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Effect of steric hinderance on junction properties of poly (3-alkylthiophene)s based schottky diodes

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Schottky diodes have been constructed from poly(3-cyclohexylthiophene) (P3cHT) and poly(3-*n*-hexylthiophene), and metals, such as, In, Ag, Al, Sn, etc. The polymers were synthesised chemically using ferric chloride as catalyst. The electrical properties of the devices have been studied by current-voltage (I-V) and capacitance-voltage (C-V) measurements. Junction parameters such as ideality factor (n) and barrier height (χ) have been calculated on the basis of thermoionic emission theory. Better performance of P3cHT/metal diode, compared to P3nHT was attributed to the steric effects produced by cyclohexyl unit present in the polymer.

Introduction

Since their discovery, conducting polymers have been extensively studied for their use as active components in semiconducting devices. These polymers offer the remarkable potential of producing materials with important electronic and optical properties of semiconductors in combination with the attractive mechanical properties and processing advantages. Several devices, such as field effect transistors (FETs), Schottky diodes, light emitting diodes (LEDs) (1-3) etc., have been developed using these conjugated materials. Semiconducting properties of both doped and undoped conjugated polymers such as polypyrrole (4), polyaniline (5), polythiophene (6), polycarbazole (7) and polyindole (8) were used in electronic device applications. However, in these devices not only the bulk properties of polymers are important but the junction properties are also of equal significance. Several types of junctions such as p-n junction, Schottky barrier junction and heterojunction have been fabricated and studied for their electrical properties (9-11). The performance of these devices is dependent on various factors such as fabrication parameters, characteristics of the polymer and the metal used. The cost and availability of material in abundance, processability and environmental stability are also deciding factors for a material to be used in device applications.

Polythiophenes constitute a particularly important class of conjugated polymers, which have been extensively studied for the relation between the geometrical structure, and the optic and electronic properties (12-13). However, the commercial applications of unsubstituted polythiophenes have been restricted due to their difficult processability. The substitution of alkyl chains to thiophene ring at 3-position not only enhances the solubility of the polymer in common organic solvents but also changes its electrical properties. These facts have been explained on the basis of steric effects on chain packing of solids (14). Poly(3-alkylthiophene)s are among important conducting polymers because they were the first soluble and even fusible conducting polymers with novel characteristics such as thermochromism (15), solvatochromism (16-17), photochromism (18-19) and thermal-dedoping (20). They have been reported to behave as p-type semiconductors (21). Since, generally, the metals with work function lower than that of the p-type polymer form rectifying contact (22), it is expected that these polymers would exhibit rectifying behaviour when interfaced with metals such as Al, In, Sn, and Sb.

We wish to report here a comparative study of the electrical properties of the junctions of poly(3-cyclohexylthiophene) (P3cHT) and poly(3-*n*-hexylthiophene) (P3nHT) with metals (Al, Ag, In and Sn). The device fabrication is simple because of direct casting of the polymers from the chloroform solution.

Experimental

Monomer Synthesis

3-cyclohexylthiophene and 3-*n*-hexylthiophene were prepared by nickel catalysed cross coupling reaction of 3-bromothiophene with cyclohexylmagnesium chloride and *n*-hexylmagnesium chlroide, respectively (23).

Synthesis of Homopolymers

Homopolymers viz. P3cHT and P3nHT were prepared by the chemical method described elsewhere (24). 3-cyclohexylthiophene and 3-hexylthiophene monomers were polymerized with $FeCl_3$ catalyst in chloroform solution under inert atmosphere. A solution of 0.12 mol $FeCl_3$ in 30ml dry chloroform was taken in a flask. To the contents, 0.003 mole monomer in 20ml chloroform was added with constant stirring under an argon atmosphere. After 24 hours, the solution was poured into 1litre methanol. Due to its high oxidation potential, the polymer was immediately reduced by methanol. The precipitate was recovered by filteration and was purified by methanol in a soxhlet extractor followed by extraction with a mixture of acetone and methanol (1:1v/v) for 48 hours. The neutral polymer thus obtained was dried under reduced pressure at 50°C.

