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## Influence of the nature of contacts on the dark and photovoltaic characteristics of the Schottky junction between n-doped silicon and poly(4,4'-dipentoxy-2,2'-bithiophene)

Received: 27 December 1997 / Accepted: 24 April 1998

**Abstract** The dark and photovoltaic characteristics of the Schottky junction between n-doped silicon and a conducting polymer in its oxidised form, poly(4,4'-dipentoxy-2,2'-bithiophene), have been determined as a function of the nature of the electrical contact on the polymer side. It was found that the dark and photovoltaic performances of the device depended strongly on this contact. An aluminium contact is oxidised by the polymer and an aluminium oxide film forms between the polymer and the contact through which the forward current is controlled by charge injection. The devices assembled with indium tin oxide, platinum and gold contacts show better characteristics than the ones with aluminium contact; in the last three cases, however, a faradic charge transfer reaction on the contact, probably the oxidation of some amount of water contained in the polymer, affects the characteristics of the junction.

**Key words** Schottky junction · n-Doped silicon · Poly(4,4'-dipentoxy-2,2'-bithiophene)

### Introduction

It is frequently assumed that the characteristics of diodes and photodiodes based on organic materials can be entirely ascribed to parameters inherent to the core of the rectifying junctions, i.e. electrical properties of the organic substance (Fermi level energy, electrical conduc-

tivity, stability under current flow, etc.) and, in the case of photodiodes, to the possibility of exciton formation and their dissociation into free charges. However, the quality of the contact through which the organic substance is connected with the external circuit is also of utmost importance in the economy of the device performance.

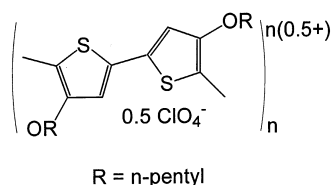
A number of papers deal with the use of conducting polymers, at various doping levels, in diode [1–5] or photodiode [5–7] construction. In all papers the characteristics of the systems were related only to the rectifying junction. Any contribution of the contacts on the organic materials was not taken into consideration.

In a previous paper, the characteristics of the Schottky junction between oxidised poly(4,4'-dipentoxy-2,2'-bithiophene) (pET2, Fig. 1), acting as a quasi-metal component, and n-doped silicon were reported [7]. The current-voltage (*i-V*) characteristic of the junction was found to be in accordance with a thermionic process of charge transfer at the Si/pET2 interface until very low forward voltage values, whereas it was found that the current flowing was space charge limited under higher forward voltages. It was thought that the reason for this behaviour could be found in the formation of a film of aluminium oxide (hydroxide) at the interface between the highly oxidised polymer and the aluminium contact. This contact would be ohmic if formation of an insulating aluminium oxide layer did not take place. The growth of the aluminium oxide film can occur because the redox potential of the oxidised polymer is low [8] and aluminium can be easily oxidised, and also because of the oxygen and water content inside the polymer.

In this paper the electrical and photovoltaic characteristics of n-Si/pET2 rectifying junctions, connected to the external circuit with different electrical contacts on the polymer, i.e. aluminium, gold, indium tin oxide (ITO) and platinum, are reported. The aim of this work is to throw light upon the influence of the electrical contacts on the device performance, when conducting polymers are used as diode components. The knowledge of this influence is very important for an accurate de-

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**Fig. 1** Oxidized form of pET2

termination of the properties and parameters inherent to the rectifying junction and for the improvement of the device performance.

## Experimental

pET2 films (with thickness ranging between 2 and 10  $\mu\text{m}$ ) were deposited on n-doped silicon plates ( $<100>$  resistivity 1  $\Omega\text{ cm}$ ) by cyclic voltammetry (from  $-0.2$  to 1.5 V against saturated calomel electrode) of a  $4.0 \times 10^{-3}$  M ET2 solution in acetonitrile (AN) with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. In order to decrease its resistivity, silicon, acting as the working electrode, was illuminated with a tungsten lamp during the cyclic voltammetry. AN (Merck VA-SOL, for spectroscopy) was dehydrated with  $\text{P}_2\text{O}_5$ , neutralised in  $\text{K}_2\text{CO}_3$  and then distilled under argon atmosphere. Before polymer deposition, the oxide film was removed from the silicon plates by dipping them in a diluted HF solution, rinsing with threefold distilled water and drying with an argon flux.

The junction was connected to the external circuit by two contacts, the first formed by vacuum evaporation of aluminium on the silicon surface, and the second formed by pressure of different materials on the polymer. The surface (0.5  $\text{cm}^2$ ) of the metallic contact on p(ET2), ring shaped in order to allow the light to strike the junction through the hole, was considered to be the junction area. The junction was assembled in a home-made cell where de-aeration of the sample with dry argon flux was possible.

The  $i$ - $V$  characteristics were obtained by using an AMEL system 5000 multifunction instrument.

The impedance measurements were done with a Solartron 1255 frequency response analyser coupled with a Solartron 1286 electrochemical interface. In all the impedance measurements the amplitude of the a.c. signal was 10 mV. Non iterative, non-linear software, previously described [9], was used for the fitting of the impedance spectra. The resistance and the capacitance of the components associated with the various semi-circles were obtained by using the resonance formula  $2\pi fRC = 1$ , where  $R$  and  $C$  are the resonance resistance and capacitance, respectively. Any dependence of the capacitance on the frequency was not taken into account as the plots of the capacitance as a function of frequency gave stable frequency values for the examined semi-circles.

The light source was a 1000 W xenon arc lamp equipped with a water filter to cut off IR irradiation. Incident light intensity was varied by using neutral density filters and measured with an Oriel thermopile.

The polymer film thickness was measured by using a Tencor profilometer, model Alpha Step 200.

All measurements were done at ambient temperature (22  $^\circ\text{C}$ ).

