Electrical Properties of Metal (Indium)/Polyaniline Schottky Devices

S. S. PANDEY,[1] M. K. RAM,[1] V. K. SRIVASTAVA,[2] B. D. MALHOTRA[1]

[1] Biomolecular Electronics and Conducting, Reasearch Group, National Physical Laboratory, New Delhi—110012, India

[2] Chemistry Department, University of Ghorakhpur, Ghorakhpur, U.P., India

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ABSTRACT: Schottky devices were fabricated by thermal evaporation of indium on chemically synthesized polyaniline, poly(*o*-anisidine), and poly(aniline-*co*-*ortho*-anisidine) copolymer. Electrical characterization of each of these devices was carried out using current (I)–voltage (V) and capacitance (C)–voltage (V) measurements. The value of various junction parameters such as rectification ratio, ideality factor, and barrier heights of an In/poly(aniline-*co*-*o*-anisidine) Shootky device were found to be 300, 4.41, and .4972 V compared to the values of 60, 5.5, and 0.5101 V obtain for an In/polyaniline device, respectively. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2745–2748, 1997

INTRODUCTION

Organic polymers having extended π-electron conjugation have recently attracted much attention largely because of their many projected applications in electrochromic displays, lightweight batteries, EMI shielding, and molecular electronics.[1–5] Conducting polymers are "molecular" analogs of inorganic semiconductors and exhibit high electronic mobilities when doped. The ability to prepare junctions with well-defined electrical properties is a key step toward the development of polymer-based solid-state electronic devices.[6,7] Among the molecular electronic devices, Schottky devices based on conjugated polymers such as polypyrrole, polythiophene, and polyaniline have received considerable attention due to their excellent electrical characteristics.[8–11] The performance of a Schottky diode is known to depend upon various junction parameters such as barrier height, ideality factor, and work function of the semiconducting polymers.[12,13]

Schottky devices based on a conducting polymer (polypyrrole/polyaniline) and metal (In, Al, Sn, and Pb) have recently been fabricated.[14,15] It was revealed that an In/polyaniline Schottky diode exhibits relatively better rectification characteristics over various other metal (Al, Sn, Pb, Sb)/polyaniline Schottky devices. One of the major problems heralding commercialization of the majority of conducting polymers including polyaniline as an active semiconducting device component pertains to their poor processibility. This is largely because most of the conducting polymers are not completely soluble in any of the known organic solvents. In this context, it was recently shown that poly(aniline-*co*-*ortho*-anisidine) is soluble in common organic solvents (chloroform, tetrahydrofuran, dimethylformamide, etc.) and exhibits a faster switching response time for its application as electrochromic display.[16]

In the present article, we report the results of our systematic studies carried out on In/polyaniline (PANI), In/poly(*o*-anisidine) and In/poly(aniline-*co*-*o*-anisidine). The results of current–voltage (I–V) and capacitance–voltage (C–V) measurements carried out on each of these devices were used to estimate the various junction parameters such as barrier height (ϕ), rectification ratio, ideality factor (n), and carrier concentration (N).

Correspondence to: B. D. Malhotra.

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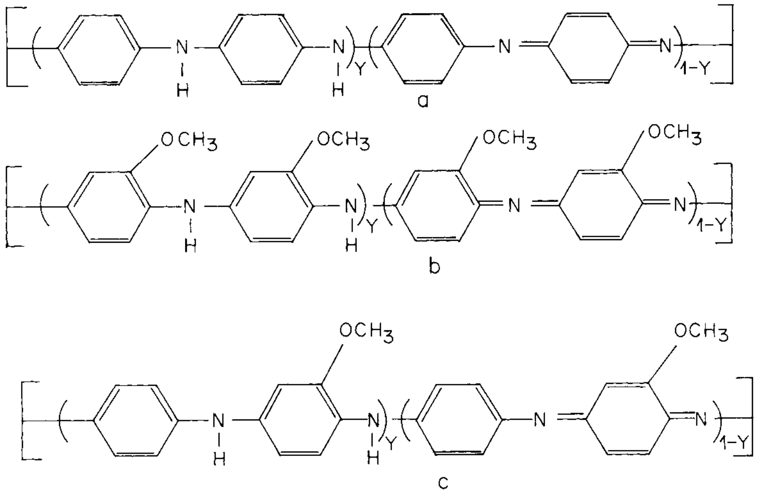

Figure 1 Structures of (a) polyaniline, (b) poly(*ortho*-anisidine), and (c) poly(aniline-*co*-*ortho*-anisidine).

