

Utilization of conducting polymers in rectifying junction construction: Dark characteristics and photovoltaic properties

N CAMAIONI, G BEGGIATO*, G CASALBORE-MICELI,
A GERI and L VENTURA

Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR, via Gobetti 101,
40129 Bologna, Italy

Abstract. The electrical characteristics of the junction obtained by depositing poly(4,4'-dipentoxy-2,2'-bithiophene) on *n*-type silicon have been investigated in the dark and under white as well as monochromatic illumination. The dark forward current is space charge limited at forward bias > 0.2 V, whereas it has an exponential trend for very low forward voltages. A Schottky barrier formation at the poly(ET2)/*n*-Si interface is demonstrated. The barrier height values, obtained both from the Mott–Schottky plot and from the dependence of the open-circuit voltage on the short-circuit current, are very similar. The short-circuit current is a linear function of the incident light intensity, as expected for silicon solar cells. The analysis of the spectral response of the junction suggests that the photocurrent is mainly due to silicon.

Keywords. Poly(4,4'-dipentoxy-2,2'-bithiophene); conducting polymers; heterojunctions; photovoltaic effect.

1. Introduction

An advantage of organic material for application in electronic technology is the wide spectrum of chemical and physical properties which can be presented by these compounds. In particular, conducting polymers, which change optical spectrum and electrical conductivity as a function of the doping level^{1,2}, seem to be very interesting for optoelectronic devices.

It has already been observed that, by interfacing oxidised conducting polymers with inorganic semiconductors, a Schottky barrier is formed at the interface^{3–6}. In these junctions, conducting polymers act as the metal due to their very high charge density (10^{20} – 10^{21} cm⁻³).

The photovoltaic effect of Schottky junctions between conducting polymers and inorganic semiconductors or between metal and semiconducting polymers has also been demonstrated^{3,6,8,9}.

In this paper, the dark and photovoltaic properties of the junction obtained by depositing on a *n*-doped silicon plate the oxidised form of poly(4,4'-dipentoxy-2,2'-bithiophene) (poly(ET2)) are reported. This conducting polymer was used as a metal-like material for its stability and high transmission in the visible region.

*For correspondence

2. Experimental

Thin (4 to 9 μm) films of poly(ET2) were deposited on *n*-Si plates ($\langle 100 \rangle$), resistivity 1 $\Omega\text{ cm}$) by cyclic voltammetry (from -0.2 to 1.5 V against saturated calomel electrode) of a 4.0×10^{-3} M ET2 solution in acetonitrile (AN) with tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte. In order to decrease its resistivity, silicon, acting as a working electrode, was illuminated with a tungsten lamp during the voltammetry cycles. Before polymer deposition, the SiO_2 film was cleaned off from the silicon by dipping the plates in a diluted HF solution, rinsing with tridistilled water and drying with an argon flux.

To test the junction, two aluminium contacts were realised, one by vacuum evaporation on silicon and the second by mechanical pressure on the polymer. The surface (0.5 cm^2) of the metallic contact on poly(ET2), ring shaped to allow the junction illumination through the hole was considered to be the junction area.

The current-voltage 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, over a frequency range of 1–500000 Hz. The light source was a 1000 W xenon arc lamp equipped with a water filter to cut off IR radiations. The intensity of the incident light was varied by using neutral density filters and measured with an Oriel thermopile. For the spectral response, a Jobin Yvon HR 250 monochromator was used. All measurements were done under ambient conditions.

3. Results and discussion

The quite low redox potential (≈ 0.04 V vs saturated calomel electrode⁷) assures a good stability to the oxidised form of poly(ET2). Indeed, the doping level of the conducting polymer undergoes only a relatively small decrease under ambient conditions, as is evident in figure 1, where the transmittance spectrum of a poly(ET2) film, deposited in oxidised form on ITO (indium-tin-oxide) and stored in ambient conditions, is compared with the transmittance of the same film in its oxidised and neutral form. The oxidised poly(ET2) is characterised by a low absorbance in the visible region of the spectrum. Therefore, by illuminating the junction *n*-Si/poly(ET2) through the polymer, part of the incident light can reach the silicon surface.

