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COMPLEX IMPEDANCE SPECTROSCOPY OF THE INTERFACE BETWEEN ALUMINIUM AND EMERALDINE BASE POLYANILINE

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ABSTRACT: Emeraldine base polyaniline (PANI) forms semiconducting organic solid films when spin coated from xylene solution. An interface between aluminium contacts to emeraldine base polyaniline films were studied using complex impedance spectroscopy and current-voltage characteristics measurements. The current density-voltage curve is asymmetric and non-ohmic and shows Schottky barrier type rectification. The complex impedance spectra are semi-circles which reveal the existence of a region depleted of mobile charge carriers. It is modelled by an equivalent circuit consisting of one parallel RC circuit. The depletion region strongly depends on externally applied bias voltage, rendering very high impedance when a reverse bias voltage is applied.

Key words/phrases: Impedance, polyaniline, Schottky barrier, semiconductor, spectroscopy,

INTRODUCTION

Metal contacts to semiconductors form interfaces that manifest basic features of many rectifiers, metal-semiconductor devices such as field-effect transistors, sensors, and other surface junction devices. Hence electrical contacts to semiconductors are critical elements in a number of important technologies.

A significant amount of research has been carried out on the use of semiconducting polymers in their neutral (or unintentionally doped) states as active materials in electronic and optoelectronic devices. The overall quantum efficiency of polymer-based light-emitting diodes (PLEDs) is strongly influenced by the injection of electrons and holes at the respective metal/polymer interface

(Parker, 1994). Usually indium-doped tin oxide (ITO) coated glass is used as a hole injecting contact, while the counter electrode is a metal having low work function that enables electron injection into the conduction band of the polymer. In this context, the overall device efficiency may be limited by the injection efficiency of the minority carriers. There has been a breakthrough in the area of PLEDs (Burroughes *et al.*, 1990; Gustafsson *et al.*, 1992; Berggren *et al.*, 1994). For instance, multicolour PLEDs were made from side-chain substituted thiophene polymers exhibiting electroluminescence over the full visible spectrum, from the blue into the near-infrared (Berggren *et al.*, 1994). White light emission from Al/PANI/ITO and Mg/PANI/ITO devices is also reported (Chen *et al.*, 1996).

Although doping increases the electrical conductivity of polymers (Shirakawa *et al.*, 1977), neutral or unintentionally doped conjugated polymers such as PANI, polypyrrole (PPy), and polythiophene (PT) have reasonably high conductivity to be categorized as semiconducting organic polymers. However, there is little information on the mechanisms that control charge carrier transport across the interface between metals and the polymers, where chemistry induced defects formed when metal atoms are deposited on the conjugated polymer surface are likely to play a crucial role (Bantikassegn Workalemahu *et al.*, 1993a,b; Dannetun *et al.*, 1993). Some interdisciplinary studies of polymer-metal interfaces show that, during the early stages of interface formation, deposited aluminium atoms form covalent bonds with the carbon atoms of the α-linkage in polythiophenes (Salaneck and Bredas, 1996). Other reports show that low work function metals such as aluminium or calcium readily react with oxygen-containing parts of the polymer or polyelectrolyte, thus forming a thin insulating layer (Bantikassegn Workalemahu *et al.*, 1993b).

Polyacetylene (PA) was found not only to be the first conducting polymer (Shirakawa *et al.*, 1977), but was also the first polymer to be tested as a semiconductor in a diode (Kaniki, 1986). Subsequent improvements in synthesis, stability, and diode processability of various organic polymers have led to numerous studies on polymeric diodes made from, for example, thiophene oligomers (Fichou *et al.*, 1989; De Leeuw and Lous, 1994; Lous *et al.*, 1995) and poly(3-alkylthiophene) (Tomozawa *et al.*, 1989; Omhori *et al.*, 1990; Gustafsson *et al.*, 1991; Assadi *et al.*, 1992; Gomes *et al.*, 1993). These

Schottky diodes were made from undoped, or unintentionally doped, conjugated polymers (having low electrical conductivity) whose currents at a forward bias were limited by bulk resistance.