EXPERIMENTAL

Conducting polymers like polyaniline (PANI), poly(*o*-anisidine) (POAS), and poly(aniline-*co*-*o*-anisidine) (PACOAS) (Fig. 1) were chemically synthesized using standard procedures reported elsewhere.[16] Each of these doped conducting polymers was filtered and dried under a dynamic vacuum. Schottky diodes were fabricated by thermally evaporating indium metal on respective pellets of each of the HCl-doped conducting polyanilines having thickness in the range of 100–150 μm for making top rectifying contact. In each case, the contact area was 3.94×10^{-2} cm^2. Back Ohmic contacts were made using an electrodag (E + 502, Acheson). A cross section of a metal/polyaniline heterojunction device is schematically shown in Figure 2.

Various In/polyaniline Schottky devices were characterized using I–V and C–V measurements conducted in a dark vacuum chamber with a microprocessor-based data acquisition system using a Kiethley (Model 617) electrometer. The I–V data were acquired by an IEEE-488 card interfaced to a personal computer.

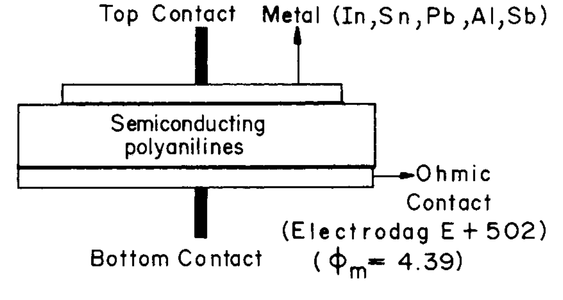

Figure 2 Schematic of a metal/polyaniline heterojunction.

RESULTS AND DISCUSSION

Figure 3 shows the results of I–V measurements carried out on an In/HCl-doped PANI/E + 502 electrodag (curve 1), In/HCl-doped POAS/E + 502 (curve 2), and In/HCl-doped PACOAS/E + 502 (curve 3) structures. The striking asymmetry ob-

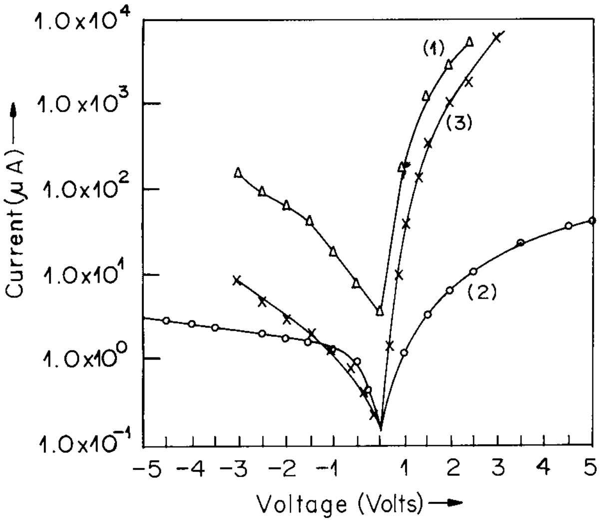

Figure 3 I–V characteristics of (1) In/HCl-doped polyaniline/E + 502 Eletrodag, (2) In/HCl-doped poly(*ortho*-anisidine), and (3) In/HCl-doped poly(aniline-*co*-*ortho*-anisidine).

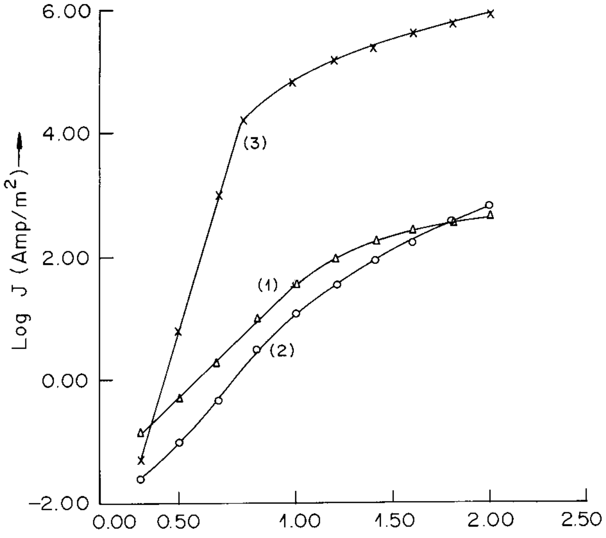

Figure 4 log J versus V plots of (1) In/polyaniline, (2) In/HCl-doped poly(*ortho*-anisidine), and (3) In/HCl-doped poly(aniline-*co-ortho*-anisidine).

served in the forward and reverse bias conditions in In/conducting polymer heterojunctions indicates the buildup of space charges at the interface. C–V characteristics as shown in Figure 3 are similar to those obtained for metal (In)/vacuum-deposited PANI and metal (In)/polypyrrole heterojunctions. The rectification ratios for In/polyaniline, In/poly(*o*-anisidine), and In/poly(aniline-*co*-*o*-anisidine) Schottky diodes obtained at 0.6 V were found to be 60, 10, and 300, respectively. It is interesting to see that indium exhibits a better rectification with polyaniline and poly(aniline-*co*-*o*-anisidine), whereas it shows poor rectification with poly(*o*-anisidine). Current passing through a Schottky barrier follows the Richardson–Schottky equation[17]:

$$J = J_0 \exp(qV/nkT) \tag{1}$$

$$J = A^{**}T^2 \exp(-q\phi/kT) \tag{2}$$

where A^{**} is the Richardson constant, k is the Boltzmann constant, T is the absolute temperature, q is the electronic charge, V is the applied bias voltage, n is the ideality factor, and J_0 is the reverse saturation current density.