## Results and discussion

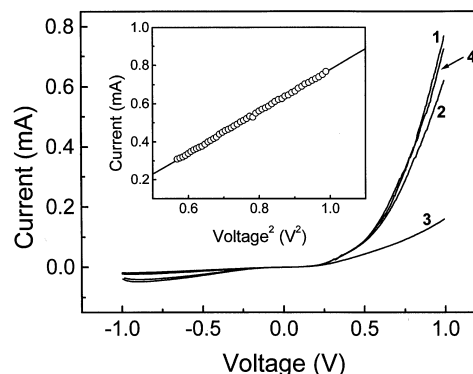
### Dark characteristic: results

#### n-Si/pET2 junction with an aluminium contact on pET2

In Fig. 2, the  $i$ - $V$  characteristics are shown for a junction stored in air, subsequently exposed to dry argon flux and again held in air. The forward current of the system exposed to air shows an exponential trend only for low bias values, and it then follows a parabolic law (Fig. 2, inset). The same system stored under dry argon flux becomes gradually more and more insulating; exposed again to air, it restores slowly the former characteristics.

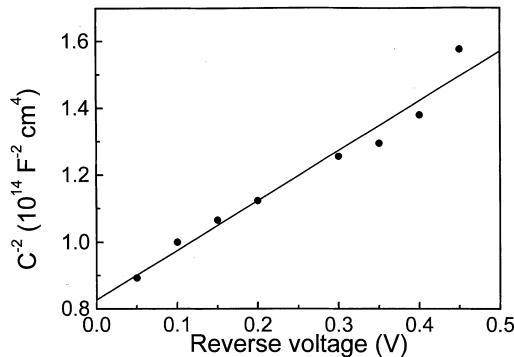
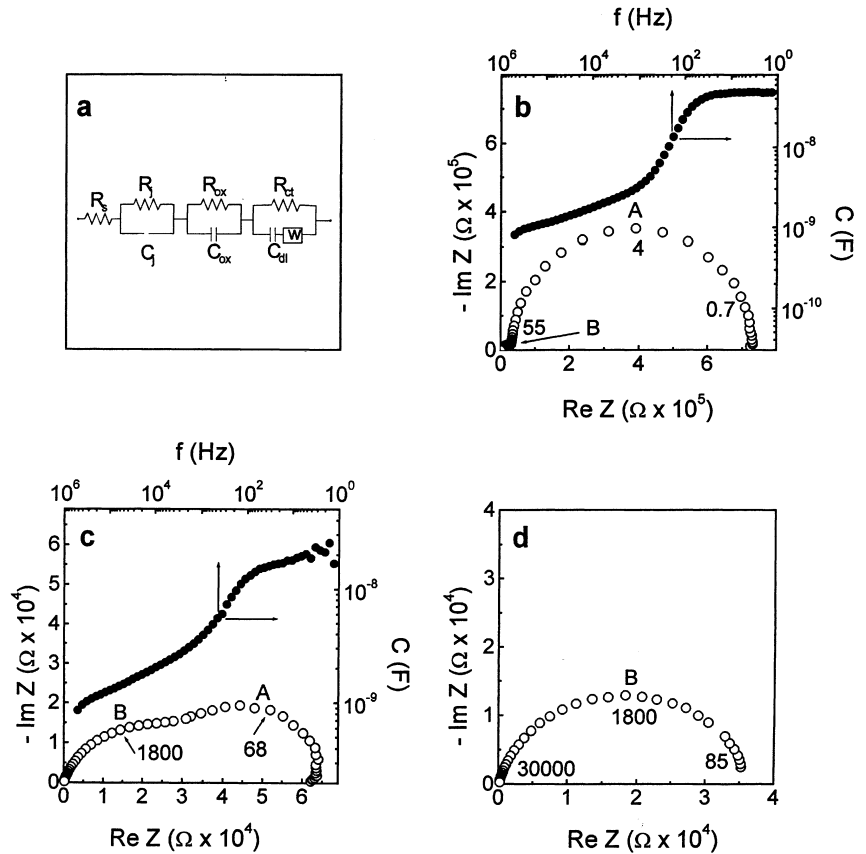
The Nyquist plots of the same system held in air show two semi-circles related to different time constants (Fig. 3). At reverse bias, semi-circle A, related to the junction impedance [7], is much greater than semi-circle B and its resonance capacitance was used to draw the Mott-Schottky plot (Fig. 4). Semi-circle B is reasonably due to a passivating film formation between the polymer and the aluminium contact and becomes comparable with semi-circle A only at forward voltages, where the junction impedance markedly decreases. The formation of this film can occur as aluminium is oxidised at potentials  $> -1$  V (vs the saturated calomel electrode) [10], and the reduction potential of oxidised pET2 is  $\sim 0$  V, if referred to the same electrode [8].

After many subsequent impedance measurements at various reverse or forward bias values, the oxidised al-



**Fig. 2** Plots of the dark ( $i$ - $V$ ) characteristic of n-Si/pET2 junction with an aluminium contact on pET2: 1 in the air; 2 under argon flux; 3 under argon flux, after subsequent sweeps; 4 again in the air. Polymer thickness ca. 9  $\mu\text{m}$ ; junction area 0.5  $\text{cm}^2$ . Inset: forward current against  $V^2$

**Fig. 3a–d** Impedance and capacitance spectra (full points: capacitance) of the same junction as Fig. 2: *a* equivalent circuit of the junction; *b* d.c. bias  $-100$  mV, frequency range  $1$ – $500\,000$  Hz; *c* d.c. bias  $+100$  mV, frequency range  $1$ – $500\,000$  Hz; *d* d.c. bias  $+800$  mV, frequency range  $1$ – $500\,000$  Hz



**Fig. 4** Mott-Schottky plot of the junction n-Si/pET2 with an aluminium contact on pET2. Junction area  $0.5\text{ cm}^2$

uminium layer becomes more and more insulating. Only if the system is allowed to adsorb water [leading to  $\text{Al}(\text{OH})_3$  formation], by resting for some hours, are the previous conditions restored. Alternatively, the insulating  $\text{Al}_2\text{O}_3$  film can be eliminated by performing a potential sweep until very high forward voltages (i.e.  $5$ – $7$  V); by this operation the high applied electric field destroys the insulating film.