We have investigated a series of polymer-based sandwich structures for which one of the electrodes is a vacuum evaporated aluminium layer. Two-terminal devices based on junctions between p-type conducting polymers doped with large polymeric anions such as polystyrenesulphonate (PSS$^-$) and low work function metals, e.g. aluminium, show symmetrical but non-ohmic current-voltage characteristics (Bantikassegn Workalemahu *et al.*, 1993a,b; Bantikassegn Workalemahu and Inganas, 1996; 1997a). For instance, when poly(3-,4-ethylenedioxythiophene) (PEDOT) and PPy were doped with PSS$^-$ anions, their contacts with aluminium show metal-insulator-semiconductor (MIS) type of junctions (De Leeuw and Lous, 1994; Lous *et al.*, 1995; Bantikassegn Workalemahu and Inganas, 1996; 1997a). However, the same polymers doped with small anions such as ClO^-_4 (Bantikassegn Workalemahu *et al.*, 1993a,b; Bantikassegn Workalemahu and Inganas, 1996; 1997a), and poly[3-(4-octylphenyl)-2,2'-bithiophene] (PTOPT) doped with PF^-_6 gave a metal-semiconductor (MS) type contacts. Diodes made of neutral (or unintentionally doped) PTOPT as an active semiconducting polymer gave a Schottky barrier type rectification of about 10^5 (Bantikassegn Workalemahu and Inganas, 1997b).

Generally, the high conductivity of organic polymers lies in their level of conjugation; the more extensive the conjugation, the higher the conductivity PANI is a peculiar polymer having different oxidation states with varying conjugation levels. These are leucoemraldine, protoemeraldine, and emeraldine base polyanilines. The three oxidation states can either partially or fully be protonated, where the nitrogen atoms that bridge the backbone benzene rings are the protonation sites. The insulator-to-semiconductor transition occurs as a result of such protonation, known as protonic acid doping. By virtue of its stability, and particularly its highly conjugated π-system, emeraldine base PANI has higher conductivity than the others. This makes it more suitable to test it as a semiconducting material in devices. We report here the electrical properties of junctions between aluminium and emeraldine base polyaniline. The complex impedance spectroscopy as well as current-voltage measurements are used for characterization. Schottky barrier theory is applied to interpret the data.

EXPERIMENTAL DETAILS

The transparent conducting ITO on glass was partly covered with photoresist, and the exposed ITO was etched with a mixture of concentrated HCl, HNO_3, and water, 48:4:48 by volume, respectively. The etched portion of the ITO/glass provided a region convenient for electrical contacts to the aluminium layer deposited later. The photoresist was removed using acetone, and then the surface was washed with detergents and distilled water, and rinsed with ethanol.

Emeraldine base polyaniline was dissolved in xylene at a 1:3 ratio by weight and stirred using a magnetic stirrer for about six hours, until a thick solution was obtained. This solution was then centrifuged for about two hours, at the end of which a clear yellowish and slightly viscous xylene solution of PANI was separated and stored in a cold environment. Using a spinner with a remote control system, ITO/glass substrate was spin coated with PANI from the xylene solution at the rate of 1000 rpm yielding uniform, high quality yellowish thin film of about 200 to 300 nm thickness.

Using Edwards Auto 306 vacuum evaporator, about 500 nm thick aluminium strips were deposited at a pressure of about 10^{-6} Torr as the required low work function metal contact to polyaniline. Part of the Al strip was over the PANI/ITO, while the remaining part was over the glass from which the ITO was etched out. This was to avoid possible damage of Al and the polymer beneath when electrical contacts are made. The active area was about 0.1 cm^2. The diode was forward biased when the aluminium electrode was connected to a negative terminal of the voltage source. The sandwich structure of Al/PANI/ITO (see Fig. 1) provided a means of current-voltage and complex impedance measurements. The samples were kept in the dark, at room temperature in dry air during all measurements.