Construction of the device-

Thin films of polymers were deposited onto SnO_2 glass substrate by spin casting technique, using a solution of the polymer (3g/l) in chloroform. The substrate was kept at 40°C for 15 minutes in order to evaporate the solvent. Finally, a thin metal layer (Al, Ag, In and Sn) was deposited onto the polymer film by thermal evaporation technique under pressure of 10^{-5} torr, using Edwards Co. U.K., turbo molecular pumping system. Metal deposition was followed by silver deposition in order to avoid deterioration of metals in ambient conditions. The effective device area was kept $1mm^2$. Devices thus prepared were kept in

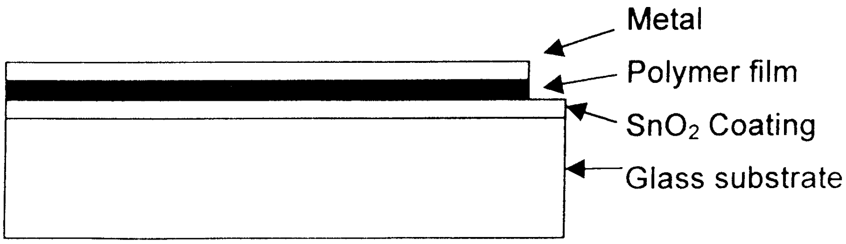

Fig. 1 Schematic diagram of the polymer/metal junction.

vacuum desiccator before testing. Figure 1 shows the schematic diagram of the Schottky diode.

Characterisation

All measurements were carried out at 25°C. Gel permeation chromatography (GPC) was carried out in tetrahydrofuran using WATERS 150-C ALC/GPC instrument equipped with a WATERS 490 programmable multi wavelength detector. Chromatograms were recorded at 254 nm at flow rate of 1 ml/min, using polystyrene curve as a reference. NMR spectra were taken on BRUKER AMX-500 spectrophotometer, in $CDCl_3$ using tetramethyl selane (TMS) as an internal standard. The current-voltage (I-V) characteristics of each device were measured in the dark using micromanipulator interfaced with an IBM compatible computer while capacitance-voltage (C-V) measurements were carried out on Hewlett-Packard LCR meter (model HP 4284A) using regulated power supply.

Results and discussion

GPC analysis of P3nHT and P3cHT shows weight-average molecular mass of $1.5x10^4$ and $1.6x10^4$, respectively.

Figure 2 shows the NMR spectra of the P3cHT and P3nHT taken in $CDCl_3$. In the ^1H NMR spectrum of P3nHT, two signals at δ2.79, and δ2.56 for the methylene protons of hexyl substituent nearest to thiophene ring are observed while in the case of P3cHT, peaks at δ3.05 and δ2.63 are observed for methine

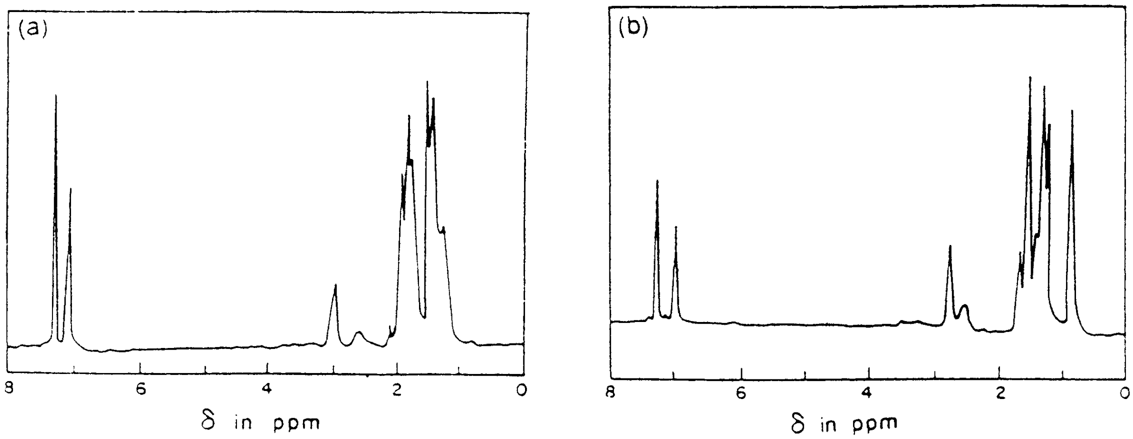

Fig.2 ^1H NMR spectra of (a) poly(3-cyclohexylthiophene) and (b) poly(3-*n*-hexylthiophene).