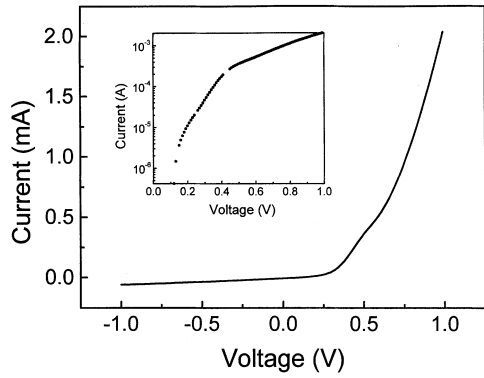
n-Si/pET2 junction with an ITO contact on pET2

The system was assembled as reported in the experimental section. ITO cannot be oxidised by the

polymer and therefore the problems found in the case of the aluminium contact could not arise. However, ITO is not a metal and its conductivity is not very high.

A dark  $i$ - $V$  plot for the pET2/Si junction with an ITO contact on the polymer (Fig. 5) shows a flex at  $\sim +0.4$  V. The logarithmic plot is quite linear up to high voltages but follows two different slopes, the flex point being the boundary between the two regions. Under dry argon flux the  $i$ - $V$  characteristics did not show meaningful changes with respect to those recorded with the same system held in air.

Impedance measurements indicate that, from reverse to forward bias up to  $+0.4$  V (Fig. 6), the system is characterised by only one semi-circle (A), inherent to the polymer/Si interface, with a constant high frequency intercept on the real axis of  $245$ – $255\ \Omega$ , mainly due to the ITO impedance (see the equivalent circuit in Fig. 6). At more positive bias, a second semi-circle (B) begins to grow with a higher time constant than semi-circle A; though semi-circle B tends to decrease on increasing the bias, it remains the only detectable semi-circle at a bias  $> 0.6$ – $0.7$  V, as that inherent to the rectifying junction decreases more rapidly with an exponential trend (Fig. 7). In these conditions the high frequency intercept on the real axis of semi-circle B is always  $\sim 250\ \Omega$ , i.e. the ITO resistance.



**Fig. 5** Plot of the dark  $i$ - $V$  characteristic of the n-Si/pET2 junction with an ITO contact on pET2. Polymer thickness ca. 2  $\mu\text{m}$ ; junction area 0.5  $\text{cm}^2$ . *Inset*: semi-logarithmic plot of the dark  $i$ - $V$  characteristic

n-Si/pET2 junction with a gold contact on pET2

Figure 8 shows the  $i$ - $V$  characteristics of the junction with a gold contact on the polymer. Although the junction area is the same as the previously considered junctions, the current is much higher in this case than in the previous ones. However, the  $i$ - $V$  curve is distorted by a flex at the same bias (+0.4 V) as found for the ITO contact (Fig. 9). The logarithmic plot is linear (Fig. 8, inset) up to +0.4 V and at higher forward voltages shows a more complex trend. The impedance measure-

ments also gave results similar to those obtained in the case of the ITO contact (Fig. 10), with two important differences; in fact, the series resistance of the system with the gold contact, detectable as the intercept at high frequency of semi-circle A, is, as expected, much lower than that shown by the system with the ITO contact, and the resistance inherent to the semi-circle B, present at a bias >0.3–0.4 V, increases linearly with the bias (Fig. 10d).

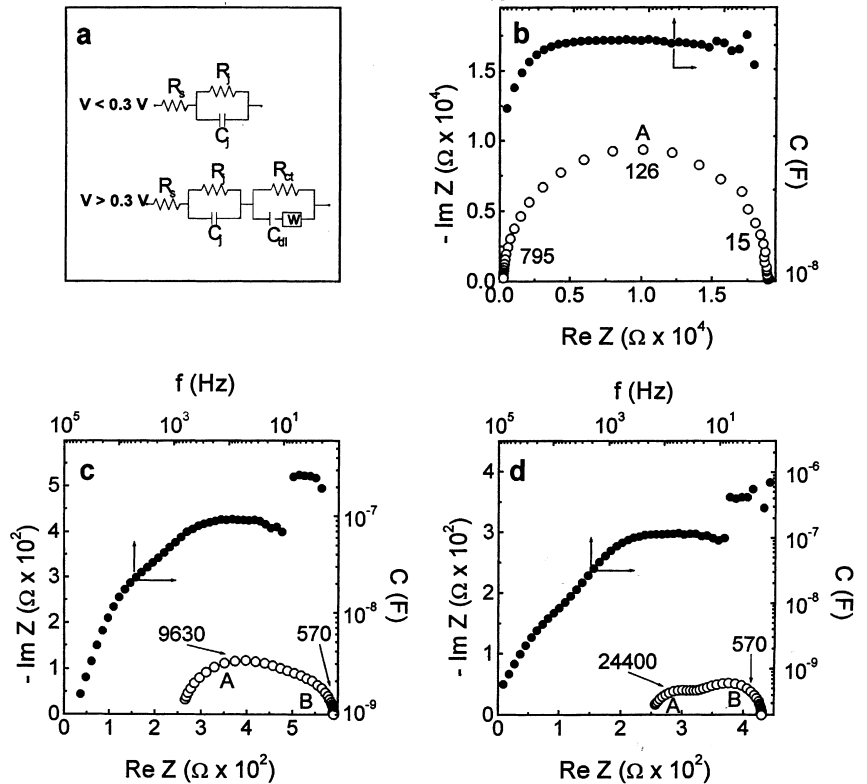
By increasing the number of subsequent sweeps, the  $i$ - $V$  characteristics of the system with the gold contact change: the forward current undergoes a regular decrease until the device becomes insulating.

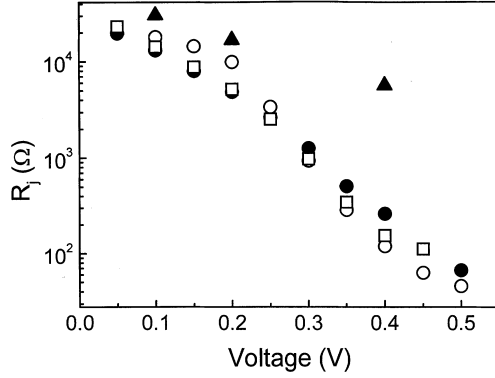
Working under dry argon flux has no great influence on the system performance. The initial characteristics of the junction can be restored only by cleaning the gold surface.

