕ_b, can be deduced using the Richardson equation,

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

where A^* is the effective Richardson constant usually taken as $120\,\mathrm{A/(cm^2\,K^2)}$ [50].

Typical J–V curves of the polyindole–tetrafluoroborate junctions with the metals (Al, In, Sb and Sn) are shown in Fig. 3(a). The ideality factor, barrier voltage and saturated current are evaluated from the $\ln J$ vs V plots (Fig. 3(b)) and the values are shown in Table 2. The current increases exponentially with increasing forward bias. In the reverse bias the current is somewhat large. The ideality factor is about 2.6 for both In and Al and about 3.6 for Sb and In-based junction devices. The J–V curve of polyindole-5-carboxylic acid–metal barriers are presented in Fig. 4(a). The junction parameters evaluated from $\ln J$–V (Fig. 4(b)) are given in Table 2. The important observation is the high saturation current in all the junction devices made from both polyindole and polyindole-5-carboxylic acid.

The J–V curves of the Schottky barriers of polycarbazole and poly(N-vinylcarbazole) are shown in Figs. 5 and 6. All the junctions show rectifying behaviour. The corresponding $\ln J$ vs V plots are also shown and the diode parameters are evaluated from these plots (Table 3). In the case of polycarbazole, the ideality factor is about 2.5 ± 0.3 for the four Schottky devices. The saturation current values are quite high as in the case of polyindole. In the case of poly(N-vinylcarbazole), all the four metal–polymer junctions show rectification, although the junction formed with antimony gives poor rectification ratio due to large currents flowing in the reverse-biased condition. The junction formed with indium metal gives the best values for ideality factor (1.5) and reverse saturation current ($1.75 \times 10^{-10}\,\mathrm{A\,cm^{-2}}$).

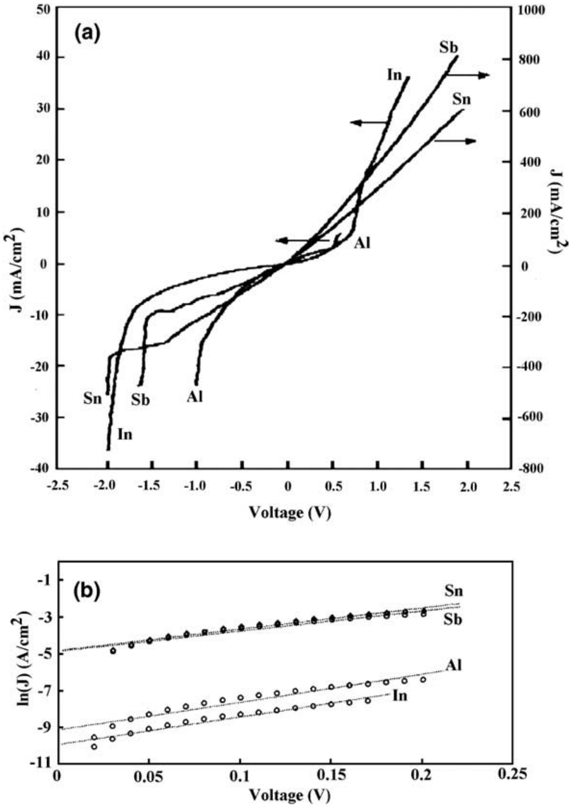

Fig. 3. (a) Dark current density vs applied voltage and (b) $\ln J$–V characteristics for ITO/polyindole-tetrafluoroborate/metal diode.

