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INDIUM/POLYPYRROLE(POLYPYRROLE DERIVATIVES) SCHOTTKY JUNCTIONS

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INDIUM/POLYPYRROLE(POLYPYRROLE DERIVATIVES) SCHOTTKY JUNCTIONS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Samples of polypyrrole, poly(N-methyl pyrrole) and their copolymer poly(N-methyl pyrrole-pyrrole) have been prepared by electrochemical polymerization technique. Their conductivity values have been optimized for fabricating indium-polymer Schottky junctions. The current-voltage characteristics of the indium-polymer Schottky junctions have been investigated. The results have been explained on the basis of thermionic emission theory.

Key Words: Polypyrrole; Poly(N-methyl pyrrole); Copolymer; Schottky junctions; Chot plots; Thermionic emission

INTRODUCTION

The applicability of conjugated polymers in microelectronic devices has been gaining importance in the recent years because of their ease of processability and stability. One of the greatest advantages of these organic conducting polymers over inorganic materials is their architectural flexibility. They can be easily shaped

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according to the requirement of a particular device. Their properties can be controlled by various preparation parameters such as, dopant concentration, applied potential, temperature of preparation, etc. This makes them useful for wide range of applications such as semiconductor devices [1] like metal-insulator semiconductor (MIS), Schottky diodes, electrochemical insertion electrodes, high conductivity low density metals, non-linear optical applications and field effect transistors (FETs), etc. In semiconductor devices like Schottky junctions, MIS, the charge can be introduced into the region of surface charge at the semiconductor/insulator or metal/semiconductor interface by application of strong electric field. It is evident from numerous publications on polypyrrole family of polymers, that it is one of the promising materials for device applications. Several reports are available on Indium-polyprrole (In-PPY) junctions [2-5] and almost all the workers have tried to explain the results on the basis of Richardson's equation of thermionic emission. Unfortunately, the charge transport mechanism has not been discussed in girth, in any of these reports. Moreover, the parameters such as dopant concentration, type of dopant, the work function of electrode metals, the conductivity of polymers, play an important role in the formation of junction. But no systematic study about these parameters is available in the literature.

In the present investigation we report a detailed study of current-voltage (I-V) characteristics of the junction between metal and different polymers viz. polypyrrole (PPY), poly(N-methyl pyrrole) [P(NMPY)] and copolymers poly(N-methyl pyrrole-pyrrole) [P(NMPY-PY)]having various compositions and conductivity values. Indium (In) has been chosen for the formation of Schottky contacts with the polymers. An ideal barrier results from depositing the metal in a carefully controlled way so as to keep the surface atomically clean. Thus, in making a Schottky barrier interface, the metal is typically deposited on to the surface either by building up metallic layer by vacuum evaporative deposition or pressing two bulk pieces together, forming bulk contacts [6]. The former process has been adopted in the present investigation.

EXPERIMENTAL

10 μm thick films of PPY, P(NMPY) and their copolymers; P(NMPY-PY) were prepared by electrochemical polymerizaion technique [7]. The concentrations of monomers taken is 0.1 M of pyrrole for PPY (designated as sample A), 0.1 M of N-methyl pyrrole for P(NMPY) (designated as sample B), 0.05 M each pyrrole and N-methyl pyrrole for P(NMPY-PY1) (designated as sample C), and 0.025 M pyrrole and 0.075 M (N-methyl pyrrole) for P(NMPY-PY2) (designated as sample D). 0.1 M tetraethyl ammonium tetrafluoroborate (Et_4NBF_4) has been used as electrolyte in the solvent propylene carbonate for the preparation of these films. The polymerization has been performed at 273 K in an inert atmosphere with an indium-tin oxide (ITO) coated glass plate as anode and platinum foil as cathode. Before polymerization the reaction mixture was thoroughly degassed by

passing dry nitrogen through the solution for 60 minutes. The dopant concentration [7] was determined (within ± 5% accuracy) from the loss of weight in these polymers after dipping them in ammonia for different intervals of time (10 seconds–30 minutes). The room temperature conductivities of all the samples of A, B, C and D have been plotted as functions of BF_4^- ion concentration in Figure 1. For making Schottky junctions, gold electrode of 5 mm diameter were vacuum deposited on one side and indium electrode of 1mm diameter on the other side of these polymer films. Before depositing indium the gold deposited films were annealed at 353 K for 100 hours. Current-voltage (I-V) characteristics were recorded with the help of Keithley's 617 electrometer, 220 current source and 2000 DMM interfaced with a PC.