n-Si/pET2 junction with a platinum contact on pET2

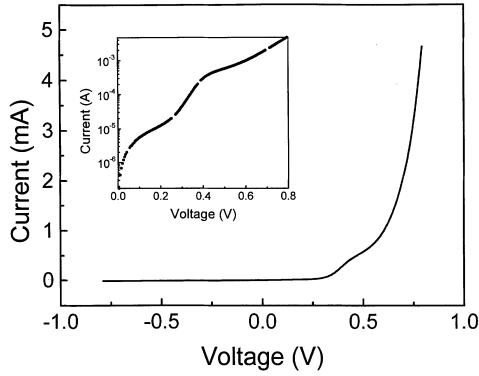
The  $i$ - $V$  characteristics of the junction with a platinum contact on the polymer, reproducible in time and for repetitive sweeps, are shown in Fig. 11. The flex at the same bias, already described in the cases of junctions with gold and ITO contacts, is clearly detectable (Fig. 9). The logarithmic plot shows the same behaviour already found in the case of the junction with the ITO

**Fig. 6a–d** Impedance and capacitance spectra (*full points*: capacitance) of the same junction as Fig. 5: *a* equivalent circuit of the junction; *b* d.c. bias -250 mV, frequency range 1–100 000 Hz; *c* d.c. bias +400 mV, frequency range 1–50 000 Hz; *d* d.c. bias +500 mV, frequency range 1–100 000 Hz

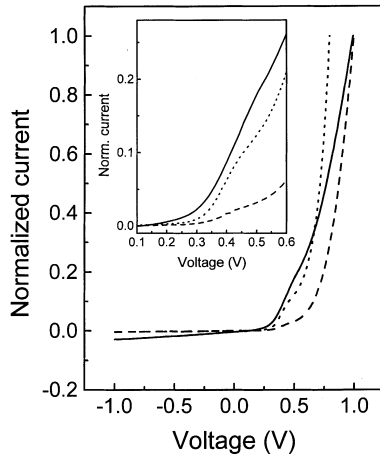




**Fig. 7** Junction resistance as a function of the forward voltage for the junction n-Si/pET2 with different contacts on pET2: aluminium (*solid triangles*), gold (*open circles*), ITO (*solid circles*) and platinum (*open squares*). The resistance values are those inherent to semi-circle A of the impedance spectra



**Fig. 8** Plot of the dark  $i$ - $V$  characteristic of the n-Si/pET2 junction with a gold contact on pET2. Polymer thickness ca. 1.6  $\mu\text{m}$ ; junction area 0.5  $\text{cm}^2$ . *Inset*: semi-logarithmic plot of the dark  $i$ - $V$  characteristic



**Fig. 9** Normalised dark  $i$ - $V$  of the junction n-Si/pET2 with different contacts on pET2: gold (*dotted line*), ITO (*solid line*) and platinum (*dashed line*). *Inset*: enlarged scale of the same plot in the voltage range 0.1–0.6 V

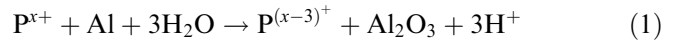
contact, as two linear trends with different slopes are observable with the boundary coincident with the flex point.

Impedance measurements gave a Nyquist plot with the expected characteristics (Fig. 12): only one semi-circle (A), due to the rectifying junction impedance, is detectable from a reverse to forward bias of  $\sim +0.3$  V; the series resistance of the device, derived from the high-frequency intercept of semi-circle A with the real axis, is very low. Sweeping towards positive bias, from  $\sim +0.3$  V a second low-frequency semicircle (B) can be detected. Although its resistance decreases with increasing bias (Fig. 12d), at a bias  $> \sim +0.5$  V it remains the only semi-circle, owing to the faster exponential decrease of the rectifying junction resistance (Fig. 7).

### Dark characteristics: discussion

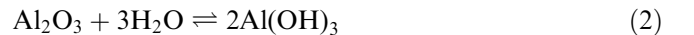
The above results show that the properties of the pET2/n-Si junction depend strongly on the electrical contact on the oxidised polymer. The characteristics of the pET2/n-Si junction with the aluminium contact are very different from those of the junction with the other contacts investigated in this work (ITO, gold, platinum). In fact, the experimental results indicate that an insulating aluminium oxide film grows at the interface between the metal and the oxidised polymer. As reported in a previous paper [10], the resistivity of  $\text{Al}_2\text{O}_3$  depends on the pH of the medium, varying in the range  $\sim 10^{11}$ – $10^{12}$   $\Omega \text{ cm}$ . In order to explain the  $i$ - $V$  forward characteristics, which depend on the water content of the system, the following hypotheses were put forward:

1. pET2 oxidises the aluminium contact and, in the presence of a little water, a passivating  $\text{Al}_2\text{O}_3$  film (maybe monomolecular) forms at the polymer/aluminium interface (Eq. 1):



Alternatively, the oxidised aluminium layer arises from the reaction between the aluminium electrode and the oxygen or water adsorbed by the polymer.

