

Study of charge transition between interfaces of hetero-structured assemblies based on phenyl-capped aniline tetramer/n(p)-silicon

Yahong Zhang^a, Yaan Cao^b, Ce Wang^{a,*}, Junbo Gao^a, Tengfeng Xie^a, Yubai Bai^a

^a Department of Chemistry, Jilin University, Changchun 130023, PR China

^b Institute for Photographic Chemistry, Chinese Academy of Science, Beijing 100101, PR China

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Abstract

Emeraldine base (PECT-EB) and leucoemeraldine base (PECT-LEB) of phenyl-end-capped aniline tetramer have been coated on n(p)-silicon wafers by spin-coating, respectively. The interfacial electron transfers of the assemblies PECT-EB/p-Si, PECT-EB/n-Si, PECT-LEB/p-Si, and PECT-LEB/n-Si were studied by surface photovoltage spectroscopy (SPS). The results indicate that PECT-EB and PECT-LEB make the surface photovoltage (SPV) response of p-Si decreasing and the SPV response of n-Si increasing. The facts imply that the mechanisms of charge transfer of the assemblies are different. Therefore, two reasonable energy band models have been built up to illustrate the transfer process of interfacial charges of p-Si and n-Si coated by PECT-EB and PECT-LEB. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hetero-structure; SPS; Interfacial charge transfer; Aniline oligomers

1. Introduction

Organic–inorganic hetero-structure has become an important study subject because of its potential application in many fields, such as light-emitting diode, photoelectrochemistry, photovoltage cell, and solar light-to-electrical conversion [1–7]. However, solar light-to-electrical conversion, as one of these study fields, has been investigated extensively in the past years, and one of the topics is related to maximizing the quantum yield of photo-to-electric conversion by making the best use of the sensitization function of dye molecules on semiconductors. For example, Grätzel and coworkers [8] utilized dye-sensitized mesoporous TiO₂ and a hole-transport material (OMeTAD) to obtain the photon-to-electron conversion efficiency with a high yield of 33%. Additionally, many polymers have been used as sensitizers for hetero-structure photovoltaic cell [9].

It is well known that polyaniline in the base form consists of two main structural units, i.e. the benzenoid diamine and quinoid diimine, and can be represented schematically by the following formula [10–12].

In principle, y can be varied continuously from one, which yields a completely reduced polymer (leucoemeraldine base,

LEB) to zero, which gives a completely oxidized polymer (pernigraniline base, PNB). For $y = 0.5$, the material is called emeraldine base (EB). They exhibit a wide absorption band in the UV/Vis region, good stability and ease of preparation, which makes polyaniline as a photosensitizer possible.

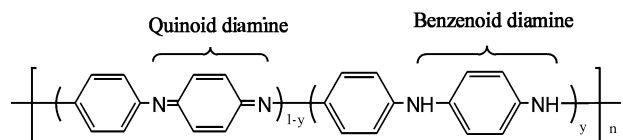
We have an interest in two oligomeric model compounds of polyaniline: PECT-EB and PECT-LEB:

One of their advantages compared to polyaniline is the ability to avoid chemical and structural imperfection and to form a good film, which is important for the efficient photoinduced charge process on the interface. We prepared PECT-EB/p-Si, PECT-EB/n-Si, PECT-LEB/p-Si, and PECT-LEB/n-Si hetero-structural assemblies. The photosensitive properties of these sensitizers were studied by SPS in detail, and the results show that the PECT-EB/n-Si assembly might be used in solar cell devices. Two reasonable energy band models were proposed.

2. Experimental

PECT-EB and PECT-LEB were prepared in our laboratory, and the preparation process has been reported in detail elsewhere [13,14]. p-Si (111, 6 Ω cm) and n-Si (111, 20 Ω cm) wafers were purchased from the Institute of Beijing Non-Ferrous Metal. For the treatment of p-Si and n-Si

* Corresponding author. Tel.: +86-431-5620387; fax: +86-431-8925459.
E-mail addresses: wjzhang@public.cc.jl.cn, wjzhang@mail.jlu.edu.cn (C. Wang).



wafer surfaces, they were first cleaned through ultrasound with chloroform, acetone, and anhydrous ethanol in succession. Then, they were boiled in a mixture of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (4:1 by volume) for 10 min, followed by etching them in a solution of NH_4F (40 wt.%) for 30 s. Finally, they were rinsed with deionized water so that the treated silicon wafer had a hydrophobic surface. The PECT-EB/p-Si, PECT-EB/n-Si, PECT-LEB/p-Si, and PECT-LEB/n-Si hetero-structure assemblies were obtained by spin-coating the corresponding solutions on the silicon wafers.