RESULTS AND DISCUSSION

Four samples of PPY have been designated as A1, A2, A3, and A4. Their bulk conductivity and the corresponding concentration of BF_4^- ions are given in Table 1. Sample A1 is fully doped sample having the conductivity of 56.2 Ω^{-1} cm^{-1}. As a representative result the forward and reverse bias current density vs. voltage (J-V) (where J = I/A, A is the area of the device) characteristics of A1 are shown in Figure 2. The forward and reverse bias characteristics of A1 are almost symmetrical, therefore rectification constant r ≈ 1. A very high value of carrier concentration (~10^{22} cm^{-3}) and a very thin depletion width (~6 Å) has been obtained

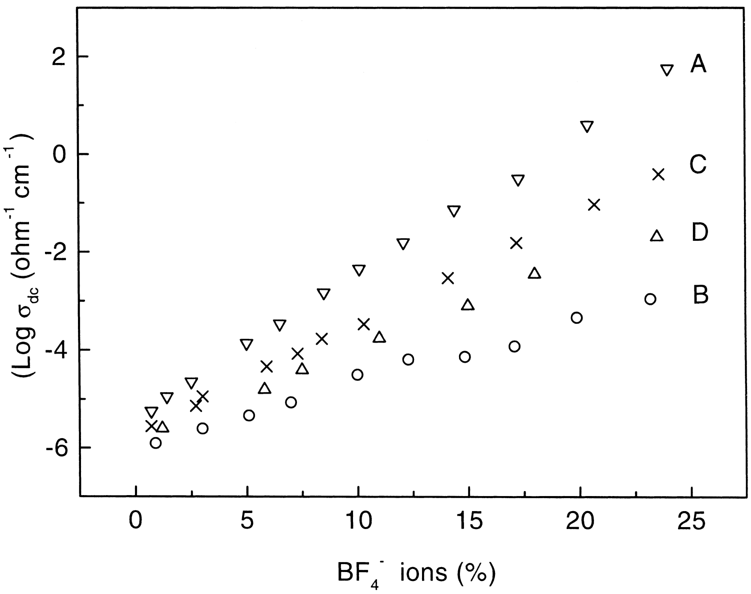

Figure 1. Variation of room temperature dc conductivity of different samples of PPY, P(NMPY), P(NMPY-PY1), and P(NMPY-PY2) with BF_4^- ions concentration.

Table 1. Different Parameters of In-Polymer Junctions for Various Samples of PPY (A), P(NMPY) (B), P(NMPY-PY1) (C), and P(NMPY-PY2) (D)

Sample No.	Bulk Conductivity σ_{dc} (Ω^{-1} cm^{-1})	BF_4^- ions concentration (%)	η	r at 0.3 V
A1	5.62×10^{1}	24.0	7.03	1.0
A2	1.58×10^{-2}	12.1	6.92	2.5
A3	2.33×10^{-4}	6.1	5.52	6
A4	1.12×10^{-5}	1.4	4.13	10
B1	1.12×10^{-3}	23.3	2.7	172
B2	1.2×10^{-4}	17.1	3.80	210
B3	2.33×10^{-5}	10.0	4.54	150
B4	2.1×10^{-6}	3.0	6.82	95
C1	3.98×10^{-1}	23.6	6.54	1.0
C2	2.93×10^{-3}	14.1	5.21	1.8
C3	8.58×10^{-5}	7.3	4.03	19
C4	7.35×10^{-6}	2.7	3.53	16
D1	2.1×10^{-2}	23.5	1.48	1808
D2	3.55×10^{-3}	18.0	1.56	1808
D3	1.58×10^{-5}	5.8	2.1	428
D4	2.52×10^{-6}	1.2	2.3	424

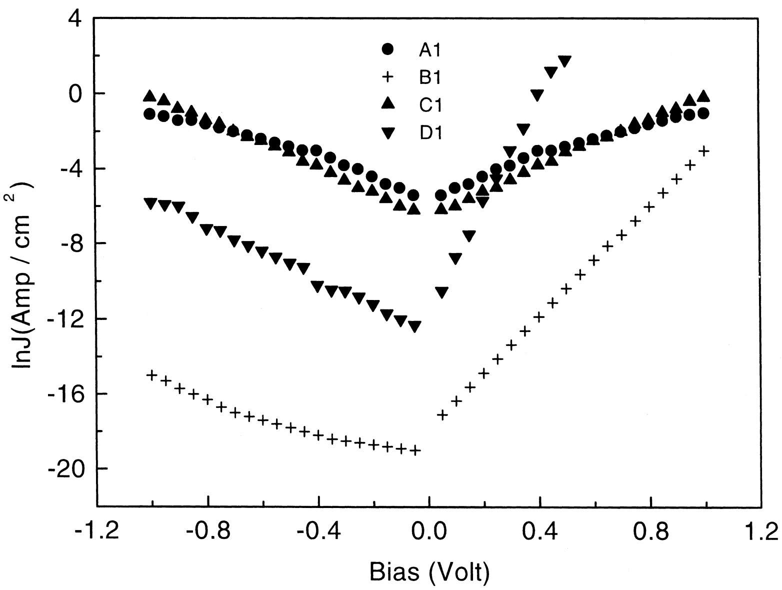

Figure 2. ln J-V characteristics of In-A1, In-B1, In-C1 and In-D1 junction.