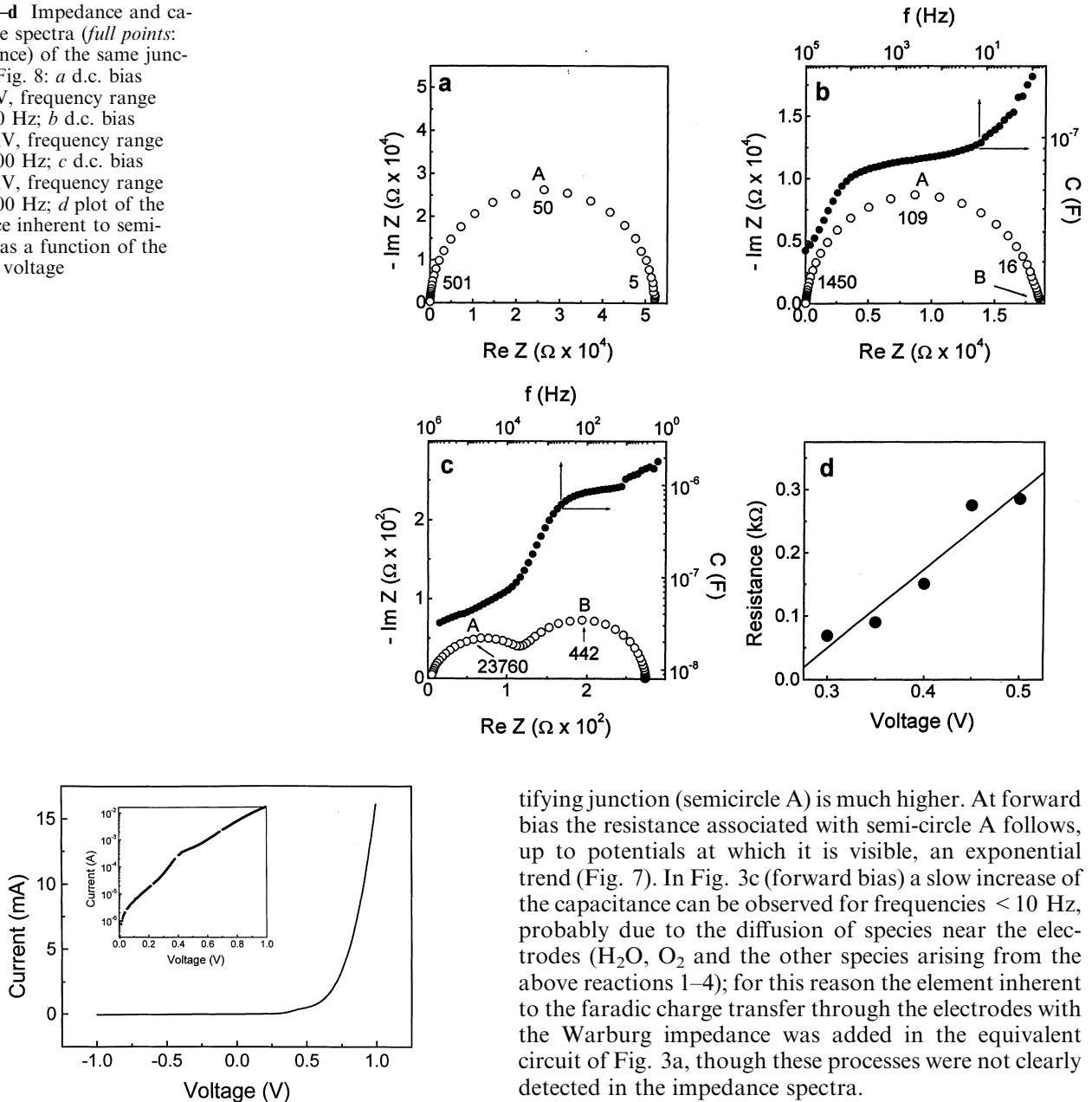
2. The aluminium oxide film adsorbs water from the air and, perhaps, from the polymer, leading to the formation of a non-coherent wet aluminium hydroxide layer (Eq. 2). The formation of aluminium hydroxide leads to the fracture of the dry  $\text{Al}_2\text{O}_3$  insulating film, and the resistance decreases.



3. When the system is held under dry argon, the film dehydrates (Eq. 2 from right to left) and a compact insulating oxide layer covers the aluminium electrode. If the system is brought back into air, the conductivity of the film at the polymer/Al interface increases again.

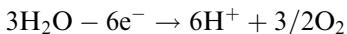
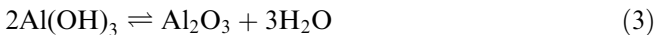
4. If the system works at bias values which induce, at the aluminium hydroxide/Al interface, the growing of

**Fig. 10a-d** Impedance and capacitance spectra (full points: capacitance) of the same junction as Fig. 8: *a* d.c. bias -250 mV, frequency range 1–10 000 Hz; *b* d.c. bias +100 mV, frequency range 1–100 000 Hz; *c* d.c. bias +400 mV, frequency range 1–100 000 Hz; *d* plot of the resistance inherent to semi-circle B as a function of the forward voltage



**Fig. 11** Plot of the dark  $i$ - $V$  characteristic of the n-Si/pET2 junction with a platinum contact on pET2. Polymer thickness ca. 2  $\mu\text{m}$ ; junction area 0.5  $\text{cm}^2$ . Inset: semi-logarithmic plot of the dark  $i$ - $V$

potentials able to oxidise or reduce water (Eqs. 3 and 4), the film, if water is adsorbed slowly, dehydrates and becomes more and more resistive.



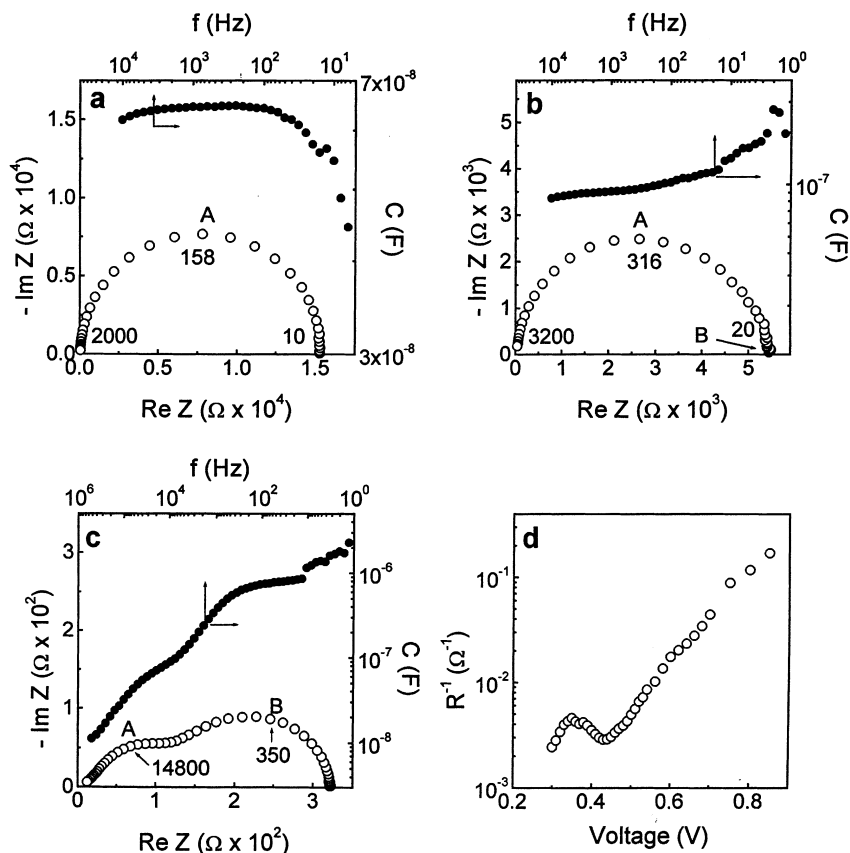
The resistance of the oxidised aluminium film has no great influence on the reverse characteristics of the system, because, at reverse bias, the impedance of the rec-