UV/Vis spectra were conducted on UV-Vis-Nir Recording Spectrophotometer Model 3100 and quartz glass was used as standard. SPS was obtained through a surface photovoltaic spectrometer at room temperature. A photovoltaic cell, ITO/sample/ITO, was used, where two pieces of ITO glasses were utilized as the top and bottom electrodes, respectively. We used a light source-monochromator-lock-in detection technique. The principle and set-up diagram of SPS were described in detail elsewhere [15,16].

3. Result and discussion

The UV-Vis absorption spectra of PECT-EB and PECT-LEB are shown in Fig. 1a and b, respectively. The absorption bands at 310 and 330 nm are attributed to $\pi-\pi^*$ electron transition of the conjugated systems [17–21]. The $\pi-\pi^*$ absorption band of PECT-LEB shows a small red shift in comparison with that of PECT-EB, which results from the extension of π -conjugation system from PECT-EB to PECT-LEB [22–26]. The extent of π -conjugation of benzenoid diamine unit is decreased because of the existence of the quinoid diimine, while quinoid diimine with a good conjugation extent contributes to the absorption at 590 nm, just like mentioned below. The wide absorption bands at 590 nm for PECT-EB and at 600 nm for PECT-LEB are assigned to electron transition from benzenoid to quinoid, i.e. bipolaron transition [18,19,21]. However, the intensity of the peak at 600 nm in Fig. 1b is weaker than that in Fig. 1a. This shows that PECT-LEB is composed of benzenoid diamine unit mainly.

In order to ascertain the energy level positions of PECT-EB and PECT-LEB, the cyclic voltammogram of PECT was

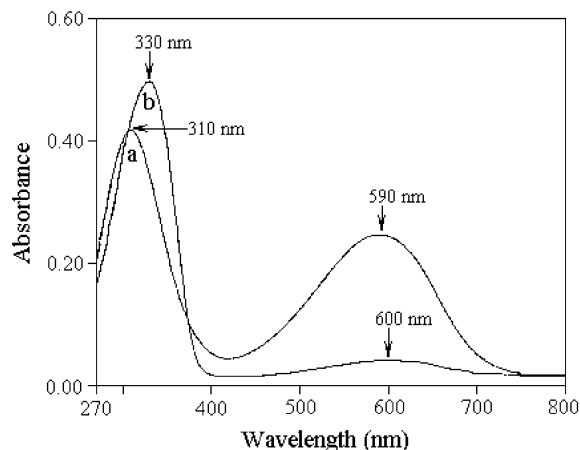


Fig. 1. UV/Vis absorption spectra of PECT-EB (a) and PECT-LEB (b) in NMP solution (concentration: 10^{-5} mol/l).

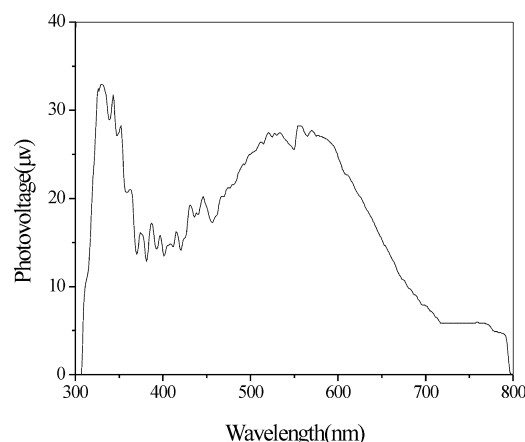
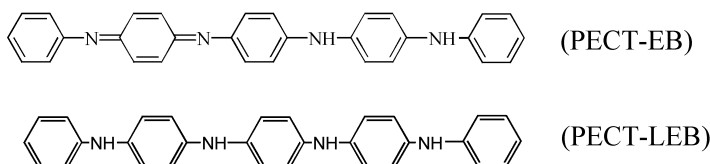


Fig. 2. SPS of PECT-EB powder.

examined, and the result is consistent with that obtained by Baughman and coworkers [21]. It can be known from the voltammogram cycle that the HOMO energy level vs vacuum energy level (VEL) of PECT-LEB is -4.99 eV, and the HOMO energy level vs VEL of PECT-EB is -5.42 eV. There is a 0.4 eV difference between HOMO energy levels of PECT-LEB and PECT-EB, which just gives a reason why the absorption peak of PECT-LEB at 330 nm has a red shift compared with that of PECT-EB at 310 nm.