from C-V characteristics (results not shown). This may be because of heavy doping, a very thin barrier is formed where transport may occur through tunneling. The forward and reverse bias characteristics of A2 and A3 were not symmetrical but the rectification constant was also not high (~2.5, 6 at 0.3 V). The rectification constant for A4 is 4 (Table 1). The slope of forward bias ln J vs. V lies in the range ≈ 5-12. The J-V behavior according to Child's law ($J \propto V^2$) [8] has not been observed even for higher voltages. However, space charge limited current (SCLC) caused by the traps at the interfacial region between metal and polymers can be possible. The other possibility of non-linear J-V characteristics for low doped samples is a bulk limited Poole-Frenkel emission. Non-linear curves have been obtained by plotting ln (J/V) vs. $V^{1/2}$ (results not shown). This rules out the possibility of Poole-Frenkel effect [9].

The Richardson's equation which has been used in the present investigation for all the samples is given by [6, 8, 10]:

$$J = J_0 \exp (eV/\eta k_B T) \tag{1}$$

where

$$J_0 = A^* T^2 \exp(-\phi_B / k_B T) \tag{2}$$

and A^* is the effective Richardson's constant, ϕ_B is the effective barrier height, k_B is the Boltzmann's constant, η is the ideality factor, V is the applied voltage, e is the electronic charge and T is the temperature at which measurements are performed. The ideality factor calculated from the slope of ln J vs. V plots is ~ 4 –7 for the samples A1, A2, A3, and A4 (Table 1). Samples A1 and A2 have a higher carrier concentration, which results in narrow depletion width and which may be the reason for poor rectifying behavior. The conductivity is proportional to the density of charge carriers and the addition of N-substituted pyrrole lowers the conductivity, which in turn may be due to the lowering of charge carrier concentration, thus resulting in a wider depletion width and better junction behavior.

The samples of P(NMPY) are designated as B1, B2, B3, and B4. The forward and reverse bias ln J- V characteristics of B1 having bulk conductivity value of $1.12 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ are shown in Figure 2. The bulk conductivity and corresponding concentration of ions of B1, B2, B3 and B4, are given in Table 1. The slope of ln J vs. V characteristics is greater than 2 and non linear ln (J/V) vs. $V^{1/2}$ characteristics rules out Poole-Frenkel emission. The rectification constant for all the samples lies in the range 100-200 (at 0.3 V). This rectification constant is better than that of In-PPY junction. The ideality factor η lies in the range ≈ 3-7 (Table 1). The higher values of η for B3 and B4 may be due to the higher insulating nature of the polymer. Therefore, in order to increase the conductivity, copolymers of pyrrole and N-methyl pyrrole have been prepared. The four samples of the copolymer P(NMPY-PY1) have been designated as C1, C2, C3, and C4. The values of bulk dc conductivities and corresponding BF_4^- ion concentration and the diodes' parameters (η and r) are given in Table 1. As a representative result forward and reverse bias characteristics of sample C1 are shown in Figure 2. The slope of these characteristics are greater than 2 and Poole Frenkel emission is also not applicable in this case. Almost symmetric characteristics have been obtained for C1. The higher values of carrier concentrations ($\sim 10^{21}$ cm^{-3}) and very thin depletion layer (~8Å) indicate the probability of tunneling mechanism in C1. For the samples C2, the ideality factor is ~ 5 and for C3 and C4, it is ~ 4 and 3.5, respectively. But the rectification constant is not high for both the samples (19 and 16 at 0.3V). It was decided to further increase the content of N-methyl pyrrole. The four samples of P(NMPY-PY2) have been designated as D1, D2, D3 and D4. Their values of bulk conductivity and BF_4^- concentration and the diodes' parameters (η and r) are given in Table 1. Forward and reverse bias J-V characteristics for samples D1, D2, D3 and D4 are shown in Figure 3. The slope of ln J vs. V plots is greater than 2 and ln (J/V) vs. $V^{1/2}$ characteristics are non-linear. The values of η and r for samples D1, D2, D3 and D4 are given in Table 1. The values of ideality factor for sample D1 and D2 are 1.48 and 1.56, respectively, and are very close to 1. Moreover sample D1 has very high rectification constant (≈ 1808). In fact, similar results were obtained for Al-polymer junction and rectification constant for Al-D1 sample was 1507 [10]. The reverse bias current increases gradually in all the samples in the entire range of measurement. This is unlike conventional semiconductors, where current increases rapidly at the break down voltage. The behavior is similar to that we obtained for Al-PPY-derivatives junctions [10].