The dark current-voltage (*I*–*V*) characteristic of the junction is clearly nonlinear and asymmetric (see figure 2), with a rectification ratio, at ± 1 V, of 2.2×10^2 . The current increases exponentially only at low voltages ($V < 0.2$ V). On the contrary, in the range 1.2–2.0 V, the current is a linear function of V^2 . According to these findings, the dark *I*–*V* characteristic can be described by two different mechanisms: thermionic emission over the polymer/Si contact barrier, at low applied voltages, and space charge injection at high voltages. Current is then given by the following equations,

$$I = I_0 [\exp(qV/nkT) - 1] \quad (1)$$

$$I = cV^2, \quad (2)$$

where q is the electronic charge, n the ideality factor, k the Boltzmann constant, T the temperature, A the junction area and c a constant. I_0 , the reverse saturation current, is given by

$$I_0 = AA^*T^2 \exp(-q\phi/kT) \quad (3)$$

where A^* is the Richardson constant and ϕ the height of the contact barrier.

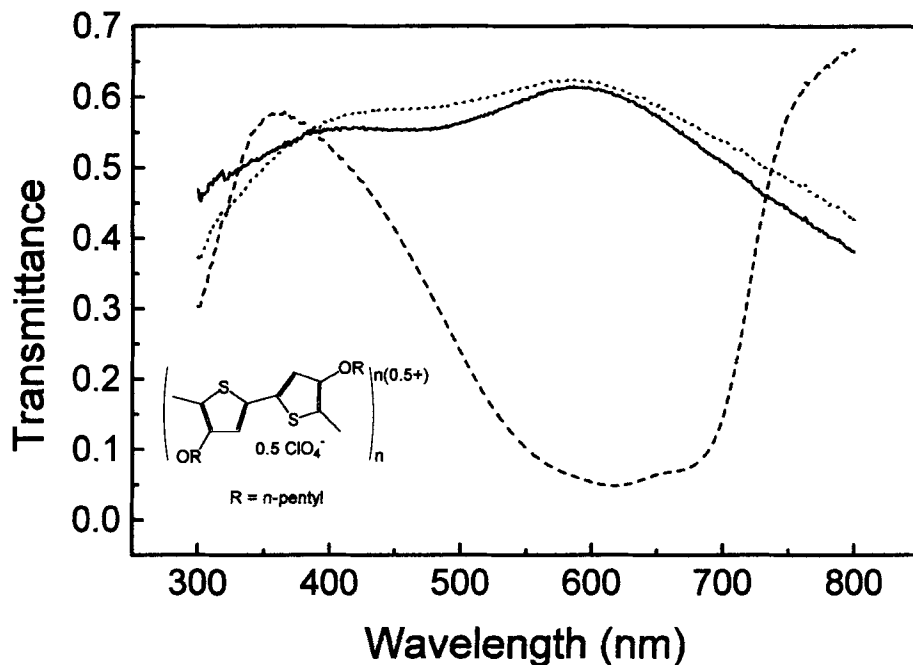


Figure 1. Transmittance of a poly(ET2) film 0.5 μm thick, deposited on ITO. Dotted line: oxidised form; dashed line: neutral form; solid line: grown in oxidised form and stored under ambient conditions. Inset: Structure of poly(ET2).

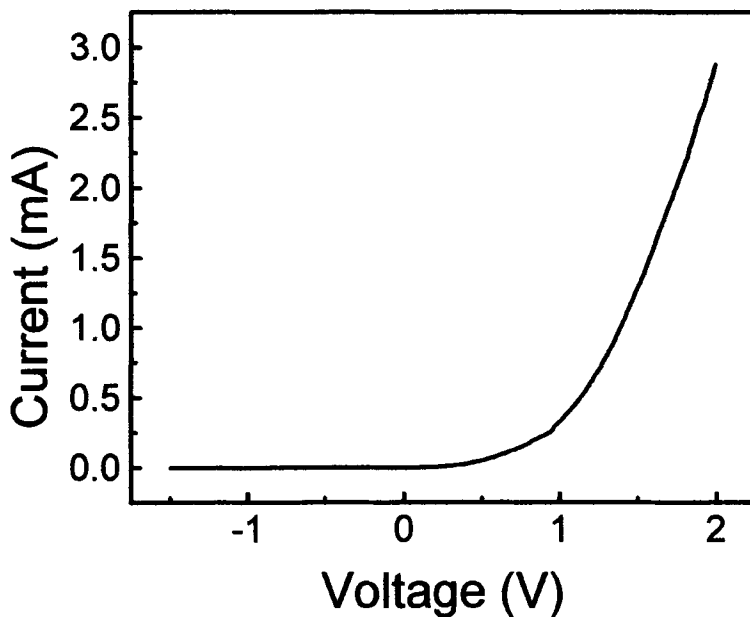


Figure 2. Dark current-voltage characteristic of poly(ET2)/*n*-Si junction. Polymer thickness $\approx 4 \mu\text{m}$; junction area 0.5 cm^2 .