SPS of PECT-EB powder, as shown in Fig. 2, matches to its absorption spectrum (Fig. 1a). The SPV response at 320 nm is assigned to electron transition of HOMO (valence band) to LUMO (conduction band) energy level of PECT-EB, and its absorption threshold, i.e. the width



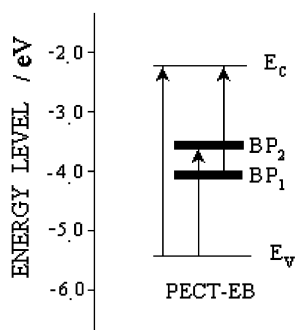


Fig. 3. Schematic diagram of energy band structure of PECT-EB. E_v is the valence band (HOMO) of PECT-EB, and E_c the conduction band (LUMO) of PECT-EB.

of band-gap between HOMO and LUMO energy level of PECT-EB is 3.2 eV. Thus, the LUMO energy level (-2.22 eV) of PECT-EB can be obtained by a simple addition of HOMO (-5.42 eV) and band-gap (3.2 eV). The SPV response at 550 nm is related to the electron transition of bipolaron (i.e. benzene to quinoid electron transition) [21]. That is, the electrons fly from the bipolaron energy level (BP_1) near to HOMO energy level of PECT-EB to its LUMO energy level as well as from HOMO energy level of PECT-EB to the bipolaron energy level (BP_2) at its LUMO energy level. In accordance with its absorption threshold, the bipolaron energy levels are located at -3.99 and -3.65 eV from the VEL, respectively. The energy band structure of PECT-EB is shown in Fig. 3.

SPS of p-Si and PECT-EB/p-Si are given in Fig. 4a and b, respectively. The p-Si shows a strong SPV response in the range 300–800 nm, which is assigned to the electron transition of valence band to the higher energy level in the conduction band. The conduction band and valence band energy level of p-Si are -4.01 and -5.1 eV, respectively [27–29], and its Fermi energy level (E_{fp}) is near to the valence band. As is well known, the Fermi energy level of ITO glass (E_{fITO}) is -4.6 eV [30]. Therefore, the band bend at the interface of p-Si/ITO is downward (Fig. 5a).

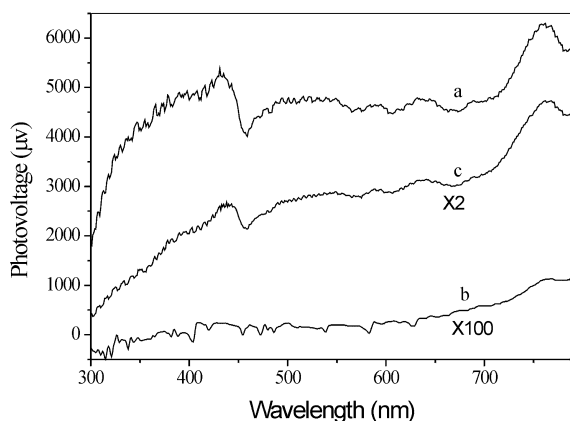


Fig. 4. SPS of p-Si (a), PECT-EB/p-Si (b), and PECT-EB/p-Si (c).

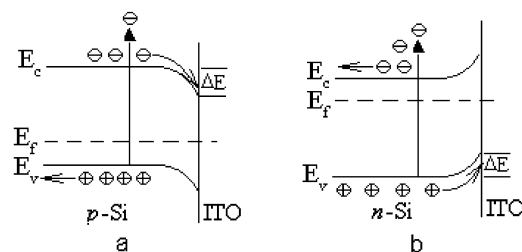


Fig. 5. Schematic diagram of band bends of p-Si/ITO (a) and n-Si/ITO (b). E_v is the top of the valence band, E_c the bottom of the conduction band, and E_f the Fermi energy level.