In order to find out whether the junction properties could be improved by changing the polymer preparation conditions, Schottky barriers are constructed with poly(N-vinylcarbazole)

Table 2
Metal–polyindole and metal–polyindole-5-carboxylic acid (PI5CA) junction parameters

No.	Device configuration	Ideality factor n	Barrier height ϕ_b (eV)	Reverse saturation current J_0 (A/cm^2)	Contact potential V_c (V)	Carrier concentration N_s (cm^{-3})	Depletion width D (Å)
1	ITO/polyindole-BF$_4$/Al	2.60	0.65	1.11×10^{-4}	0.66	6.34×10^{18}	62
	ITO/polyindole BF$_4$/In	2.60	0.67	4.91×10^{-5}	0.64	5.51×10^{18}	66
	ITO/polyindole BF$_4$/Sb	3.55	0.53	8.13×10^{-3}	0.56	7.85×10^{18}	51
	ITO/polyindole BF$_4$/Sn	3.77	0.54	7.77×10^{-3}	0.55	6.45×10^{18}	57
2	ITO/PI5CA/Al	1.28	0.64	1.16×10^{-4}	0.66	6.33×10^{18}	61
	ITO/PI5CA/In	1.08	0.70	1.11×10^{-5}	0.64	5.50×10^{18}	66
	ITO/PI5CA/Sb	2.58	0.63	2.38×10^{-4}	0.63	7.25×10^{18}	57
	ITO/PI5CA/Sn	2.08	0.61	4.72×10^{-4}	0.61	4.99×10^{18}	69

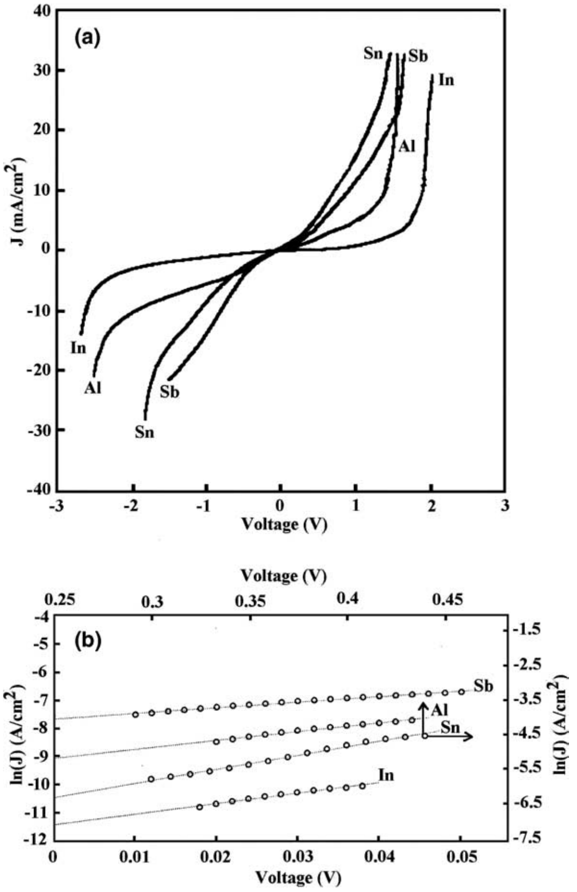

Fig. 4. (a) Dark current density vs applied voltage and (b) ln J–V characteristics for ITO/polyindole-5-carboxylic acid/metal diode.