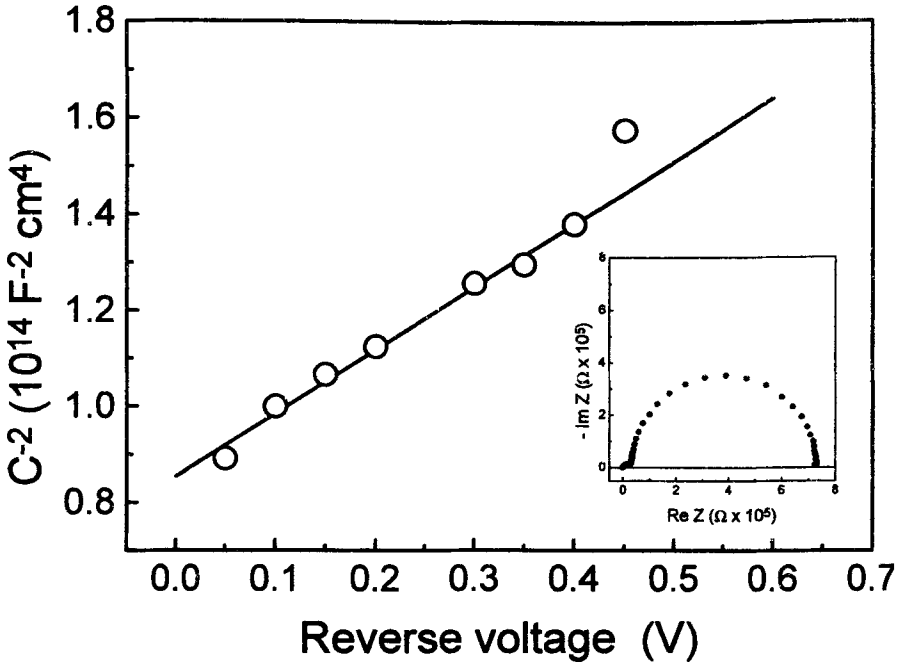


Figure 3. Mott-Schottky plot of the junction poly(ET2)/n-Si. Inset: Impedance spectrum of the junction of figure 2, in the frequency range $1-5 \times 10^5$ Hz and with a DC bias of -50 mV.

For forward voltages ranging from 0.2 to 1.2 V, both the above mentioned mechanisms coexist; therefore the current-voltage plots cannot be described by only one equation. By using (1), values of 2.1 for the ideality factor and of 1.3×10^{-7} A for the reverse saturation current were obtained from the I-V plot in the range 0-0.2 V.

As said above, at higher forward potentials, the current undergoes space charge conditions. As aluminium is an easily oxidisable metal, the formation of a highly resistive aluminium oxide (hydroxide) film at the interface Al/poly(ET2), can be assumed to give rise to the space charge limited current.

To understand the junction properties better the capacitance variation as a function of the reverse bias was studied. In figure 3 (inset) a typical Nyquist plot, obtained for reverse polarisation, is reported. The semicircle at lower frequencies, lowered only by a very small angle ($0-1^\circ$), can be ascribed to the n-Si/poly(ET2) interface. By plotting C^{-2} as a function of the reverse bias V_R (where C is the resonance capacitance per unit area inherent to the semicircle at lower frequencies) a good straight line is obtained (figure 3), as expected for a Schottky junction. For an ideal Schottky barrier, the capacitance per unit area under reverse bias V_R is given by (4),

$$C = \left(\frac{qN\epsilon_s}{2} \right)^{1/2} \left(\phi - \zeta + V_R - \frac{kT}{q} \right)^{-1/2}$$

where ϵ_s is the semiconductor permittivity, N the semiconductor carrier concentration and ζ the depth of the Fermi level below the conduction band. From the slope of C^{-2} vs

V_R , the carrier concentration of silicon was determined to be $9 \times 10^{16} \text{ cm}^{-3}$. This value agrees fairly well with the silicon resistivity ($1 \Omega \text{ m}$). From the intercept on the horizontal axis of the C^{-2} vs V_R , a built-in potential (V_i) of 0.65 V was obtained as,

$$V_i = \phi - \zeta - \frac{kT}{q}, \quad (5)$$

a value of 0.8 eV was calculated for the barrier height. The width of the depletion layer (W) is related to the built-in potential and to the semiconductor carrier concentration by,

$$W = \left(\frac{2\epsilon_s V_i}{qN} \right)^{1/2}. \quad (6)$$

By using the calculated values of V_i and N , a value of 95 nm was found for W .

