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Analysis of photocurrent spectra at polybithienyl film coated on Pt

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Abstract Photoelectrochemical measurements have been performed at a polybithienyl (PBT) film (doping level of $1 \times 10^{18}/\text{cm}^3$) deposited on a platinum electrode. The cathodic photocurrents and negative slope of the Mott-Schottky plot indicate that the PBT film has the features of a p-type semiconductor. The cathodic photocurrents are interpreted in terms of the Gaertner-Butler model on the basis of the theory of the semiconductor|solution interface. The $(i_{\text{ph}}/h\nu)^{2/n}$ vs. $h\nu$ plots taken from the photocurrent spectra show two linearities for $n=1$ in the wavelength range from 460 nm to 490 nm and for $n=4$ in the wavelength range $\lambda > 490$ nm. The band gaps of the PBT film were determined to be 2.05 ± 0.05 eV for $n=1$ and 1.55 ± 0.05 eV for $n=4$. The flat-band potential is 0.33 V (vs SCE). From the slope of the Mott-Schottky plot at the modulation frequency of 3 kHz, the dielectric constant ϵ of the film and the thickness of the depletion layer W_0 of the PBT film were determined to be 7.4 and 0.29 μm , respectively.

Key words Polybithienyl · Organic semiconductor · Photocurrent · Gaertner-Butler model · Band gap energy

Introduction

The photoelectrochemical properties of electric conducting organic polymers (ECOPs) are very interesting owing to their applications in solar energy conversion and optical displays. Therefore, investigation of the

photoelectrochemical behaviour of ECOPs is significant. In the last decade, much more work in this field has been reported [1–9]. Most reports are about poly-3-methylthiophene (PMT), but few about polybithienyl (PBT) [5–7, 9]. Recently, Plieth and co-workers [8] and Semenikhin et al. [9] have reported the photoelectrochemical behaviour of polybithienyl (or polybithiophene) (PBT) in aqueous and non-aqueous solutions, respectively. However, there is a lack of the analysis in detail. Therefore, we have tried to analyse the photocurrent spectra of PBT using the Gaertner-Butler model [10, 11] on the basis of an assumption that the PBT film is a quasi-semiconductor and the behaviour of the PBT|solution interface corresponds with the theoretical model of the semiconductor|electrolyte interface as suggested in the literature [12, 13]. The results of this analysis are surprisingly good. In the present paper we report these results and attempt to interpret them.

Experimental

Preparation of the PBT films

The equipment employed for the electrochemical synthesis of PBT film is described in detail in a previous paper [14]. The PBT film for the photocurrent measurements was galvanostatically synthesized at a current density of 1 mA cm^{-2} on Pt disc electrodes (0.071 cm^2) in a propylene carbonate + 0.1 M LiClO_4 + 0.01 M BT solution under nitrogen atmosphere at room temperature. The thickness of the PBT film was determined by interferometry to be 1.3 μm [15]. It is assumed that the film thickness is independent of the doping level $d_{\text{PBT}} = 2Q_{\text{ox}}/Q_{\text{gr}} = 0.2\%$ where Q_{ox} is the charge for PBT oxidation and Q_{gr} is the charge needed for chain growth of the PBT [14, 15]. The anion doping concentration (or PBT cation concentration) is $N_A = 1 \times 10^{18}/\text{cm}^{-3}$, defined as follows:

$$N_A = \frac{K}{V_{\text{PBT}}} = \frac{d_{\text{PBT}} \frac{V_{\text{PBT}}}{V_{\text{BT}}}}{V_{\text{PBT}}} = \frac{d_{\text{PBT}}}{V_{\text{BT}}} \quad (1)$$

where K is the charge number of the oxidized PBT, $(\text{BT})_m^{K+}$, and V_{PBT} and V_{BT} are the total volume of the doped PBT film and BT monomer unit volume, respectively. Since the thiophene oligomers are subject to a strong rotational disorder instead of a planar one [16], it is assumed that the BT monomer unit is a cylinder with a

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diameter of 0.85 nm and a length of 1.7 nm which is double the distance between two 2,5-thienylene units of a neutral polythiophene molecule [17].