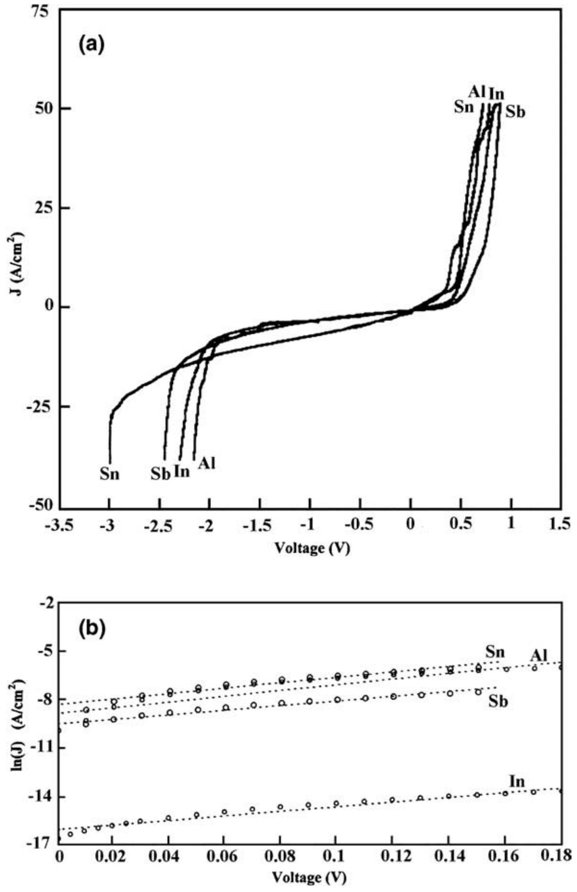

Fig. 5. (a) Dark current density vs applied voltage and (b) ln J–V characteristics for ITO/polycarbazole-tetrafluoroborate/metal diode.

electrodeposited from a non-aqueous medium viz. acetonitrile containing 0.1 M lithium perchlorate as electrolyte. The film was prepared by applying a constant potential of 1.2 V vs Ag. The J–V data

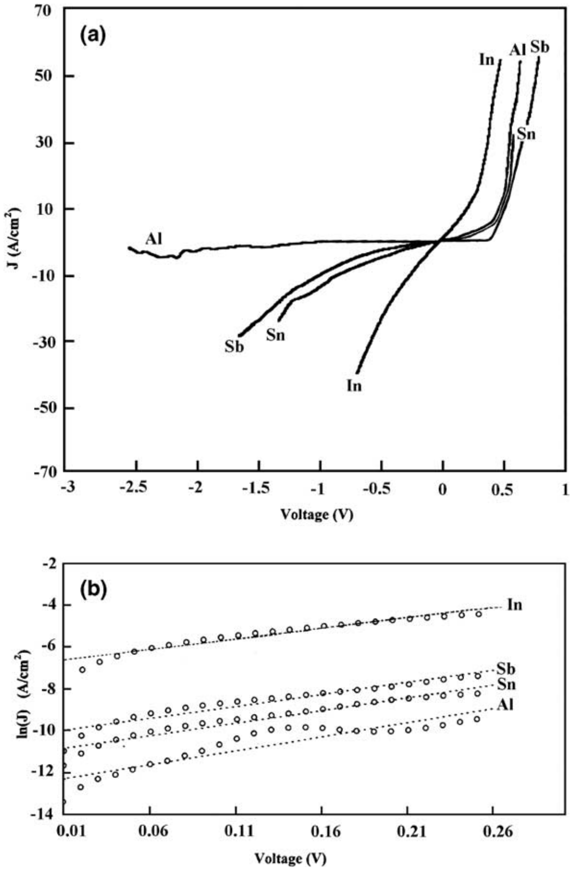

Fig. 6. (a) Dark current density vs applied voltage and (b) $\ln J$–V characteristics for ITO/poly(N-vinylcarbazole)-tetrafluoroborate/metal diode.