tifying junction (semicircle A) is much higher. At forward bias the resistance associated with semi-circle A follows, up to potentials at which it is visible, an exponential trend (Fig. 7). In Fig. 3c (forward bias) a slow increase of the capacitance can be observed for frequencies < 10 Hz, probably due to the diffusion of species near the electrodes ( $\text{H}_2\text{O}$ ,  $\text{O}_2$  and the other species arising from the above reactions 1–4); for this reason the element inherent to the faradic charge transfer through the electrodes with the Warburg impedance was added in the equivalent circuit of Fig. 3a, though these processes were not clearly detected in the impedance spectra.

After many subsequent impedance measurements at various reverse or forward bias values, the oxidised aluminium becomes more and more insulating as the reactions of Eqs. 3 and 4 continue. Only by allowing the system to adsorb water, by resting for some hours, are the previous conditions restored. Alternatively, the insulating  $\text{Al}_2\text{O}_3$  film can be eliminated by extending the sweep up to very high forward bias values; in this way the electric field growing between the polymer and aluminium can destroy the passivating film. Therefore, the reported experiments indicate that good ohmic contacts cannot be established between conducting polymers and aluminium electrodes, at least if the conducting polymers are heavily doped and able to oxidise aluminium.

Some gaseous products ( $\text{H}_2$ ,  $\text{O}_2$ ) must arise from the above reactions; however, maybe for the reason that they tend to diffuse out of the system, their influence on

**Fig. 12a–d** Impedance and capacitance spectra (*full points*: capacitance) of the same junction as Fig. 11: *a* d.c. bias  $-250$  mV, frequency range  $1$ – $10\,000$  Hz; *b* d.c. bias  $+200$  mV, frequency range  $1$ – $10\,000$  Hz; *c* d.c. bias  $+400$  mV, frequency range  $1$ – $500\,000$  Hz; *d* plot of the resistance inherent to semi-circle B as a function of the forward voltage



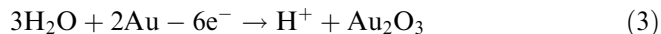
the  $i$ - $V$  plots or on the impedance spectra could not be determined, either for the case of the aluminium contact or for the cases of the other three contacts (ITO, gold and platinum).

The behaviour shown by the devices assembled with ITO, gold and platinum contacts on the polymer is similar, but with some important differences. All three systems show  $i$ - $V$  curves with a flex at about  $+0.3$ – $0.4$  V (Fig. 9). An explanation of this can be found by taking into account the presence of a small amount of water, already hypothesised in the case of the aluminium contacts, which undergoes oxidation at a forward bias of  $+0.3$ – $0.4$  V; at this bias value the electrochemical potential acting at the interface of the polymer/electrical contact cannot be evaluated.

The  $i$ - $V$  plots indicate that the systems with platinum and ITO contacts can supply currents following an exponential trend as a function of the forward bias until  $\sim 1$  V, but the logarithmic curves of the same plots show two different slopes, the first acting up to  $\sim +0.4$  V and the second at higher bias. The system with the gold contact also shows a good linear trend of the logarithmic plot up to  $\sim +0.4$  V, but at higher forward bias it follows a more complicate trend.

Differently from the ones with ITO and platinum contacts, the device with the gold contact on the polymer gradually loses its good performance and, finally, cannot

supply current anymore. This behaviour is not easily understandable; in any case, at forward bias the overall oxidation process leads to the formation of an insulating layer on the gold contact, the nature of which was not determined. The formation of an insulating  $\text{Au}_2\text{O}_3$  film on the gold surface, caused by water oxidation, could be hypothesised according to the overall Eq. 5:



Gold (and platinum) oxides are known to be unstable; however, it was reported that the formation of an  $\text{Au}_2\text{O}_3$  layer on a gold electrode coated with a polyaniline occurs when electrolysing an acid solution on this electrode at  $1.4$ – $1.7$  V vs the standard hydrogen electrode [11]. In the present case, the electrode potential and the chemical species acting at the gold contact cannot be easily determined.

Also the impedance spectra of the junctions with ITO, gold and platinum contacts are similar. At reverse bias and at a forward bias up to  $+0.3$  V the Nyquist plots show only one semi-circle (A) inherent to the rectifying junction; the Mott-Schottky plots obtained with the resonance capacitance of these semi-circles (Fig. 13) lead, in the three cases, to very similar junction parameters (see Table 1). At a forward bias  $>0.3$  V a second semi-circle (B) begins to rise, owing to the oxidation of water (and, maybe, of other species present inside the

polymer) and to related subsequent reactions at the contacts. The impedance of ITO can be estimated by the high-frequency intercept of semi-circle A.

In the case of ITO, gold and Pt contacts (see Figs. 6c, 6d, 10b, 10c, 12b, 12c), an increase of the capacitance was detected, for a forward bias, at frequencies  $< 10$  Hz. This was probably due to the diffusion of the mobile species ( $\text{H}_2\text{O}$ , but also  $\text{ClO}_4^-$  and  $\text{O}_2$ ); the symbol of the Warburg impedance was therefore added to the relative equivalent circuits.

The formation of an insulating film at a bias  $> +0.3$  V is supported, in the case of the gold contact, by the reported impedance measurements, which show an increase of the resistance, associated with semi-circle B, linear with voltage (Fig. 10d). Indeed, the formation of insulating oxide layers, whose thickness was proportional to the polarisation potential, was previously reported by electrolysing aqueous solutions with different pH values on Al electrodes, at potentials ranging from 0 to +2 V vs the saturated calomel electrode [9].