Before and after the photoelectrochemical measurements the stability of the PBT films was tested by means of cyclic voltammetry at a potential range of -1.0 V to 0.6 V vs. SCE in a deoxygenated 0.2 M LiClO_4 aqueous solution. The cyclic voltammograms obtained are peakless and prove that the PBT film is electrochemically stable in this aqueous electrolyte solution [15].

Photocurrent measurement

A potentiostat/galvanostat (EG&G model 273) was used to control the electrode potential in photoelectrochemical measurements, which were performed in a three-electrode photoelectrochemical cell with a quartz window. A monochromator with a wavelength range of 250 – 1500 nm and a light chopper working at a modulation frequency of 0.1 Hz were used. An argon plasma lamp, operating at 300 W, served as the light source. The photocurrent was amplified by a two-phase lock-in amplifier (EG & G model 278) and recorded by a x - y recorder (Linseis). The photoelectrochemical measurements were performed at several potential points in the range of -1.0 V to 0.6 V (vs SCE) in 0.2 M LiClO_4 aqueous solution.

Results and discussion

The working electrode for the photoelectrochemical measurements was a PBT film ($\delta = 1.3$ μm , $d_{\text{PBT}} = 0.2\%$, $N_{\text{A}} = 1 \times 10^{18}/\text{cm}^{-3}$) coated on a Pt disc electrode (0.071 cm^2). The PBT films synthesized by the galvanostatic method have a regular morphology and compact structure which can be seen from the scanning electron microscopy (SEM) diagram in Fig. 1.

Fig. 1 Scanning electron microscopy diagram of a PBT film formed by galvanostatic synthesis



The photocurrent spectra were measured at several constant electrode potentials of 0.6 , 0.5 , 0.4 , 0.3 , 0.2 , 0.0 , -0.2 , -0.4 , -0.6 , -0.8 and -1.0 V. At the first three potentials no photocurrent was observed. The cathodic photocurrent spectra of the PBT on Pt in 0.2 M LiClO_4 aqueous solution obtained at different electrode potentials are shown in Fig. 2. Each photocurrent spectrum exhibits a current maximum which is similar to that of the absorption spectra of PBT films in oxidized and reduced forms at almost the same wavelength [18] (Fig. 3).

Photocurrent spectra such as these with a maximum depending on the electrode potential (E), were obtained on PMT in an aqueous electrolyte [19] and are similar to the photocurrent spectra of a passive layer on Sn called an amorphous semiconductor [13]. On such materials there is no sharp band edge as in a crystalline semiconductor. The mobility of the electrons and holes in these materials follows a hopping mechanism due to energy distribution and delocalization [13]. The maxima of the photocurrent spectra at $E \geq -0.2$ V appear at the same wavelength of 455 nm (λ_{max}) which shifts slowly to a longer wavelength with the potential negative change until $\lambda_{\text{max}} = 467$ nm at $E = -1.0$ V (Fig. 2). This λ_{max} shift implies a decrease of the transition energy between HOMO and LUMO in the PBT molecules. At $E = 0.0$ V and -0.2 V, the photocurrent spectra show a considerable photocurrent shoulder in the neighbourhood of 550 nm. With the negative change of the potential, this shoulder changes gradually and disappears at -0.4 V after which the photocurrent spectra are almost symmetrical. This photocurrent shoulder could be considered as the overlapped band gap edge as described in the conventional model of the semiconductor/solution interface, because of a linearity of the