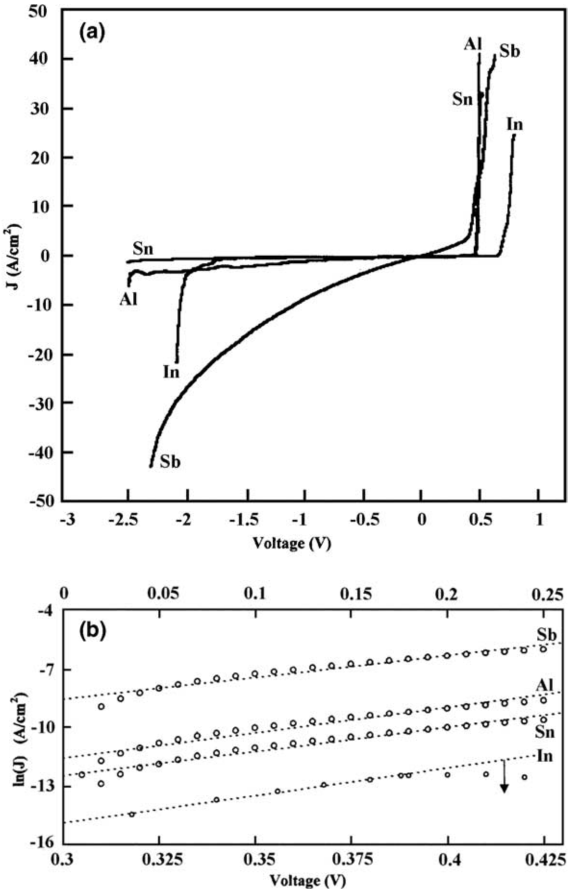

Fig. 7. (a) Dark current density vs applied voltage and (b) $\ln J$–V characteristics for ITO/poly(N-vinylcarbazole)-perchlorate/metal diode. Polymer was prepared from acetonitrile containing 0.1 M $LiClO_4$.

Table 3
Metal–polycarbazole and metal–poly(N-vinylcarbazole) junction parameters

No.	Device configuration	Ideality factor n	Barrier height ϕ_b (eV)	Reverse saturation current J_0 (A/cm^2)
1	ITO/polycarbazole-BF_4/Al	2.30	0.64	1.49×10^{-4}
	ITO/polycarbazole-BF_4/In	2.90	0.82	1.05×10^{-7}
	ITO/polycarbazole-BF_4/Sb	2.80	0.66	7.53×10^{-5}
	ITO/polycarbazole-BF_4/Sn	2.40	0.62	2.58×10^{-4}
2	ITO/poly(N-vinylcarbazole)-BF_4/Al	2.20	0.72	6.29×10^{-6}
	ITO/poly(N-vinylcarbazole)-BF_4/In	1.50	0.99	1.75×10^{-10}
	ITO/poly(N-vinylcarbazole)-BF_4/Sb	2.60	0.64	1.32×10^{-4}
	ITO/poly(N-vinylcarbazole)-BF_4/Sn	2.40	0.74	2.67×10^{-4}
3	ITO/poly(N-vinylcarbazole)-ClO_4/Al	2.67	0.60	6.71×10^{-4}
	ITO/poly(N-vinylcarbazole)-ClO_4/In	2.63	0.59	8.46×10^{-4}
	ITO/poly(N-vinylcarbazole)-ClO_4/Sb	2.68	0.63	1.94×10^{-4}
	ITO/poly(N-vinylcarbazole)-ClO_4/Sn	2.70	0.81	1.96×10^{-7}

obtained for this polymer film-metal junctions are shown in Fig. 7. The diode parameters for these junctions do not show any improvement over the devices constructed with the polymer film prepared from aqueous-methanolic solution. The ideality factor is close to 2.5 and the saturation current is about $10^{-4}\,\mathrm{A\,cm^{-2}}$ (Table 3).

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 [20]. The capacitance of the metal–polymer junction can be expressed by the following equation:

$$C^{-2} = [2(V_c - V)]/(A^2 e\epsilon\epsilon_0 N_s) \tag{4}$$

Here V_c is the contact potential, A is the effective area of the diode, ϵ_0 is the permittivity of free space and N_s is the carrier concentration. ϵ, the dielectric constant of the polymer is assumed to be 3.4 [18]. The intercept of the Mott–Schottky plot of C^{-2} vs voltage 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 (μ) and depletion width (D) by the following equations:

$$\sigma = N_s e\mu \tag{5}$$

where σ is the electrical conductivity of the p-doped polymer.

$$D = [2\epsilon\epsilon_0(V_c + V)/(eN_s)]^{1/2} \tag{6}$$

The capacitance–voltage curves obtained at three different frequencies for polyindole-tetrafluoroborate and polyindole-5-carboxylic acid are shown in Fig. 8. Although the Mott–Schottky plots should be independent of the measuring frequency, such results are infrequently observed for amorphous semiconductor electrodes [51]. Surface roughness, dielectric relaxation and impedance across the sample surface have all been advanced as possible explanations for frequency dispersion in Mott–Schottky plots [52]. The depletion width