Current-voltage characteristics were measured with the HP 4145B semiconductor parameter analyzer together with the HP 16058A test fixture. The applied voltage was scanned between -3V and +3V. A computer interfaced HP 4192A LF impedance analyzer was used to measure the complex impedance. The bias voltage applied to the diode ranged between -3V and +3V in steps of 1V. For every bias voltage used, a sinusoidal oscillation voltage of $V_{rms} = 10$ mV was applied. The frequency was scanned between 300 Hz and 10^6 Hz for each bias. With the help of the EQUIVCRT programme (Boukamp, 1993), Cole-Cole plots were generated and analyzed.

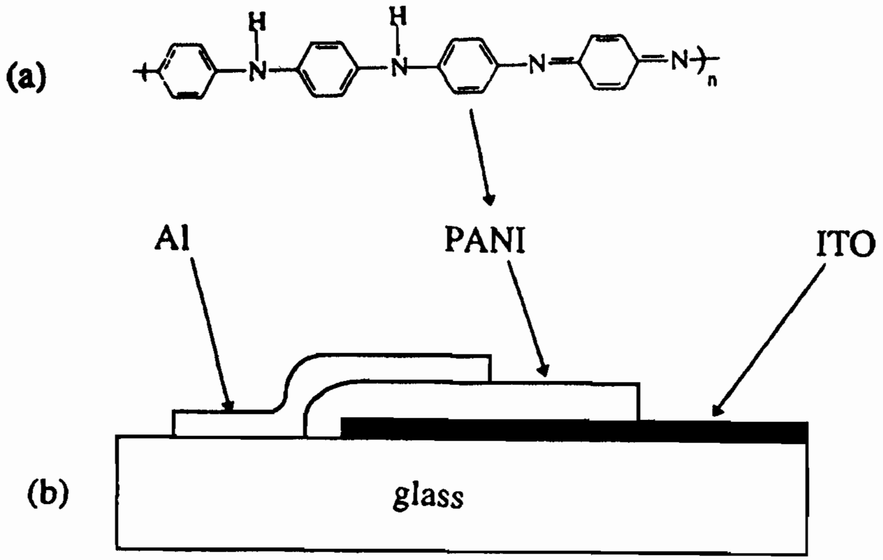

Fig. 1 (a) Geometric structure of emeraldine base polyaniline (PANI), and (b) Schematic diagram of Al/PANI/ITO/glass device.

RESULTS AND DISCUSSION

Doping (in most cases oxidation) of polymers creates new electronic states in the forbidden energy gap providing new optical transitions in addition to the interband transition. These transitions from the valence band to the new band gap states are referred to as bipolaron transitions because polarons are rarely observed, since it is energetically favourable for the polarons to combine and form bipolarons (Onodera, 1984). It was reported that PTOPT/Al junction forms a Schottky-type barrier (Bantikassegn Workalemahu and Inganas, 1997b).

J-V characteristics

Figure 2 shows the J-V characteristics of the Al/PANI/ITO device in the dark. The forward voltage corresponds to the Al being negative. The J-V curves are asymmetric and non-linear. The forward current increases exponentially at low voltage regions. The device clearly exhibits a rectification behaviour in the dark with a turn-on voltage at about 1V.