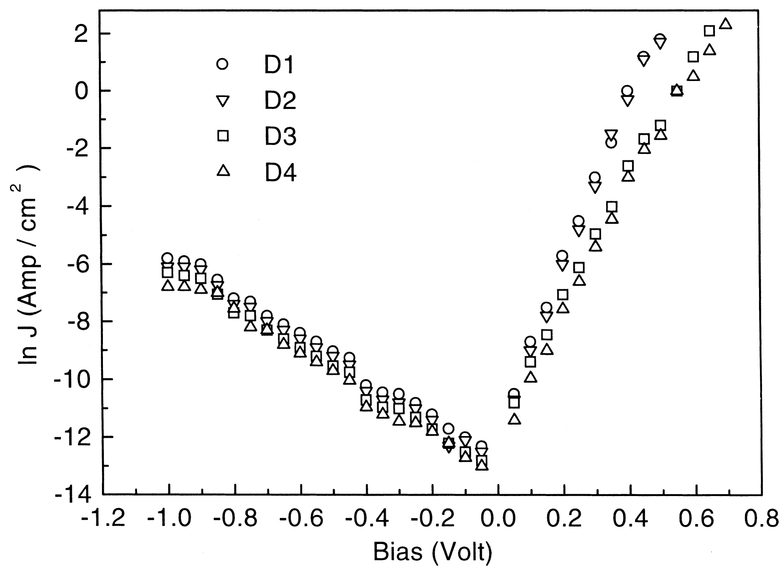

Figure 3. ln J-V characteristics of various In-P(NMPY-PY2) junctions on the samples D1, D2, D3, and D4.

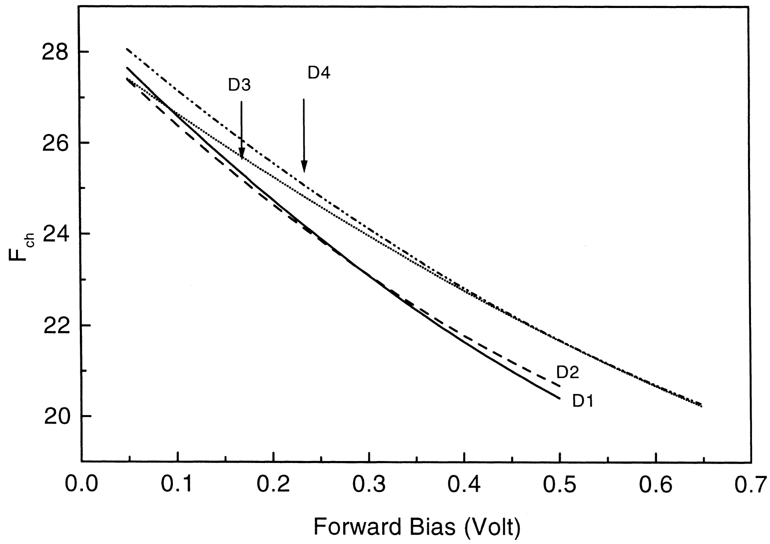

Figure 4. Chot plots of ln-P(NMPY-PY2) junctions.

The Chot plots [10, 11] for all the samples were obtained by using the expression:

$$F_{ch} = (eV / 2\eta\, k_B T) - \ln (JA/BT^2) \quad (3)$$

where B is a unit current constant (1 Amp/K^2). The Chot plots of all the samples decrease with an increase in applied voltage. This indicates that the junction primarily controls J-V behavior [10, 11]. The Chot plots of A1, B1, C1, and D1 are shown in Figure 4.

It is not very successful attempt to make an ideal Schottky junction but samples D1 and D2 are promising candidates for making Schottky junction diodes, from copolymer of pyrrole and N-methyl pyrrole. One can conclude that by optimizing dopant concentration and optimizing the conductivity values a good junction behavior can be obtained.

CONCLUSION

Out of the various polymers prepared in the present investigations the copolymer with 0.025 M pyrrole and 0.075 M N-methyl pyrrole having bulk conductivity ~ $10^{-2} - 10^{-3}\ \Omega^{-1}\ cm^{-1}$ is a promising candidate, for making Schottky junction devices because of better values of η and r. Search for other polymers with suitable conductivity values for making Schottky junctions is under investigation.

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