For the systems with ITO and platinum contacts on the polymer, an insulating layer on the contact does not form. In both cases the resistance of semi-circle B decreases with bias and follows, for a bias  $> +0.4$  V, an exponential trend, as shown in Fig. 12d, where  $1/R$  as a function of bias is reported. This trend could be due to an oxidation reaction on the contacts, probably water oxidation (Eq. 3), which would not damage meaningfully the polymer, as the characteristics of the device remain unchanged over time and after repetitive sweeps. Therefore, the resistance of semi-circle B could be re-

lated to a charge transfer and obey the Tafel law (Eqs. 6 and 7):

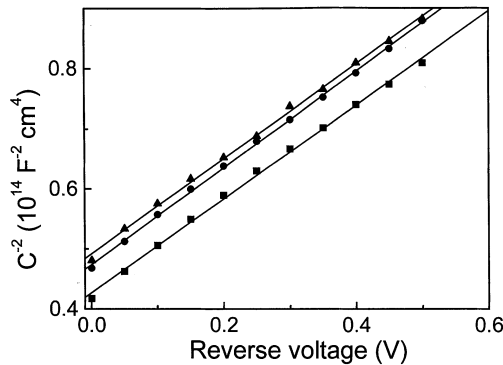
$$i = I_0 \exp(\beta n F \eta / RT) \quad (6)$$

where  $\eta$  = overvoltage and  $\beta = 1 - \alpha$ ,  $\alpha$  being the transfer coefficient. Then, the charge transfer resistance ( $R_{ct}$ ) can be obtained:

$$1/R_{ct} = di/d\eta = (\beta n F / RT) i_0 \exp(\beta n F \eta / RT) = A \exp(B\eta) \quad (7)$$

The behaviour of  $1/R_{ct}$  vs bias for low bias values (Fig. 12d) can be due to the adsorption on the contact of some species coming from the electrode reaction (i.e.  $\text{H}^+$ ). The difference between the systems kept in the air and under dry argon flux can be observed only at a bias  $> 0.3$ – $0.35$  V. At these bias values, in the case of the platinum contact semi-circle B of the system under argon flux gives a resistance 1.35 times higher than that derived from the corresponding semi-circle shown by the system in air ( $\sim 40\%$  relative humidity). On the other hand, a deeper understanding of the reaction related to the charge transfer at the interface between Pt, Au or ITO contacts and oxidised pET2 needs more investigation, centred also on the chemical characteristics of the polymer, and this is now in progress. An important consequence of the electron transfer reaction at platinum/polymer and ITO/polymer contacts is that the resistance connected to this reaction, showing an exponential decay like that inherent to the rectifying junction, and at a forward bias higher than  $+0.5$ – $0.6$  V, becomes the predominant impedance of the circuit; for this reason, the logarithmic plots of the current as a function of forward bias show two different slopes with a flex at  $\sim +0.3$ – $0.4$  V. From the above results it can be inferred that the polymer contains some amounts of water, which is reasonable if the high content of the counter-ion and a possible inclusion of some amount of supporting electrolyte, coming from the electrolysis solution during the polymerisation, are taken into consideration.

Platinum is the most suitable material for ohmic contacts on conducting organic polymers. ITO, for its transparency, could be very profitable for contacts in photovoltaic applications; moreover, it cannot be oxidised, but introduces a relevant series resistance. The gold contact on oxidised pET2, in spite of the high work function of this metal and the initial good performances of the junction, is not convenient for the proposed diode, as, during the potential sweep, the progressive formation of an insulating layer takes place on the gold surface.

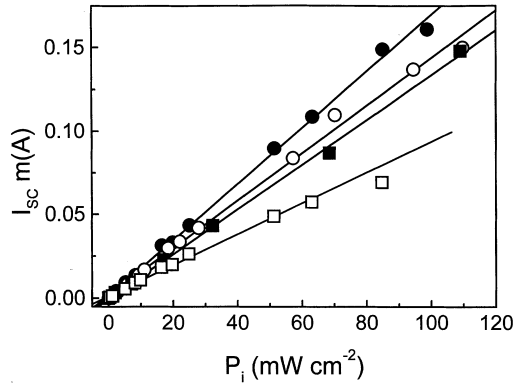


**Fig. 13** Mott-Schottky plot of the junction n-Si/pET2 with different contacts on pET2: gold (solid triangles), ITO (solid circles) and platinum (solid squares). Junction area  $0.5 \text{ cm}^2$

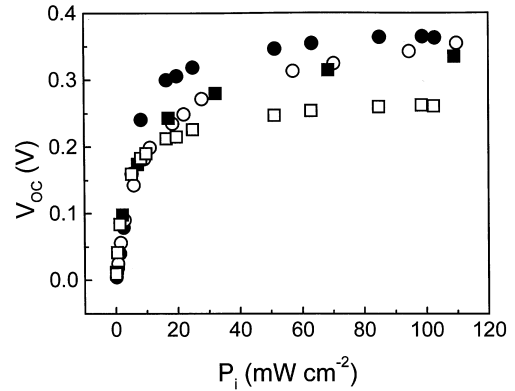
**Table 1** Parameters derived from the Mott-Schottky plots of the junction n-Si/pET2 with various electric contacts on pET2 (N: silicon donor concentration;  $V_i$ : built-in potential;  $qF$ : barrier height;  $E_F$ : Fermi level energy of the polymer)

	N ( $\text{cm}^{-3}$ )	$V_i$ (V)	$qF$ (eV)	$E_F$ (eV)
Gold	$(1.52 \pm 0.02) \times 10^{17}$	$0.623 \pm 0.012$	$0.782 \pm 0.015$	$4.83 \pm 0.10$
Platinum	$(1.54 \pm 0.02) \times 10^{17}$	$0.546 \pm 0.012$	$0.705 \pm 0.016$	$4.75 \pm 0.1$
ITO	$(1.50 \pm 0.01) \times 10^{17}$	$0.588 \pm 0.07$	$0.747 \pm 0.009$	$4.80 \pm 0.05$
Aluminium	$(8.09 \pm 0.63) \times 10^{16}$	$0.555 \pm 0.065$	$0.731 \pm 0.083$	$4.78 \pm 0.56$