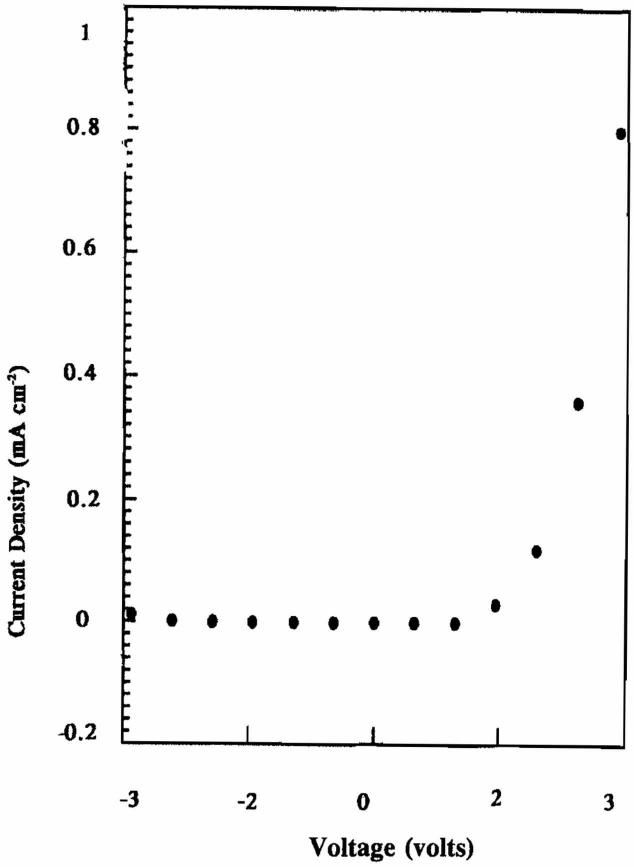

Fig. 2. J-V characteristics of emeraldine base polyaniline/aluminium diode.

A semi-logarithmic plot (see Fig. 3) of the forward current density (J) versus the applied voltage (V) shows that the forward current increases exponentially in the applied voltage between 0.5V and 1.5V. This exponential dependence can be attributed to a formation of the depletion region near the Al/PANI interface (see also the section, complex impedance spectroscopy).

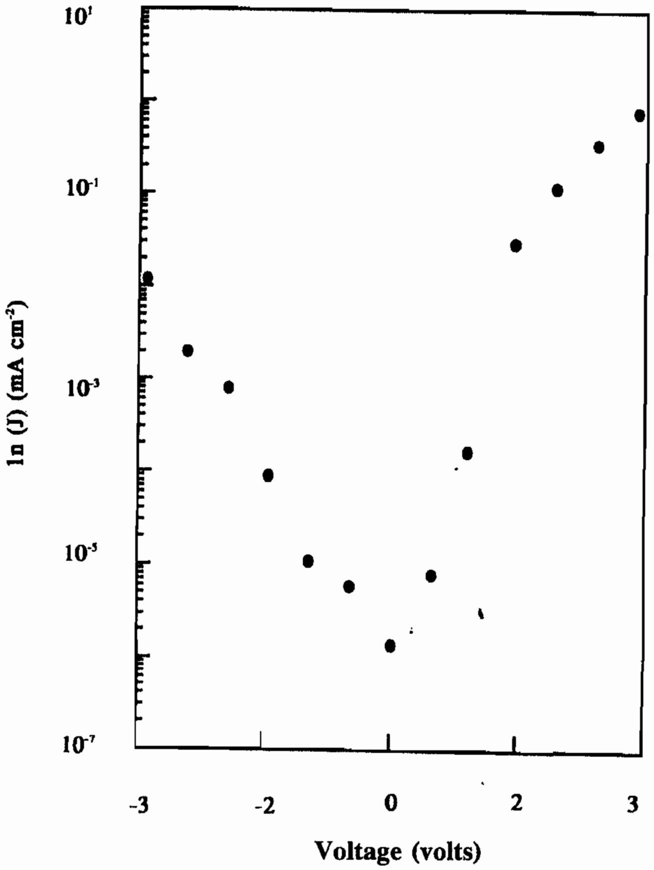

Fig. 3. Semilog of J-V curve of emeraldine base PANI/Al diode.

According to the Schottky barrier theory (Sze, 1981), p-type semiconductors form a rectifying barrier at the interface when the work function of the metal is smaller than that of the semiconductor. However, if the work functions are in the reverse order, such as in the sandwich structure of Au/PPy(PSS)/Au, (where PPy is doped with PSS$^-$), the device gives an ohmic J-V characteristics rather than rectifying (Bantikassegn Workalemahu *et al.*, 1993b). Since neutral

PANI behaves as a p-type semiconductor, its work function is in between those of Al (4.2eV) and ITO (4.9eV), yielding a rectifying contact with aluminium.