group of the cyclohexyl substituent. In the 3-substituted thiophenes, the α-position of the thiophene subunits may either be coupled via the 2-2', or 5-5' or 5-2' positions which are regarded as head-to-head (HH), tail-to-tail (TT) and tail-to-head (TH) coupling, respectively. The HT-HT coupling is considered as regioregular coupling and other couplings viz. TT-HH, TT-HT and HT-HH are considered as regio-irregular or miscoupled polymeric systems. In analogous with similar assignments in case of poly(*n*-alkylthiophene)s, the signal at δ2.63 was assigned to the methine protons of HH coupled subunits (irregular) and the signal at δ3.05 to HT coupled subunits (regular) of the polymer (25-26). The ratio of regioregular coupling to miscouplings was calculated from the integrals of the NMR peaks. This ratio was estimated as 7:5 for the cyclohexyl substituted and 18:7 for hexyl substituted polymer. Therefore, the amount of regioregularity of P3nHT is significantly higher than that of P3cHT. Since one repeating unit of the polymer is bound by two neighbouring thiophene rings, the regiochemistry of both bonds affects the resonance of the aromatic proton at 4-position. Since the 2-position may either be a part of a HH or TH coupling and the 5-position be a part of a TH or TT coupling, four different triads of thiophene rings are possible (HH-TT, TH-TT, HH-TH and TH-TH coupling) which may result in four different signals in the NMR of the thiophene subunits (24). However, the fine splitting of the signals are not shown in the NMR spectra of the poly(3-*n*-hexylthiophene) and poly(3-cyclohexylthiophene).

The current voltage (I-V) characteristics of the metal/polymer junction with different metals such as Al, In, Sn, Ag are shown in figure 4. It is clear from the figure that Al, In, and Sn metals make rectifying junctions with polymer whereas the Ag/polymer interface exhibits ohmic character. It is also clear from the figure that forward and reverse bias characteristics of P3nHT/metal interface have little difference in contrast to P3cHT/metal interface. The large leakage current for the

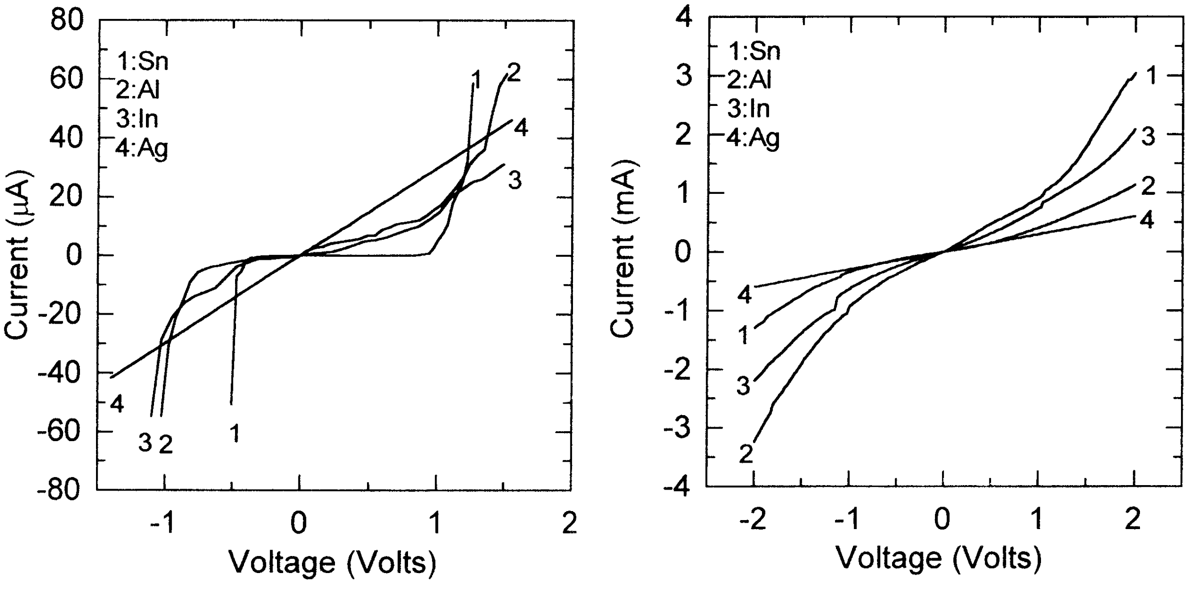

Fig. 4 Current-voltage (I-V) characteristics of junction of (a) poly(3-cyclohexylthiophene) and (b) poly(3-*n*-hexylthiophene) with various metals.