**Fig. 14** Short-circuit current as a function of the incident light intensity of the junction n-Si/pET2 with different contacts on pET2: gold (solid circles), ITO (open circles), platinum (solid squares) and aluminium (open squares). Polymer thickness: 9  $\mu\text{m}$ , 2  $\mu\text{m}$ , 2  $\mu\text{m}$  and 9  $\mu\text{m}$ , respectively. Solid lines: linear fitting of the experimental data. Junction area 0.5  $\text{cm}^2$



**Fig. 15** Open-circuit voltage as a function of the incident light intensity of the junction n-Si/pET2 with different contacts on pET2: gold (solid circles), ITO (open circles), platinum (solid squares) and aluminium (open squares). Polymer thickness: 9  $\mu\text{m}$ , 2  $\mu\text{m}$ , 2  $\mu\text{m}$  and 9  $\mu\text{m}$ , respectively. Junction area 0.5  $\text{cm}^2$

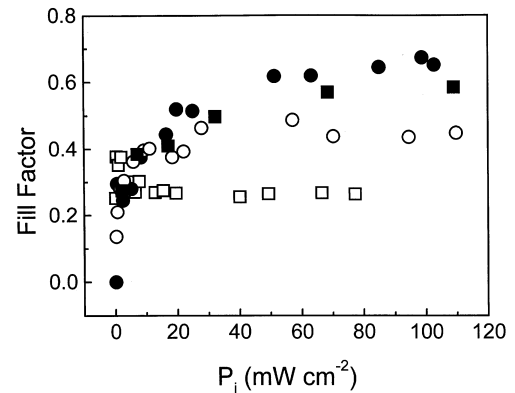
### Photovoltaic characteristics: results and discussion

pET2, in its fully oxidised form, is characterised by a high transmission in the visible spectral region and acts as a semi-transparent metal in the Schottky junction pET2/n-Si [7]. By illuminating the junction through the polymer, a photovoltaic effect occurs in all four systems described above. In Figs. 14, 15 and 16 the variations of the short-circuit current ( $I_{SC}$ ), open-circuit voltage ( $V_{OC}$ ) and fill factor ( $FF$ ), as a function of the incident light intensity ( $P_i$ ), are respectively shown.

The  $I_{SC}$  is a linear function of  $P_i$ , confirming that the photocurrent is mainly due to silicon. It is not possible to compare the photocurrent values in the four cases, because of the difference in the polymer thickness (and therefore in the polymer transmittance).

As Figs. 15 and 16 show, the nature of the contact on pET2 strongly affects two important photovoltaic parameters:  $V_{OC}$  and  $FF$ . The  $V_{OC}$  values, at an incident power intensity of about 100  $\text{mW cm}^{-2}$ , are very similar in the cases of the Au, ITO and Pt contacts ( $\sim 0.35$  V, 0.37 V being the highest value obtained), whereas a considerably lower photovoltage ( $\sim 0.25$  V) can arise with an aluminium contact on the polymer. These results can be easily understood by taking into account the formation of the insulating oxide layer in the case of the aluminium contact: the voltage drop across this space charge layer lowers the  $V_{OC}$  [12].

The more the dark  $i$ - $V$  characteristic diverges from the ideal one, the more the  $FF$  decreases. Very good  $FF$  values are obtained in the cases of gold and platinum contacts ( $\sim 0.7$ ) (Fig. 16); a not so high  $FF$  can be expected in the case of aluminium. In the system with the ITO contact on pET2 the  $FF$  ( $\sim 0.5$ ) is clearly limited by the ITO resistance, which considerably increases the series resistance.



**Fig. 16** Fill factor as a function of the incident light intensity of the junction n-Si/pET2 with different contacts on pET2: gold (solid circles), ITO (open circles), platinum (solid squares) and aluminium (open squares). Polymer thickness: 9  $\mu\text{m}$ , 2  $\mu\text{m}$ , 2  $\mu\text{m}$  and 9  $\mu\text{m}$ , respectively. Junction area 0.5  $\text{cm}^2$

### Conclusions

The results of this investigation throw some light upon the origin of the impedance, due to some construction details, that can strongly affect the performances of rectifying junctions based on organic compounds and, in particular, on conducting polymers.

The dark characteristic changes of the rectifying junction, obtained by interfacing n-doped silicon with the fully oxidised form of pET2, were investigated by connecting the system with the measurement circuit through four different electrical contacts on the polymer: aluminium, ITO, gold and platinum. The performances of the junctions were found to be strongly dependent on the nature of the contact.

Aluminium is easily oxidised, leading to the formation of a non-conductive oxide film, the resistance of which depends on the environmental humidity. In the

presence of humidity, the current flow is no longer controlled by the thermionic emission across the junction but by the charge injection through the film arising between the polymer and the aluminium contact. In a dry atmosphere this film becomes insulating and completely deactivates the device. This behaviour, which was found to be reversible, was explained with the hypothesis that the oxidised polymer and the aluminium oxide film adsorb water from the atmosphere and, consequently, part of the aluminium oxide reacts with water, giving rise to wet aluminium hydroxide; by dehydration, the formation of a pure, highly insulating aluminium oxide film occurs, which disconnects the junction from the measurement circuit.

The adsorption of water by the polymer could also explain the influence of the other three kinds of contacts on the junction performance. The characteristics of the junctions with ITO, gold and platinum contacts are similar. A flex in the  $i$ - $V$  plots is shown by these systems at a forward bias of  $\sim +0.4$  V; at a higher forward bias, impedance measurements indicate that a process, probably water oxidation, is active at the polymer/metal or polymer/ITO interface. This process causes a slow formation of an insulating layer on the gold contact, which slowly deactivates the device. In contrast, ITO and platinum contacts are not oxidised and the device performance remains unchanged in time and with repetitive potential sweeps. Platinum is the most suitable material in order to achieve good contacts on conducting polymers; in fact, ITO shows a non-negligible resistivity, which is a serious problem in photovoltaic applications.

Good photovoltaic properties correspond to good dark properties; a satisfying  $V_{OC}$  value ( $\sim 0.35$  V) was obtained with platinum and ITO contacts, but the ITO resistance limited the FF value to  $\sim 0.5$ , being 0.7 in the case of platinum contact.

As a closing remark, it can be stressed that, as far as rectifying junctions based on conducting polymers are concerned, the nature of the electrical contact on the organic material is very important and has to be taken into consideration.

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