By illuminating the junction through the polymer, a photoeffect is observed. In figure 4 the variations of the short-circuit current (I_{SC}) and of the open-circuit voltage (V_{OC}) as a function of the incident light intensity (P_i) are shown. For $P_i < 30 \text{ mW cm}^{-2}$, I_{SC} is a linear function of P_i , as expected for silicon solar cells. At higher values of the incident light intensity, the slight deviation from the linear trend is probably due to thermal effects. V_{OC} values are smaller than the calculated built-in voltage (V_i) the reasons why the values of the open-circuit voltage are significantly less than V_i can be found in the high reverse saturation current and ideality factor, and in the voltage drop across the space charge layer¹¹.

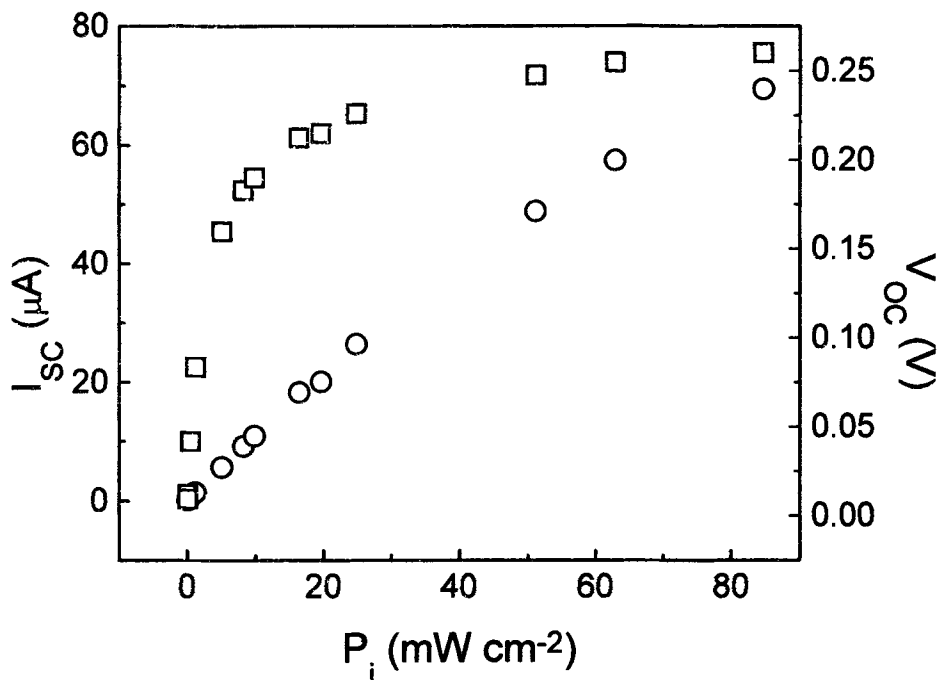


Figure 4. Short-circuit current (○) and open-circuit voltage (□) of the junction poly(ET2)/n-Si as a function of the incident light intensity. Polymer thickness $\approx 9 \mu\text{m}$; junction area 0.5 cm^2 .