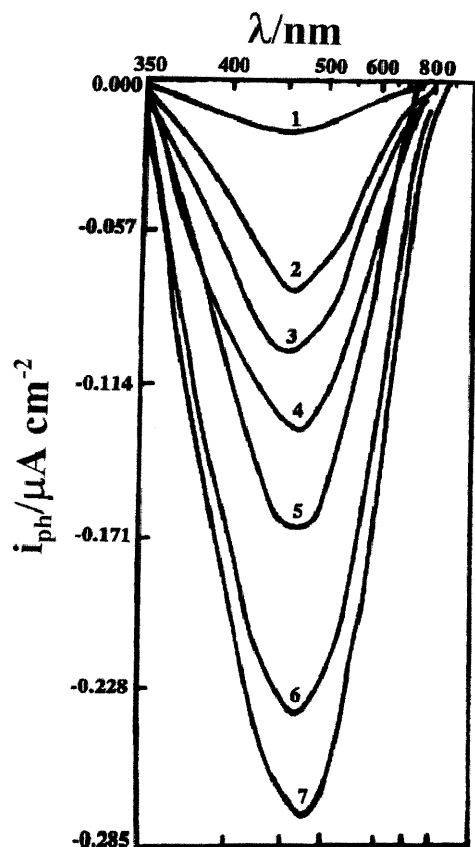


Fig. 2 Cathodic photocurrent spectra of PBT film at the potentials: 1 0.3 V, 2 0.0 V, 3 -0.2 V, 4 -0.4 V, 5 -0.6 V, 6 -0.8 V, 7 -1.0 V in $\text{H}_2\text{O} + 0.2 \text{ M LiClO}_4$ solution (pH 4.8)

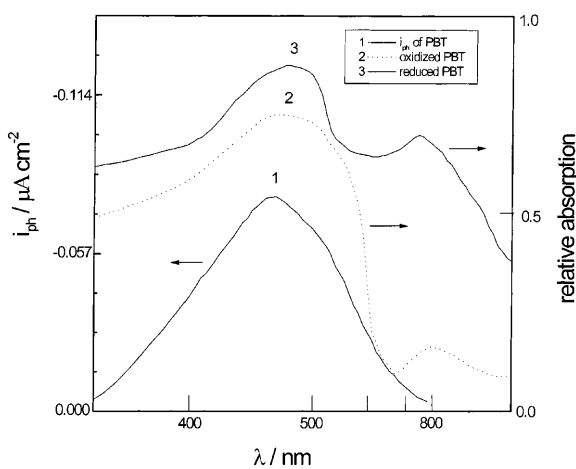


Fig. 3 Photocurrent spectrum of PBT at $E = 0.0 \text{ V}$ (curve 1) taken from Fig. 2 (no. 2) in comparison with visible absorption spectra of the oxidized and neutral PBT forms (curves 2, 3) taken from [18]

Mott-Shottky plot and also photocurrent behaviour in this potential range as mentioned in the following text. The potential dependence of the photocurrent is shown in Fig. 4 where the photocurrent shows a plateau at $E > -0.4 \text{ V}$ and then rises. This behaviour is identical

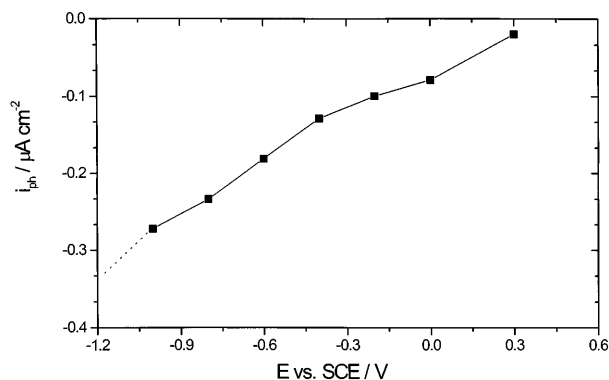


Fig. 4 Potential dependence of the cathodic photocurrents at $\lambda = 460 \text{ nm}$, taken from the photocurrent spectra in Fig. 2

to that of PBT obtained under the potential sweep [8] and similar to that of PMT in aqueous solutions [20].

The photocurrent spectra in Fig. 2 are analysed using the Gaertner-Butler model [10, 11] on the basis of an assumption that the PBT film remains unchanged under the illumination and behaves as a quasi-semiconductor. In this case, the photocurrent density (i_{ph}) is a function of the total photon flux (Φ_0), monochromatic absorption coefficient (α) and thickness of the depletion layer (W), written as

$$i_{\text{ph}}(v) \sim f[e, L_p, \Phi_0(v), \alpha(v), W(E)] \quad (2)$$

where e , v and L_p are elementary charge, wavenumber and diffusion length of minority carriers, respectively. If $\alpha L_p \ll 1$ and $\alpha W \ll 1$, according to the equation