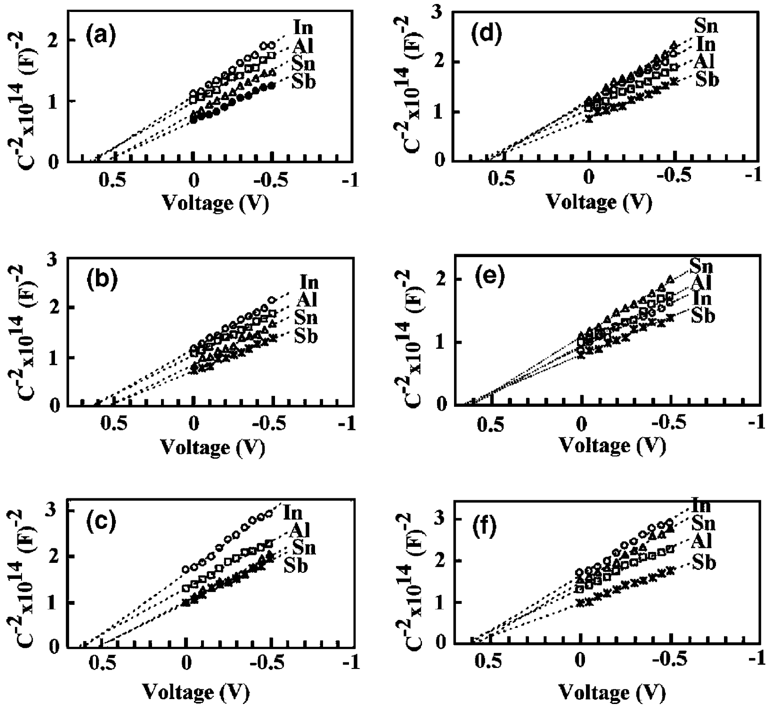

Fig. 8. C^{-2} vs applied voltage at (a) 100 Hz, (b) 1 kHz and (c) 10 kHz for ITO/polyindole-tetrafluoroborate/metal diode and (d) 100 Hz, (e) 1 kHz and (f) 10 kHz for ITO/polyindole-5-carboxylic acid/metal diode.

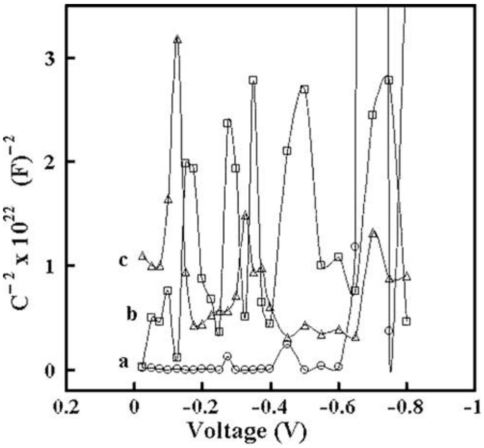

Fig. 9. C^{-2} vs applied voltage at (a) 100 Hz, (b) 1 kHz and (c) 10 kHz for ITO/poly(*N*-vinylcarbazole)-tetrafluoroborate/Al diode.

and carrier concentration calculated from the plots at 1 KHz are given in Table 2. The work function of polymer can be obtained using Eq. (7) [18]:

$$\phi_{sp} = qV_c + \phi_m \quad (7)$$

where ϕ_{sp} and ϕ_m are the work functions of the semiconducting polymer and metal respectively. The contact potential estimated from the *C–V* plots are given in Table 2. 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) [53] and the contact potentials, the work functions are evaluated to be 4.78 and 4.75 eV for polyindole and polyindole-5-carboxylic acid. In the case of polycarbazole and poly(*N*-vinylcarbazole), the capacitance–voltage curves at different frequencies (Fig. 9) indicate the presence of surface defects and interface states in the polymer [15,54–56]. No good linear fit could be obtained between C^{-2} and voltage.