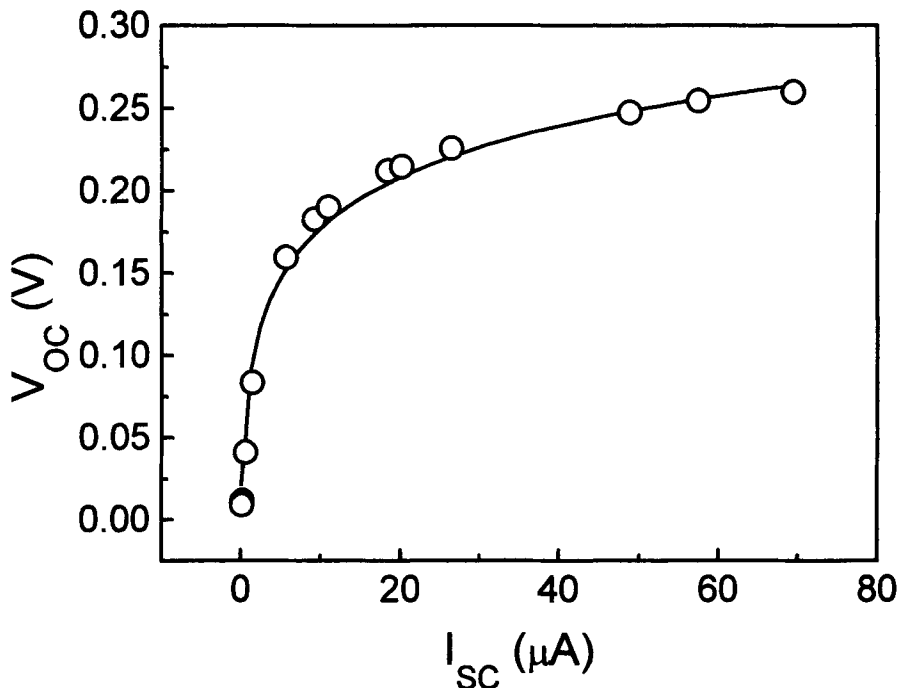


Figure 5. Open-circuit voltage of the junction of figure 4 as a function of the short-circuit current. Open circles: experimental data; solid line: fitting of the experimental data with equation 7.

For an ideal junction the open-circuit voltage is related to the short-circuit current by (7),

$$V_{oc} = n \frac{kT}{q} \ln \left(\frac{I_{sc}}{I_0} + 1 \right). \quad (7)$$

As shown in figure 5, a good fitting of the experimental data with (7) was obtained, which led to an estimation of n (1.8) and I_0 (1.9×10^{-7} A), values very close to those obtained from the dark I-V characteristic. From (3), a value of the barrier height ($q\phi = 0.77$ eV), very similar to that estimated from the Mott-Schottky plot, was obtained, which is a further indication that a Schottky junction is really formed at the interface between n -silicon and poly(ET2).

In the case of a junction with a 2 μm thick poly(ET2) film, values of 0.47 and 0.55% respectively, were found for the fill factor and the external conversion efficiency¹⁰. The latter parameter is strongly dependent on the polymer thickness and therefore very thin poly(ET2) films could give rise to a significant improvement of the junction capability in transforming luminous into electric energy.

In figure 6 the experimental spectral response (i.e. photocurrent/constant photon flux), in the range 300–800 nm, is compared with the one expected for a silicon Schottky photodiode with a metal transmittance equal to that of poly(ET2). According to the theory of inorganic Schottky solar cells, the two main contributions to the