When the incident light irradiates on the surface of p-Si, the photo-generated electrons fly into the surface of ITO through the band bend and produce an SPV response. It is found that the shape of curve (b) is similar to that of curve (a) in Fig. 4, whereas its intensity has been reduced 1000-fold in scale. It is suggested that no SPV response of PECT-EB itself appears in the curve (b). As a result, curve (b), the SPV response of PECT/p-Si, is produced by the p-Si, while PECT-EB makes its SPV response decreasing.

In an effort to illustrate this “quenching” behavior of PECT-EB for the SPV response of p-Si, an energy band model (Fig. 6a) was built-up on the basis of HOMO and LUMO and also Fermi energy levels of p-Si, PECT-EB, and ITO. Here, a hetero-structure was formed between the interfaces of PECT-EB and p-Si, whereas “Schottky junction” was formed between the interfaces of PECT-EB and ITO. Furthermore, it is known that the PECT-EB is a p-type material [31], and so the Fermi energy level of PECT-EB is near to its valence band. By using such a model, the decrease in SPV response of PECT-EB/p-Si can be explained as follows. When the PECT-EB/p-Si was irradiated, the PECT-EB layer is so thin (about $1 \mu\text{m}$) that the monochromatic light is able to pass through the PECT-EB layer and illuminate on the surface of p-Si, and makes p-Si generate electron transition. There, the photo-generated holes in the valence band, which cannot exceed a large barrier (ΔE_2) to flow to the surface of ITO, only move to the bulk of p-Si. The photo-generated electrons in the conduction band can be transferred to the hetero-structured interface of

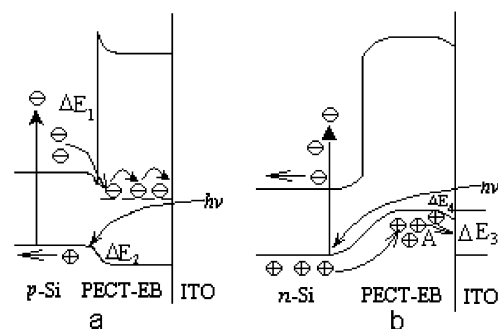


Fig. 6. Energy band model for p-Si/PECT-EB/ITO (a) and n-Si/PECT-EB/ITO (b).

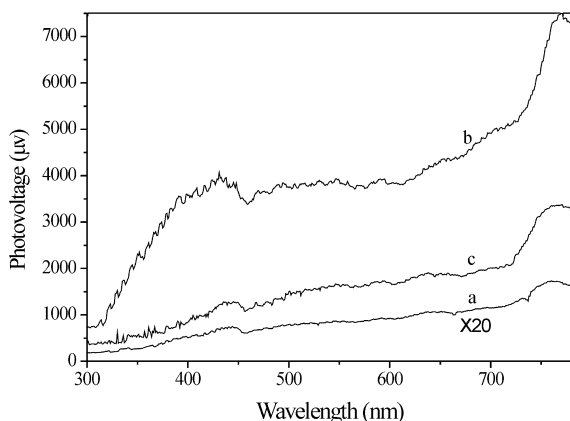


Fig. 7. SPS of n-Si (a), PECT-EB/n-Si (b), and PECT-LEB/n-Si (c).

p-Si/PECT-EB along the band bend. But, the higher barrier (ΔE_1) at the interface of p-Si/PECT-EB prevent electrons flowing further, and only a few of electrons with higher energy can pass through the interface and hop across the located energy level of bipolaron to get to the surface of ITO [32]. Thus, the separation of electron-hole pairs is reduced because of the obstruction of high barrier, so the SPS response of PECT-EB/p-Si is lower than that of p-Si.