A Schottky barrier device with a rectifying J-V characteristics usually follows the standard thermionic emission/diffusion theory for conduction across the junction (Sze, 1981). In this theory the current is assumed to be controlled only by the transfer of carriers across the interface of Al/PANI. The J-V relationship for the Schottky barrier diode is given by:

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

where J is current per unit area, J_0 the reverse saturation current density, q the electronic charge, V the applied forward voltage, T the absolute temperature, *k* the Boltzmann constant, and n the ideality factor of the diode. When $n = 1$ the Schottky barrier is ideal, whereas for higher values, *e.g.*, $n \geq 2$, a mid-gap recombination of electrons and holes occurs.

The barrier height ϕ_b can be deduced from J_0 using the Richardson equation (Tomozawa *et al.*, 1987) given by:

$$J_0 = A^*T^2\exp(-q\phi_b/kT) \tag{2}$$

where A* is the effective Richardson constant taken to be 120 $Acm^{-2}K^{-2}$ for a free electron. This value is usually assumed for a Schottky diode with p-type organic semiconductor in barrier height calculations (Tomozawa *et al.*, 1987; Koezuka and Etoh, 1983). When J_0 is very small compared with the current density of experimental interest, the contact will effectively block current flow for one sign of the applied voltage (reverse bias). This type of device will also display an exponentially increasing current when the bias voltage is of the opposite polarity (forward bias). When all other factors are held constant, the very low value of J_0 corresponds to a better rectification property. For such a low value of the reverse saturation current density, J_0, the barrier height is considered high. This phenomenon occurs when electropositive (low work function) metals are in contact with p-type semiconductors (Kumar *et al.*, 1993).

From eqn. (1), with $qV >> kT$, ln J versus V is expected to be linear in the vicinity of the turn-on with the intercept corresponding to J_0. All I-V characteristics may involve more than one type of charge transport mechanism, such as tunnelling (Assadi *et al.*, 1992), generation-recombination, and leakage currents (Barus and Donoval, 1993). As observed from the semi-logarithmic plot of the J-V curve, there could be more than one mechanism of charge transport. The upper limit of the interval is influenced by the series resistance which is indicative of electrical transport that is dominated by space charge limited current (SCLC) (Gomes *et al.*, 1993; Lous *et al.*, 1995), while possibly other current transport mechanisms, especially for structures like Al/PANI/ITO having high barrier height, push the lower interval limit up, thus reducing the linear region. It is therefore difficult to choose the linear range that corresponds to the exponential increase of the current at a forward bias. According to Fig. 3, a linear relationship in the forward bias indicates the formation of a Schottky barrier. The saturation current density (J_0) (see eqn. 2) is obtained from the intercept of the linear plot of Fig. 3. Parameters extracted from Fig. 3 are listed in Table 1.

Table 1. Parameters from the J-V curve of Fig. 3. J_0, the reverse saturation current density; ϕ_b, barrier height; n, the ideality factor; γ, the rectification ratio.

J_0 (A cm^{-2})	ϕ_b (eV)	n	γ
1.0×10^{-10}	1.6	2.3	10^2

Complex impedance spectroscopy

Information about the bulk resistance and the Schottky barrier junction can be obtained by complex impedance measurements. Figure 4 shows the impedance spectroscopy results of the interface between aluminium and neutral polyaniline as a function of frequency and applied voltage. For each of the -3V and -1V reverse bias, and 1V and 3V forward bias voltages, on to which the V_{rms} = 10 mV sinusoidal oscillation voltage is added, the frequencies range between 300 Hz and 1 MHz. The filled points are the measured co-ordinates of the real and imaginary parts of the impedance. Theoretically Cole-Cole plot of the complex impedance is a semi-circle with its centre, the zero-frequency and the infinite-frequency intercepts on the Z_{real} axis (Cole and Cole, 1941). Usually the zero-frequency real impedance is obtained by extrapolation.