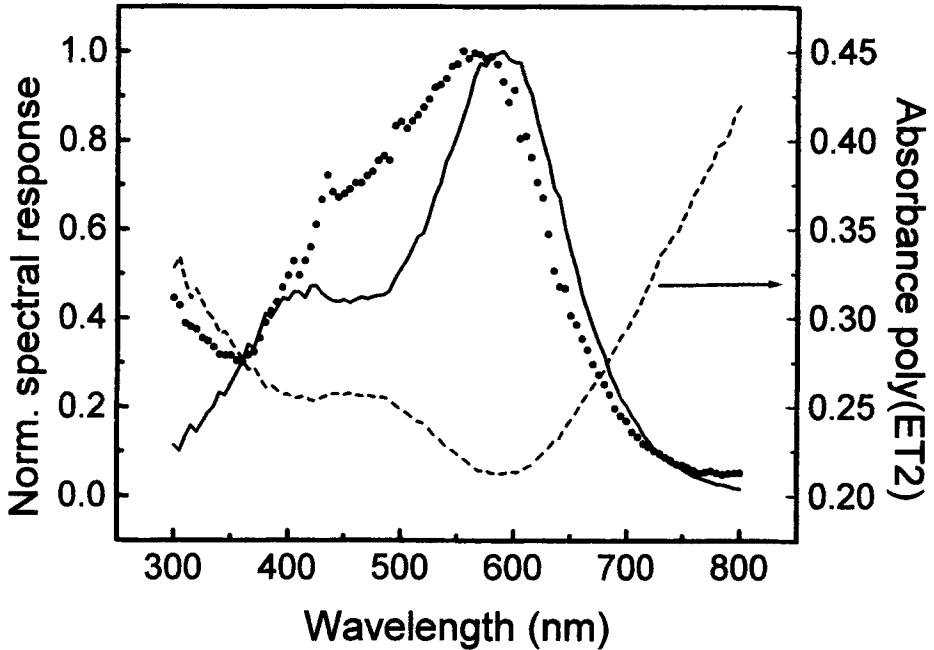


Figure 6. Dotted line: experimental spectral response of the junction of figure 4. Solid line: calculated spectral response by using equation 10 for the expected photocurrent. Dashed line: absorbance of a 0.5 μm thick poly(ET2) film deposited in oxidised form on ITO.

photocurrent, and then to the spectral response, come from the depletion layer and from the bulk of the semiconductor¹². The former is given by,

$$J_{dl} = qT(\lambda)F(\lambda)(1 - \exp(-\alpha(\lambda)W)) \quad (8)$$

whereas the latter,

$$J_b = \left(\frac{qF(\lambda)\alpha(\lambda)L}{\alpha(\lambda)L + 1} \right) T(\lambda)\exp(-\alpha(\lambda)W) \quad (9)$$

where $T(\lambda)$ is the transmittance of the metal, $F(\lambda)$ is the incident photon flux, $\alpha(\lambda)$ the semiconductor absorption coefficient, W the width of the depletion layer and L the diffusion length of holes (being the semiconductor n -type). The total photocurrent (J_T) is then given by,

$$J_T = J_{dl} + J_b. \quad (10)$$

Assuming a value of 50 μm for the diffusion length, the expected spectral response was calculated by using (10) for the photocurrent. Its shape, very similar to that of the experimental one, suggests that the photocurrent is mainly due to silicon. A study to reveal a polymer contribution in the wavelength range 300–500 nm is in progress.

4. Conclusions

Poly(ET2) is stable in its oxidised form and has a good transmittance in the visible region of the spectrum. The poly(ET2)/ n -Si junction shows rectification properties and

photovoltaic response. For forward bias, the dark I - V characteristic exhibits two different conduction modes: thermionic emission over the polymer/inorganic semiconductor contact barrier dominates for voltages less than 0.2 V, whereas at high voltages a space charge limited current model must be assumed. By studying the junction properties, both in the dark and under illumination, the formation of a Schottky barrier at the interface poly(ET2)/silicon has been demonstrated. Due to its high carrier concentration, poly(ET2) acts as a semi-transparent metal in the Schottky junction. The short-circuit current is linear with the incident light intensity. The analysis of the spectral response suggests that the photocurrent is mainly due to silicon. By using very thin polymer films, good photovoltaic performances could be achieved.

References

1. Salaneck W R, Clark D T, Samuelsen E J (eds) 1991 *Science and applications of conducting polymers* (Bristol: Adam Hilger)
2. Brédas J L, Chance R R (eds) 1990 In *Conjugated polymeric materials: Opportunities in electronics, optoelectronics, and molecular electronics* (Dordrecht: Kluwer Academic Publishers)
3. Frank A J, Glenis S and Nelson A 1989 *J. Phys. Chem.* **93** 3818
4. Campos M, Casalbore-Miceli G and Camaioni N 1995 *J. Phys. D: Appl. Phys.* **28** 2123
5. Compos M, Camaioni N, Casalbore-Miceli G, Geri A, Giro G and Zini Q 1995 *Synth. Met.* **75** 61
6. Cong H N, Sene C, Chartier P 1996 *Sol. Energy Mater. Sol. Cells* **40** 261
7. Zotti G, Gallazzi M C, Zerbi G, Meille S V 1995 *Synth. Met.* **73** 217
8. Glenis S, Tourillon G and Garnier F 1986 *Thin Solid Films* **139** 221
9. Fang Y, Chen S-A, Chu M L 1992 *Synth. Met.* **52** 261
10. Camaioni N, Beggiato G, Casalbore-Miceli G, Gallazzi M C, Geri A and Martelli A 1997 *Synth. Met.* **85** 1369
11. Kanicki J 1986 In *Handbook on Conducting Polymers* (ed.) T J Skotheim (New York: Marcel Dekker) pp. 625
12. Novel H J 1975 *Semiconductor and semimetals, Vol. 11, Solar cells* (New York: Academic Press) pp. 114