$$(i_{\text{ph}} h\nu)^{2/n} = (e\Phi_0 W A_n)^{2/n} (h\nu - E_g) \quad (3)$$

the $(i_{\text{ph}} h\nu)^{2/n}$ vs $h\nu$ plots should be linear. Here h and E_g are respectively Planck's constant and the band gap energy, A_n is a constant essentially representing the electronic transition probability and is independent of the illumination; $n = 1$ represents a direct electronic transition and $n = 4$ holds for an indirect transition. In the wavelength range from 460 nm to 490 nm, the $(i_{\text{ph}} h\nu)^2$ vs $h\nu$ plots are linear (Fig. 5A), which indicates a direct electron transition and is similar to the photoelectrochemical behaviour of lead oxide thin films [21]. The intercepts of the $h\nu$ axis give an energy value of $2.05 \pm 0.05 \text{ eV}$ which agrees with the value of the band gap energy of PMT given in the literature [19, 20, 22]. The slopes of these plots, $(e\Phi_0 W A_1)^2$, depend on the electrode potentials because W is a function of the electrode potential E , expressed as

$$W = W_0 \left(E_{\text{fb}} - E - \frac{kT}{e} \right)^{1/2} \quad (4)$$

where W_0 is the thickness of the depletion layer at the potential difference $E_{\text{fb}} - E - kT/e = 1 \text{ V}$ and E_{fb} , k and T are flat-band potential, Boltzmann constant and absolute temperature, respectively. In a small potential region, $E \geq -0.2 \text{ V}$, the $(e\Phi_0 W A_1)^2/E$ plot exhibits a

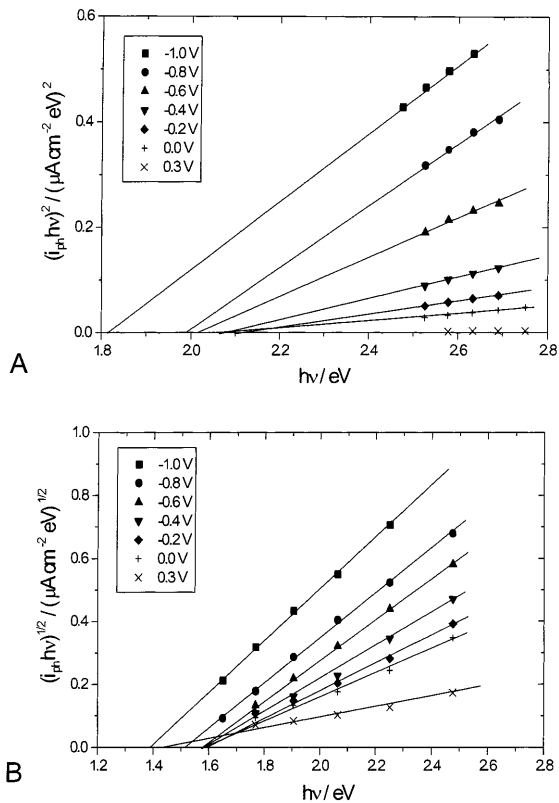


Fig. 5 A $(i_{ph}hv)^2$ vs hv plots; B $(i_{ph}hv)^{1/2}$ vs hv plots of the PBT film. The data for these plots are taken from the photocurrent spectra in Fig. 2

linearity and intersects the E axis at 0.3 V (Fig. 6A) in agreement with that obtained from the i_{ph}^2/E plot (Fig. 7A) and the Mott-Schottky plot (Fig. 7B) in the same potential region corresponding to the equations

$$i_{ph}^2 = (e\Phi_0\alpha W_0)^2 \left(E_{fb} - E - \frac{kT}{e} \right) \quad (5)$$

and

$$\frac{1}{C_{sc}} = \frac{2}{\varepsilon\varepsilon_0eN_A} \left(E_{fb} - E - \frac{kT}{e} \right) \quad (6)$$

where C_{sc} , ε , and ε_0 are the capacity of the space charge layer, the semiconductor dielectric constant and the vacuum dielectric constant. The flat-band potential is determined from the intersects of the Mott-Schottky plot and i_{ph}^2/E plots at the E axis, being 0.33 V vs. SCE [15]. This value is near to the flat-band potential of PMT ($E_{fb} = 0.35$ V vs. SCE) in aqueous solution [20]. From the slope of the Mott-Schottky plot the dielectric constant of PBT film is evaluated to be $\varepsilon = 7.4$. Inserting the parameters ε , ε_0 , e and N_A in the equation

$$W_0 = \left(\frac{2}{\varepsilon\varepsilon_0eN_A} \right)^{1/2} \quad (7)$$

gives $W_0 = 0.29$ μm . Using Eq. 4, the parameter W is then estimated for PBT film at different electrode