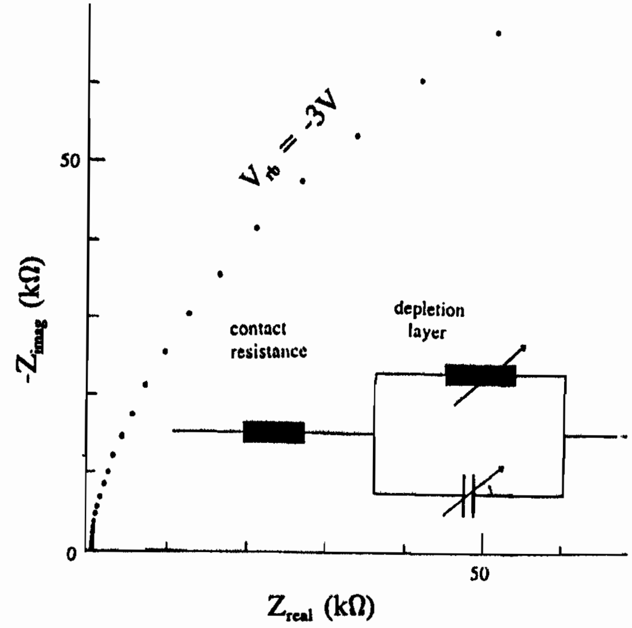
50
0
50
-Z_imag (kΩ)
Z_real (kΩ)
V_b = -3V
contact
resistance
depletion
layer

Fig. 4a.

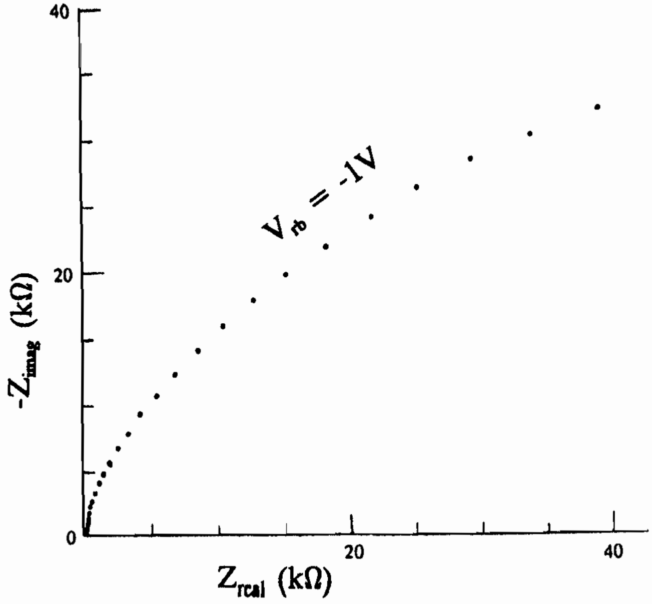
40
20
0
20
40
-Z_imag (kΩ)
Z_real (kΩ)
V_b = -1V

Fig. 4b.