4. Conclusions

For both polyindole and polyindole-5-carboxylic acid, the junctions formed with In metal have given better rectification characteristics. Polycarbazole and poly(*N*-vinylcarbazole) appear to be not suitable for the construction of ideal photovoltaic devices. It is essential to optimize the synthesis conditions for the preparation of these polymer films. The electrochemical method of preparation may not be a good choice. Template polymerization or the use of Langmuir–Blodgett method of film deposition may result in the formation of defect-free polymers. Also it is essential to improve the conductivity of the two polymers atleast by one order of magnitude higher. The energy band gap of the two polymers need to be tuned below a value of 2.5 eV.

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References

[1] V. Saxena, B.D. Malhotra, Current Appl. Phys. 3 (2003) 293.
[2] G.G. Wallace, P.C. Dastoor, D.L. Officer, C.O. Too, Chem. Innovation 30 (1) (2000) 14.
[3] R.M. Faria, O.N. Oliveira Jr., Braz. J. Phys. 29 (1999) 360.
[4] H.S. Nalwa, Adv. Mater. 5 (1993) 341.
[5] Y. Yang, E. Westerwecle, C. Zhang, P. Smith, A.J. Heeger, J. Appl. Phys. 77 (1995) 694.
[6] M.S. Roy, G.D. Sharma, S.K. Gupta, Thin Solid Films 310 (1997) 279.
[7] S.A. Chen, Y. Fang, Synth. Met. 60 (1993) 215.
[8] J. Tsukamoto, H. Ohigashi, K. Matsumare, A. Takahashi, Synth. Met. 4 (1982) 177.
[9] J.J.M. Halls, K. Pichler, R.H. Friend, S.C. Moratti, A.B. Holmes, Appl. Phys. Lett. 68 (1996) 3120.
[10] G.D. Sharma, S.G. Sangodkar, M.S. Roy, Thin Solid Films 278 (1996) 129.
[11] J. Kanicki, Mol. Cryst. Liq. Cryst. 105 (1984) 203.
[12] P.M. Grant, T. Tani, W.D. Gill, M. Krounbi, T.C. Clarke, J. Appl. Phys. 52 (1981) 869.
[13] O. Inganas, T. Skotheim, I. Lundstrom, J. Appl. Phys. 54 (1983) 3639.
[14] M. Campos, L.O.S. Buthoes, C. Lindino, Sensors Actuat. A 87 (2000) 67.
[15] A. Turut, F. Koleli, J. Appl. Phys. 72 (1992) 818.
[16] I.B. Nazarova, V.I. Krinichnyi, L.M. Goldenberg, Synth. Met. 53 (1993) 399.
[17] S.A. Chen, Y. Fang, H.T. Lee, Synth. Met. 55–57 (1993) 4082.

[18] P. Syed Abthagir, R. Saraswathi, J. Appl. Polym. Sci. 81 (2001) 2127.

[19] P. Syed Abthagir, R. Saraswathi, J. Mater. Sci.: Mater. Electron. 15 (2004) 81.

[20] J. Kanicki, in: T.A. Skotheim (Ed.), Handbook of Conducting Polymers, vol. 1, Marcel Dekker, New York, 1986, p. 544.

[21] E.B. Maarouf, D. Billaud, E. Hannecart, Mater. Res. Bull. 29 (1994) 637.

[22] D. Billuad, E.B. Maarouf, E. Hannecart, Synth. Met. 69 (1995) 571.

[23] H. Talbi, D. Billaud, Synth. Met. 93 (1998) 105.

[24] H. Talbi, D. Billaud, G. Louarn, A. Pron, Spectrochim. Acta Part A: Mol. Biomol. Spectr. 56 (2000) 717.

[25] H. Talbi, A. Pron, G. Louarn, D. Billaud, Synth. Met. 101 (1999) 117.