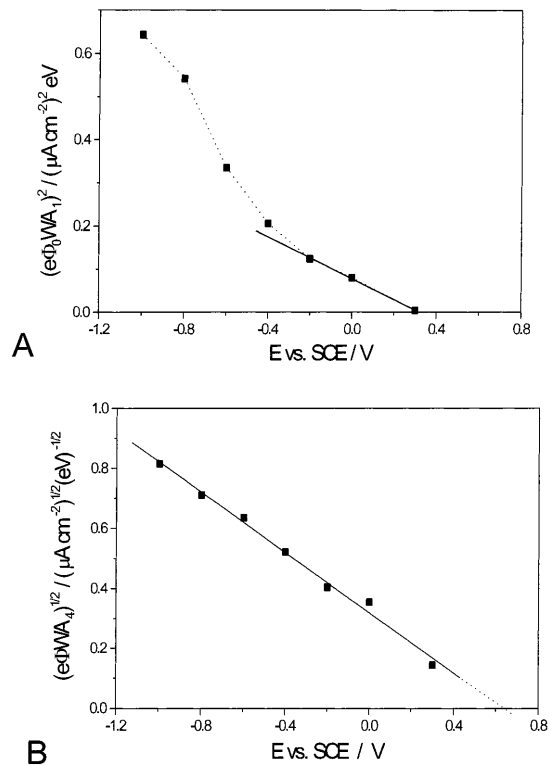


Fig. 6 Potential dependence of slopes of: A $(i_{ph}hv)^2/hv$ plots and B $(i_{ph}hv)^{1/2}/hv$ plots, obtained from the photocurrent spectra in Fig. 2

potentials (Table 1). As mentioned above, in a potential region $E \geq -0.2$ V the photoelectrochemical behaviour of the PBT film accords well with Eqs. 5 and 6, which completely describe the behaviour of photocurrents in a Mott-Schottky junction at the semiconductor|solution interface. The linearity behaviour of the Mott-Schottky plot for ECOPs is little reported in the literature except for [8] by reason of the irregular morphology and structure of the ECOPs. Generally, The ECOPs are regarded as porous electrodes because of their rough morphology and porous structure [18]. However, the PBT film reported in this paper has a regular morphology and compact structure like the crystal lattices in an inorganic semiconductor (see Fig. 1), which is an important prerequisite to form the Mott-Schottky junction at the semiconductor|solution interface. Nevertheless, the surface state (or structure) of the PBT film depends on many factors, for example the electrode potential which could change the surface state of the PBT film leading to a distinction of the photocurrent behaviour at $E < -0.2$ V from that at $E \geq -0.2$ V where the Gaertner model is valid (Figs. 5–7).

In the wavelength range $\lambda > 490$ nm, the $(i_{ph}hv)^{1/2}$ vs hv plots are linear for $n = 4$ (indirect transition) (Fig. 5B), which corresponds to an absorption peak in the absorption spectra of the PBT films at $700 \text{ nm} < \lambda < 900 \text{ nm}$ in Fig. 3 [18]. The intercepts of the hv axis give an energy value of 1.55 ± 0.05 eV which could represent the transition from valence band to the upper bipolaron state being inside the band gap