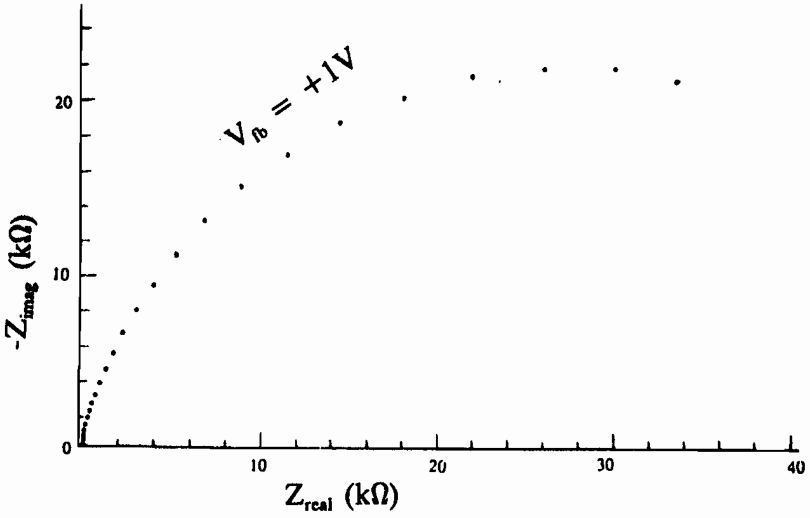

Fig. 4c.

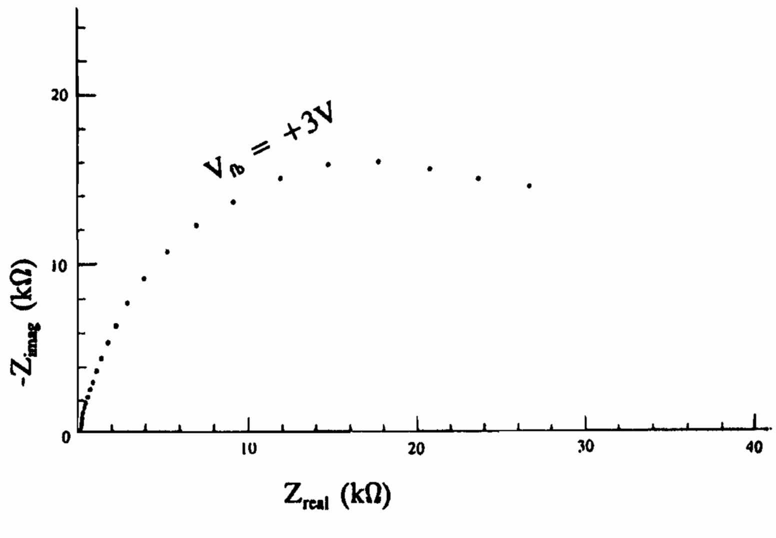

Fig. 4d.

Fig. 4. Cole-Cole plots of Al/PANI/ITO diodes. The equivalent circuit model is shown in the inset of (a), where the arrows indicate that the depletion layer depends on the applied bias voltage. (a) V_{rb}=-3V, (b) V_{rb} =-1V, (c) V_{fb}=1V, and (d) V_{fb}=3V, where rb and fb stand for reverse and forward bias, respectively.

The Cole-Cole plot thus generated is part of a semi-circle, each measured point being characteristic of the corresponding frequency value. Schottky barrier diodes are commonly analyzed by using an equivalent circuit as shown in the inset of Fig. 4(a). For complex impedance spectra of sandwich structures such as Al/PEDOT(PSS)/ITO and Al/PPy(PSS)/ITO, where PSS-doped PEDOT and PPy were used as active semiconductors, the diodes manifest two slightly overlapping semi-circles (Bantikassegn Workalemahu and Inganas, 1996; 1997a) which can be modelled by an equivalent circuit consisting of two parallel RC circuits in series. In the case of Al/PTOPT/ITO (Bantikassegn Workalemahu and Inganas, 1997b) and Al/PANI/ITO, where neutral polyaniline and PTOPT are used as active semiconductors, however, the complex impedance is a single semi-circle that can be represented by one parallel RC circuit in series with the contact resistance at infinite frequency, R. This single semi-circle supports a model where a single barrier, at the Al/PANI interface, is dominating the charge transport through the diode. There is no evidence for a partially or completely overlapping second semi-circle due to a barrier at the interface of the other electrode.