diode made of P3nHT indicates incomplete blocking of charge carriers at the P3nHT/metal interface. The non-linear I-V characteristics of the polymer/metal junction could be due to space-charge-limited conduction (SCLC), Poole-Frenkel emission, or thermoionic emission (27). The log I-log V curves were found to be non-linear which excludes the possibility of SCLC process. The plot of In(I/V) versus $V^{1/2}$ should give a straight line in the case of Poole-Frenkel emission. However, these curves were observed non-linear which rules out the possibility of this effect. This suggests that the thermoionic emission theory can be applied to evaluate junction parameters such as, ideality factor and barrier height of the device.

According to the thermoionic emission model (28), the forward current (I) for the Schottky device may be written as

$$I = I_0 \exp (eV/nkT) \qquad (1)$$

Where V is the voltage, e is the electronic charge, n is the ideality factor, k is the Boltzmann constant and T is the absolute temperature.

The value of the reverse saturation current (I_0) can be given by

$$I_0 = A^* T^2 \exp (-e\chi/kT) \qquad (2)$$

Where A^* is Richardson constant (120 A/deg^2/cm^2 for free electron) and χ is the barrier height.

Electronic parameters, n and χ for the metal/polymer junctions were calculated using above relations (equation 1 & 2). Table I summarizes the barrier height and ideality factor for each device. As indicated in the table I, there is no clear dependence of barrier height on the metal work function. This behaviour indicates the presence of surface states, which in turn determines the final barrier height. High ideality factor of the P3nHT/metal junction device suggest poor junction property in comparison with that of P3cHT/metal interface. The large measured value of ideality factor may be due to the following effects:

(i) high probability of electron and hole recombination in depletion region
(ii) occurrence of tunneling current.

Almost symmetrical I-V curves of P3nHT metal junction may be attributed to the narrow depletion width. This, in turn, causes tunneling of charge carriers through the barrier under the reverse voltages and thereby, a large current for the junction. From linear I-V curves, the conductivities for P3cHT and P3nHT were estimated to be $5.0\text{x}10^{-8}$ and $8.0\text{x}10^{-7}$ S/cm, respectively. The low conductivity of P3cHT as compared to P3nHT could be explained on the basis of steric effects (24). The substitution of bulky cyclohexyl group in thiophene ring

Table I. Ideality factor (n) and barrier height (χ) of polymer/metal Schottky junctions.

Metal	Work Function (eV) (29)	Ideality Factor		Barrier Height (Volts)	
		P3cHT	P3nHT	P3cHT	P3nHT
Al	3.74	9.13	20.58	0.80	0.46
In	4.12	12.3	21.89	0.78	0.49
Sn	4.11	4.60	25.10	0.84	0.48
Ag	4.28	Ohmic	Ohmic	------	------

decreases the coplanarity of the main chain and thereby decreases the π-π overlapping and hence the conjugation length. The decrease in conjugation length results in decrease in the conductivity of P3cHT. The low conductivity of P3cHT may be responsible for wider depletion width and thereby better rectifying character of P3cHT/metal diode in comparison with P3nHT/metal junction.

The results of capacitance-voltage (C-V) measurements for the device, at a frequency of 1 KHz, are shown in figure The plot of $1/C^2$ as a function of reverse bias voltage is linear which is indicative of the formation of Schottky junction (30). Therefore, it should follow the standard Mott-Schottky relationship-

$$\frac{1}{C^2} = \frac{2(V_{in}-V)}{e\varepsilon\varepsilon_0 N} \tag{3}$$

Where V_{in} ($=V_{bi}$-kT/e) is the intercept voltage, ε is the polymer dielectric constant, ε_0 is the vacuum permittivity, k is the Boltzmann constant and N is the ionised carrier density.