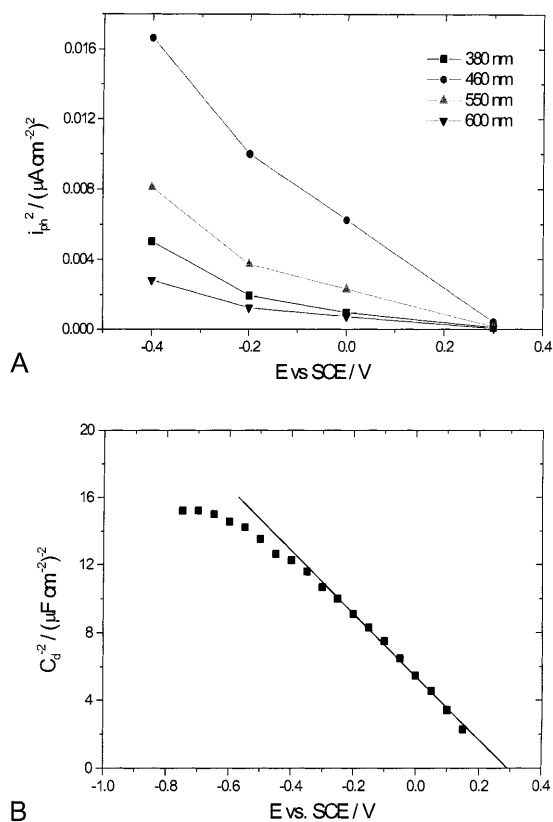


Fig. 7 A i_{ph}^2 vs E plot at wavelengths of 380, 460, 550 and 600 nm obtained from the photocurrent spectra in Fig. 2; B Mott-Schottky plot of PBT film in $\text{H}_2\text{O} + 0.2 \text{ M LiClO}_4$ solution at a frequency of 3 kHz

Table 1 Thicknesses W of the depletion layer of PBT film on Pt in $\text{H}_2\text{O} + 0.2 \text{ M LiClO}_4$ solution at different electrode potentials E

E (V)	-1.0	-0.8	-0.6	-0.4	-0.2	0.0	0.3
W (μm)	0.33	0.30	0.28	0.24	0.21	0.17	0.02

between the valence band and the conduction band, such as that in polythiophene (PT) [23]. The slopes of $(i_{\text{ph}}/h\nu)^{1/2}$ vs $h\nu$ plots are proportional to the electrode potential, i.e. the $(e\Phi_0WA_4)^{1/2}/E$ plot is linear over the whole potential range (Fig. 6B). Its extension intersects the E axis at 0.63 V more positive than the flat-band potential.

As mentioned above, at $E < -0.2 \text{ V}$ the photocurrent behaviour deviates from linearity and the obtained band gap energies decrease with the negative potential change, especially at $E = -1.0 \text{ V}$ (see Fig. 5). These phenomena cannot be interpreted by the common theory of the semiconductor because of the special character of the PBT film for example, the one dimensional conducting system, polaron and dipolaron charge carriers, the π -conjugated electrons in the aromatic ring and the mesomeric forms have different band gaps, which can be strongly influenced by the electric field. However, the known Franz-Keldysh effect given by $\Delta E = 2.8 \times 10^{-7} F^{2/3}$ [24], i.e. electric field influence on the band gap, is here very small ($\Delta E = 0.007 \text{ eV}$) and hence negligible.

According to the summary in the literature [16], the band gap of the aromatic ECOPs is determined by five factors: (1) the energy related to the degree of bond length alternation $E^{\delta r}$, (2) the mean deviation from planarity of the polymer molecule E° , (3) the aromatic resonance energy of the cycle E^{res} , (4) the substituent effect E^{sub} and (5) intermolecular or interchain coupling in the solid state E^{int} . From this one can easily understand the variance of the photocurrent behaviour of the PBT film. E^{sub} does not exist in PBT, but the other four factors are all related to the electric field, i.e. the electrode potential. Among these, E^{res} is related to the π -conjugated system and plays a main role in the final value of E_g . Obviously, the negative potential is favoured for the delocalization length or confinement length in the aromatic π -conjugated system leading to a decrease of the band gap in the PBT film.

Conclusion

The cathodic photocurrents and the Mott-Schottky plot with a negative slope indicate that PBT film has features of a p-type semiconductor. By a detailed analysis of the photocurrent spectra and Mott-Schottky plot, we have obtained some important parameters such as E_g , E_{fb} , ε , W_0 and W as well as other important information on the PBT film. The theories of conventional semiconductor electrochemistry and photoelectrochemistry can be applied to interpret the photocurrent behaviour of the organic semiconductor ECOPs. The validity of this application depends strongly on the morphology and structure of the ECOPs. In fact, PBT is a mixture of various chain lengths [14, 15], and the ratio of the oligomers to polymer depends strongly on the conduction of the PBT formation. This can make the photoelectrochemical behaviour of PBT more complicated and difficult to understand than that of the conventional semiconductor.

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