With the help of the EQUIVCRT programme, a circular fit for the complex impedance representation was performed, where the constant phase element (CPE), $Q = 1/[(j\omega)^n C]$, was used to estimate the value of the capacitance. When $n = 1$, the fit was ideal, and Q represented the imaginary component of the complex impedance yielding the corresponding capacitance, C. The parameters from the Cole-Cole plot are listed in Table 2. The resistance of the depletion region, and the corresponding depletion width decrease with increasing bias voltage, being largest at the highest reverse bias (R = 160 kΩ, and d = 196 nm at -3V), and smallest at the highest forward bias (R = 35 kΩ, and d = 30 nm at +3V). The corresponding capacitance increases. This is consistent with the J-V rectification characteristics.

Table 2. Parameters obtained from the Cole-Cole plots of the Al/PANI/ITO device. The negative sign represents the reverse bias voltage.

V_b (volts)	R (kΩ)	C (nF cm^{-2})	d (nm)
-3	160	15	196
-1	85	53	50
1	60	80	33
3	35	83	30

There are several possible factors that cause the formation of the interfacial insulating thin layer between aluminium and the bulk of the polymer. One important fact that needs to be considered, especially as many studies dealing with metal-polymer interphases have the low work function metals evaporated in a vacuum of 10^{-5} to 10^{-6} Torr, is the formation of the oxides of the deposited metals. Auger profiling analysis of Al/PPy and Au/PPy interfaces was reported (Inganas and Lundstrom, 1984/85) to manifest the formation of an insulating intermediate phase in the case of Al/PPy due to oxides of aluminium between the metal and the polymer, since the oxygen present in the polymer is more than sufficient for the formation of the insulating oxide at the Al/PPy interface. However, the Au/PPy junction showed only distinct metal and polymer phases (Inganas and Lundstrom, 1984/85). Moreover, reactions between aluminium and conjugated polymers are not unexpected. For instance, XPS and He(I)-UPS studies have shown that Al strongly reacts with surfaces of conjugated polymers, which leads to the formation of sp^3-carbon sites that influence the re-orientation of the molecular backbone (Dannetun *et al.*, 1993).

In our earlier studies of doped polymer junctions (Bantikassegn Workalemahu, *et al.*, 1993a,b; Bantikassegn Workalemahu and Inganas, 1996; 1997a,b), it was reported that reactions occur between the oxygen-containing group and the Al, thereby forming a highly resistive thin interfacial layer. The structural, chemical, and electrical nature of such interfaces play an important role in charge transport processes because dopant migration in conjugated polymers might lead to spontaneous undoping, thereby forming a graded dopant profile.

Other reports reveal that the distribution of dopants is inhomogeneous in the semiconducting polymers and can be changed by the application of bias voltage (Gustafsson *et al.*, 1990). Thus an important parameter that determines such a behaviour is the mobility of the dopants. A simple estimate of electric field ($E=V/d$) in the junction between the metal and the polymer yields 10^5 to 10^6 Vcm^{-1} for d = 100 to 10 nm at 1V. In this field even the low ionic mobility of 10^{-13} cm^{2}V^{-1}s^{-1} (Delabouglise, 1995) will give an ionic drift velocity of about 1 nm s^{-1}, high enough to change the profile of dopants in a very short time, influencing the electrical parameters during measurements. This may be a general mechanism affecting charge transport in metal/polymer junctions. However, further investigation is necessary to verify the mechanism.

CONCLUSION

We have constructed a Schottky-type device consisting of emeraldine base polyaniline polymer as an active semiconducting material and a low work function metal (Al) as a contact. The thermionic emission/diffusion model has been applied in order to interpret the J-V characteristics of the diode. The J-V measurements on Al/PANI/ITO sandwich structures show a Schottky barrier type diode with a rectification ratio of 10^2 at +3V/-3V, and an ideality factor of 2.3. The impedance of the depletion region at reverse bias voltages is much larger than the impedance at the corresponding forward bias, as seen from the complex impedance spectroscopy data. This is consistent with the rectification behaviour observed from the J-V curve. The complex impedance spectra clearly show that a single element, modelled as one parallel RC equivalent circuit, is sufficient to account for the diode. There are no extra layers at the interface.

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