With the help of equation-3, the values of V_{bi} and N can be determined from the intercept and slope of the $1/C^2$ -V plot. The results are summarised in Table II. Using the carrier density N obtained above, the carrier mobility μ can be determined from the expression for conductivity σ = Neμ, with the assumption that all carriers take part in the conduction. These results are summarized in Table III. As clear from the table III, the conductivity of polymer is proportional to the density of charge carriers. The substitution of bulky cyclohexyl group to thiophene ring lowers the conductivity, which in turn may be due to the lowering of the charge carrier concentration, thus resulting in a wider depletion width and better junction behaviour. It is also clear from the table III that as compared to

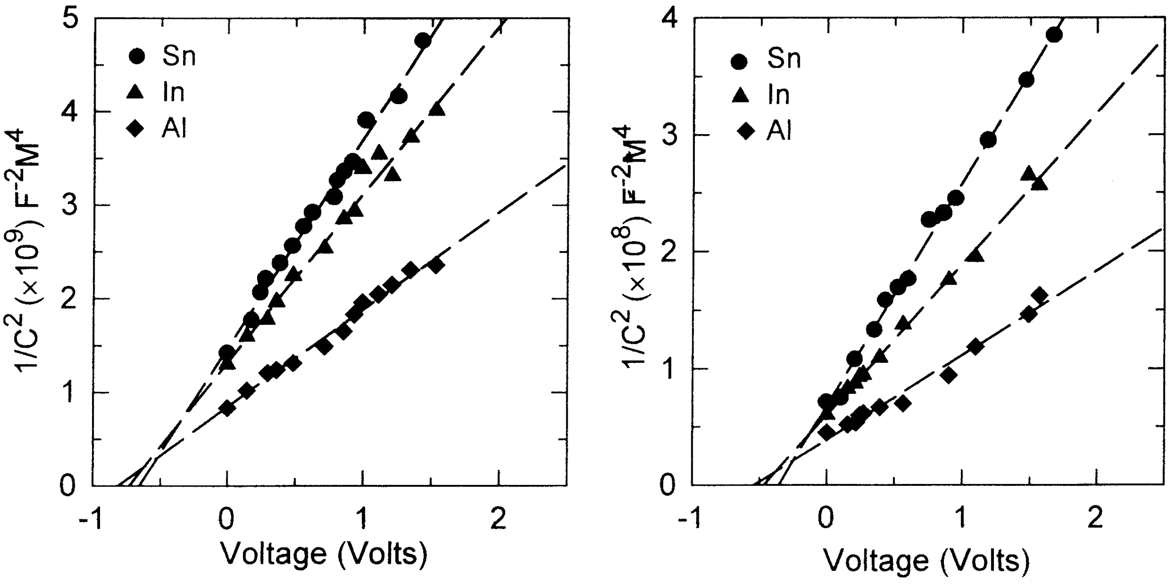

Fig. 5 Capacitance-voltage (C-V) characteristics of junction of (a) poly(3-cyclohexylthiophene) and (b) poly(3-*n*-hexylthiophene) with various metals.

Table II. Carrier density (N) and barrier height (V_{bi}) of polymer/metal Schottky junctions.

Metal	Carrier density (x10^{14}) cm^{-3}		V_{bi} (volts)	
	P3cHT	P3nHT	P3cHT	P3nHT
Sn	0.63	12.4	0.69	0.38
In	0.78	18.2	1.39	0.49
Al	1.36	32.5	0.83	0.57

Table III. Conductivity (σ), mobility (μ) and dielectric constant (ε) of poly(3-cyclohexylthiophene) and poly(3-*n*-hexylthiophene).

Polymer	Conductivity (S/cm)	Mobility μ (cm^2/Vs)	ε
P3cHT	$5.0\text{x}10^{-8}$	$2.30\text{x}10^{-3}$	10
P3nHT	$8.0\ \text{x}10^{-7}$	$1.54\text{x}10^{-3}$	6

large difference in conductivity of P3cHT and P3nHT, there exists a small change in their mobility. This suggests that the mobility is approximately constant, as in conventional semiconductors (31).

Conclusion

We have constructed the Schottky type device consisting of the chemically prepared poly(3-cyclohexylthiophene) and poly(3-*n*-hexylthiophene) and metal. The thermoionic emission model has been applied to interpret I-V characteristics of the diode. Electrical properties of the P3cHT/metal and P3nHT/metal junctions were compared. Better rectification properties of the P3cHT/metal junctions were attributed to the decreased conductivity, which results due to the steric hindrance caused by cyclohexyl units present in the thiophene ring.

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