[26] J.G. Mackintosh, A.R. Mount, J. Chem. Soc. Faraday Trans. 90 (1994) 1121.

[27] P.N. Bartlett, J. Farrington, Bull. Electrochem. 8 (1992) 208.

[28] F. Koleli, M. Asglam, A. Turut, H. Efeoglu, Turk. J. Chem. 18 (1994) 22.

[29] R.B. Kawde, N.B. Laxmeshwar, K.S.V. Santhanam, Sensors Actuat. B 23 (1995) 35.

[30] R. Saraswathi, M.M. Verghese, B.D. Malhotra, J. Appl. Polym. Sci. 74 (1999) 145.

[31] S. Aravamuthan, C.L. Clement, S. Madhavan, K.S.V. Santhantham, J. Power Sources 32 (1990) 1.

[32] R.N. O'Brien, N.S. Sundaresan, K.S.V. Santhanam, J. Elecrochem. Soc. 131 (1984) 2028.

[33] M.M. Verghese, M.K. Ram, H. Vardhan, B.D. Malhotra, S.M. Ashraf, Polymer 38 (1996) 1625.

[34] D.B. Romero, M. Schaer, M. Leclerc, D. Ades, A. Siove, L. Zuppiroli, Synth. Met. 80 (1996) 271.

[35] S.Y. Abe, J.C. Bernede, M.A. Delvalle, Y. Tregouet, F. Ragot, F.R. Diaz, S. Lefrant, Synth. Met. 126 (2002) 1.

[36] K.D. Almeida, J.C. Bernede, S. Marsillac, A. Godoy, R.F. Diaz, J. Electroanal. Chem. 248 (1988) 233.

[37] V. Rani, K.S.V. Santhanam, J. Solid State Electrochem. 2 (1998) 99.

[38] S. Aravamuthan, C. Levy, S. Madhavan, K.S.V. Santhanam, J. Power Sources 32 (1990) 1.

[39] G. Wang, C. Yuan, H. Wu, Y. Wei, J. Appl. Phys. 78 (1995) 2679.

[40] B. Hu, Z. Yang, F.E. Karasz, J. Appl. Phys. 76 (1994) 2419.

[41] C. Zhang, H.V. Seggern, K. Pakbaz, P. Kraabel, H.W. Schmitta, A.J. Heeger, Synth. Met. 62 (1994) 35.

[42] F. Michelotti, F. Borghese, M. Bertolotti, E. Cianci, V. Foglietti, Synth. Met. 111–112 (2000) 105.

[43] S.O. Djobo, J.C. Bernède, S. Marsillac, Synth. Met. 122 (2001) 131.

[44] X. Jiang, Y. Liu, X. Song, D. Zhu, Synth. Met. 87 (1997) 175.

[45] K.S.V. Santhanam, M. Sharon, Photoelectrochemical Solar Cells, Elsevier, New York, 1998, p. 174.

[46] M.S. Tyagi, Introduction to Semiconductor Materials and Devices, John Wiley & Sons, Singapore, 2000, p. 94.

[47] E.O. Kane, Solid State Electron. 28 (1985) 3.

[48] W. Schottky, Z. Phys. 15 (1914) 872.

[49] E.H. Rhoderick, Metal–Semiconductor Contacts, Clarendon Press, Oxford, 1978.

[50] H. Koezuka, S. Etoh, J. Appl. Phys. 54 (1983) 2511.

[51] M.N. Latto, D. Jason Riley, P.W. May, Diamond Relat. Mater. 9 (2000) 1181.

[52] W.P. Gomes, F. Cardon, Prog. Surf. Sci. 12 (1982) 155.

[53] S.M. Sze, Physics of Semiconductor Devices, Wiley, New York, 1969.

[54] A. Singh, Solid State Electron. 28 (1985) 223.

[55] P. Cova, A. Singh, Solid State Electron. 33 (1990) 11.

[56] A.M. Goodmann, J. Appl. Phys. 34 (1963) 329.