The ideality factors and barrier heights were calculated by plotting log J versus V (Fig. 4). The results are given in Table I, which also includes the values of other electronic parameters obtained for metal/conducting polymer heterojunctions. The nonlinearity seen at about 1.2 V in Figure 4 (curve 1) for the In/polyaniline heterojunction is perhaps due to the existence of a space charge limited region or the effect of bulk resistance.[18]

Figure 4 (curve 2) shows log J versus V characteristics for the In/HCl-doped poly(*o*-anisidine) interface. It can be seen that the fit is nonlinear, indicating that the origin of current is either due to the Poole Frenkel effect or to the presence of space charges.[19]

Curve 3 (Fig. 4) shows the variation of log J versus V obtained for the In/HCl-doped (aniline-*co*-*o*-anisidine) heterojuction. The linearity seen in the log J versus V plot up to about 0.8 V indicates excellent Schottky characteristics. The absence of any Schottky behavior beyond 0.8 V is perhaps due to the presence of bulk resistance at the In/polyaniline interface. The improved rectification obtained for In/poly(aniline-*co*-*o*-anisidine) junctions can perhaps be due to modulation of its surface during copolymerization resulting in its more intimate contact with In metal. Similarly, results with regards to the improved switching response were obtained in the case of electrochromic displays fabricated using poly(aniline-*co*-*o*-anisidine). These results suggest that copolymerization perhaps modifies the symmetry of the polymer chain and modulates both intramolecular and intermolecular forces in such a manner that poly(aniline-*co*-*o*-anisidine) exhibits physical and mechanical properties far different from those of the parent homopolymers,[20] polyaniline and poly(*o*-anisidine).

The value of ideality factors obtained for In/polyaniline and In/poly(*o*-anisidine) and In/poly(aniline-*co*-*o*-anisidine) heterojunctions were found to be 5.5, 9.65, and 4.4, respectively. The higher values of ideality factors obtained for In/conducting polymer heterojunctions perhaps arises due to the presence of a large number of defects containing trapped charges in the amorphous conducting polymer. Besides this, various other phenomena like bulk resistance and Poole–Frenkel effects may perhaps be responsible for the observed higher values of ideality factors.

It is known that the barrier height of a metal/semiconductor heterojunction is largely dependent upon the value of the carrier concentration. The carrier concentration of each of these devices (Table I) was estimated using the following Mott–Schottky equation[21]:

$$N = -2A/q\epsilon\epsilon_0\{dV/d(1/C^2)\} \tag{3}$$

Table I Electronic Parameters for Various In/Polyaniline Heterojunctions

Heterojunction Materials	Rectification Ratio	Barrier Height (V)	Ideality Factor (n)	Carrier Concn (N)
In/polyaniline	60	0.5101	5.50	1.0×10^{17}
In/poly(*ortho*-anisidine)	10	0.4907	9.65	1.2×10^{15}
In/poly(aniline-*co*-*ortho*-anisidine)	300	0.4972	4.41	2.0×10^{16}

where N is the charge carrier concentration, q is the electronic charge, A is the area of contact, ϵ^0 is the permitivity of free space, ϵ is the dielectric constant of material, C is the capacitance, and V is the reverse voltage.

Results of $C-V$ measurements performed on In/polyaniline, In/poly(*o*-anisidine), and In/poly(aniline-*co*-*o*-anisidine) were used to estimate the value of various other junction parameters obtained for these devices. The poor diode characteristics obtained for In/poly(*o*-anisidine) were attributed to low barrier hight (0.4907 V) and a fairly high ideality factor (9.65).

The improved diode performance obtained for In/polyaniline-*co*-*o*-anisidine in spite of low carrier concentration and barrier height, compared to In/polyaniline and In/poly(*o*-anisidine), is perhaps due to structural modulation in poly(aniline-*co*-*o*-ansidine, allowing it to make a better contact with the In metal.

CONCLUSIONS

It has been shown that it is possible to fabricate Schootky diodes based on polyaniline, poly(*o*-anisidine), and poly(aniline-*co*-*o*-anisidine). Excellent rectification has, however, been obtained in the case of In/poly(aniline-*co*-*o*-anisidine junction at 0.6 V. The observed deviation from the Schootky behavior for these devices seen at higher voltage has been explained in terms of either the Poole–Frenkel effect or due to the presence of a large number of defects containing the trapped charges present at the In/conducting polymer interfaces.

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