In Fig. 7, the SPV response of n-Si (Fig. 7a) is attributed to the electron transition from the valence band to the higher energy level in the conduction band in the range 300–800 nm also. In accordance with the principle of SPS, the Fermi energy level of n-Si (E_{f_n}) is between -4.01 and -4.55 eV and adjacent to its conduction band, and $E_{f_{ITO}}$ is -4.6 eV. So, the band bend of the hetero-structure is upward at the interface of n-Si/ITO (Fig. 5b). When the incident light irradiates n-Si, the electron transition occurs. The photo-generated electrons in the conduction band move to the bulk and the photo-generated holes in the valence band flow into the surface of ITO to engender the SPV response. From Fig. 7a and b, we can see that the shape of peak of SPV response of PECT-EB/n-Si is similar to that of n-Si, and there is no SPV response of PECT-EB at 320 and 590 nm. So it can be sure that the SPV response of PECT-EB/n-Si is produced by n-Si as well, whereas the function of PECT-EB is to make the SPV response of n-Si enhanced greatly (100 times). Referred to relative positions of the conduction band, valence band, and Fermi energy levels of n-Si, PECT-EB, and ITO, this result can be explained by the principle of SPS and a model of energy level structure of ITO/PECT-EB/n-Si, as shown in Fig. 6b. There, the band bend of n-Si is upward at the interface of PECT-EB/n-Si, and the both band bends of PECT-EB at the interface of PECT-EB/n-Si and PECT-EB/ITO are downward. As the incident light irradiates the surface of n-Si, the photo-generated electrons in the conduction band, due to the existence of the band bends, transferred into the bulk, and the photo-generated holes in the valence band flow into the valence band of PECT-EB through the inter-

face of PECT-EB/n-Si. And the electrons accumulate in A region. The photo-generated holes in A region is prone to pass through the barrier (ΔE_4) of the interface of PECT-EB/ITO and concentrate on the surface of ITO. ΔE_3 , a larger driving force of separation of photo-generated electrons and holes pairs, results in the increase in photo-generated holes getting to the surface of the ITO glass. Consequently, the SPV response of PECT-EB/n-Si is increased about 100 times compared with that of n-Si.

It is known that the relationship of the SPV responses of PECT-LEB/n-Si (Fig. 7c) are akin to that of PECT-EB/n-Si (Fig. 7b). However, the difference between Fermi energy levels of PECT-LEB ($E_{f_{LEB}}$) and E_{f_n} are lower than that of $E_{f_{EB}}$ and E_{f_n} (Fig. 6b), since the HOMO energy level of PECT-LEB is 0.4 eV higher than that of PECT-EB. This means that the hetero-structured potential barrier of the interface of PECT-LEB/n-Si is smaller than that of PECT-EB/n-Si (ΔE_3). Thus, the incremental extent of SPV response of PECT-LEB/n-Si vs n-Si is smaller than that of PECT-EB/n-Si vs n-Si. With respect to PECT-LEB/p-Si, the difference between Fermi energy levels of PECT-LEB ($E_{f_{LEB}}$) and E_{f_p} is larger than that of $E_{f_{EB}}$ and E_{f_p} (Fig. 6a), since the HOMO energy level of PECT-LEB is higher than that of PECT-EB. This implies that the band bending at the interface of PECT-LEB/p-Si gets steeper than that at the interface of PECT-EB/p-Si. Therefore, the much more photo-generated electrons in the conduction band can get to the surface of ITO through PECT-LEB layer along the band bend by irradiating. In this way, the SPV response of PECT-LEB/p-Si (Fig. 4c) vs p-Si (Fig. 4a) has a smaller depression than PECT-EB/p-Si (Fig. 4b) vs p-Si.

4. Conclusions

Four hetero-structured assemblies have been prepared based on phenyl-capped aniline tetramer in oxidation state (PECT-EB) and reduction state (PECT-LEB) and p-Si and n-Si wafer, respectively. The charge transfers at these interfaces were investigated by SPS. Two reasonable energy band models were supposed to analyze the interfacial charge-transition processes. It is suggested that the lowering of SPV response of PECT-EB/p-Si and PECT-LEB/p-Si vs p-Si be caused by the blocking of a higher potential barrier at the interface of p-Si/PECT. The enhancement of SPV response of PECT-EB/n-Si and PECT-LEB/n-Si vs n-Si is assigned to the increase in the hetero-structured potential barrier at the interface of PECT/n-Si. A larger hetero-structured potential barrier results in the increase of the photo-generated holes getting to the surface of ITO through the PECT layer along the band bend, which brought forth a stronger SPV response. Additionally, the extent of the decrease or increase of the SPV responses of PECT-LEB/Si vs Si wafer is smaller than that of PECT-EB/Si vs Si wafer, since the HOMO energy level of PECT-LEB is 0.4 eV higher than that of PECT-EB.

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