

# Photoinduced charge carriers at surfaces and interfaces of poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] with Au and GaAs

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The electronic structure and photoinduced surface/interface charge transfer processes have been studied in poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) thin films spin-coated on Au and *n*-GaAs(111) substrates using surface photovoltage spectroscopy. The results show that the MEH-PPV film is a *p*-type semiconductor with an optical band gap of around 2.1 eV and a surface work function of 4.7 eV, and its photovoltaic response is dominated by its free surface rather than the interface with the substrate. In addition, an acceptor surface state at 0.5 eV above the valence-band edge is found in films produced at low spinning rate, perhaps due to surface roughness. Efficient photoinduced electron injection from MEH-PPV films into the GaAs substrates is observed and found to have a strong dependence on the solvent used in the MEH-PPV spin deposition. These findings are discussed in view of the electronic and physical structure of the films.

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## I. INTRODUCTION

For the last decade, poly-(paraphenylene vinylene) (PPV) and its derivatives have received much attention due to their application prospects in devices, such as light-emitting diodes and photovoltaic cells. They have two main advantages in comparison with traditional inorganic semiconductors: ease of forming large-area custom-shaped devices and adjustable chemical structure of the conjugated chain and/or side groups. The latter may control the film electron affinity and ionization potential, enabling high-efficiency charge transfer into underlying substrates. Of the PPV derivatives, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is a typical model material. Due to its low ionization potential and hence efficient hole injection from indium tin oxide (ITO) electrodes, it has been extensively studied for applications of light-emitting diodes.<sup>1,2</sup>

Photoinduced charge transfer at interfaces, whether inorganic/inorganic,<sup>3,4</sup> organic/inorganic,<sup>5,6</sup> or organic/organic,<sup>7,8</sup> is important for fundamental understanding of interface electronic processes and their application for photovoltaic devices. Incorporation of an organic thin film as a sensitizer may extend the photoresponse intensity and energy range of a semiconductor. With its low electron affinity, MEH-PPV has been found to display efficient photoinduced charge transfer (a photosensitization effect) at many interfaces, such as with CdSe, CdS,<sup>9,10</sup> TiO<sub>2</sub> nanoparticles,<sup>11,12</sup> C<sub>60</sub>,<sup>8,13,14</sup> and poly(2,5-hexyloxy *p*-phenylene cyanovinylene)(CN-PPV).<sup>15,16</sup>

To the best of our knowledge, direct observation of photoinduced charge separation in MEH-PPV thin films has not been reported. This may provide insight into charge transport processes and surface/interface electronic structure. Photoinduced interface charge transfer from MEH-PPV to semiconductors is commonly explained by exciton dissociation at the interface due to the favorable energy match without considering the role of the interfacial electric field.<sup>9,10</sup> Experimen-

tally, the conventional analytical tools that have been used are often restricted.

In this paper, we have studied the contact potential difference (CPD) spectra of MEH-PPV thin films (prepared by spin coating) using surface photovoltage spectroscopy (SPS).<sup>17</sup> We have determined the electronic structure and the photoinduced charge separation/transfer processes at MEH-PPV/metal and MEH-PPV/semiconductor heterostructures, and propose a mechanism for photoinduced charge transfer at these semiconductor heterostructures. Additionally, we have studied the effect of the film thickness and preparation conditions, such as spinning rate and solvent type, on the film electronic structure and photoinduced charge transfer.

## II. EXPERIMENTAL METHODS

MEH-PPV thin films were obtained by spin-coating MEH-PPV, dissolved at about 1% weight/volume in tetrahydrofuran (THF), onto Au-coated glass and *n*-GaAs(111) substrates.<sup>18</sup> The GaAs was doped with a concentration of  $2 \times 10^{16} \text{ cm}^{-3}$  of Sn, which locates its Fermi level 0.15 eV below the conduction-band edge. Before spinning, the Au and GaAs substrates were treated as follows. The Au substrate was cleaned with acetone and isopropanol, then blow dried with nitrogen. The GaAs substrate was ultrasonically cleaned in *n*-hexane, acetone, methanol, and deionized water for 5 min each, rinsed in deionized water again, and blow dried with nitrogen.

To study the possible influence of the solvent on the photoinduced charge transfer, MEH-PPV was also dissolved in chlorobenzene (CB) with the same concentration as the THF solution, and spun onto Au and GaAs substrates. All the film/substrate samples were heat-treated at 55 °C in air for 5–6 h to evaporate the solvent residue. The thickness of the films was controlled by the spinning speed and measured by a profilometer.

All the CPD spectra were measured in ambient temperature using a Kelvin probe arrangement (Delta-Phi Electronic,

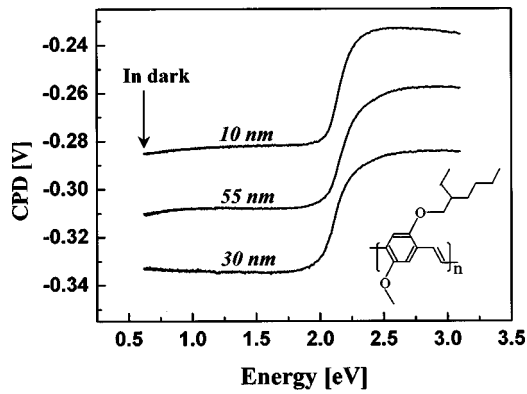


FIG. 1. CPD spectra of MEH-PPV/Au for three films of different thicknesses coated using a THF solution of 1% weight/volume. The inset shows the molecular structure of MEH-PPV.

Jülich, Germany). The CPD was measured between the sample and a vibrating reference probe. It is described by<sup>17</sup>  $V_{\text{CPD}} = (1/e)(W_S - W_R)$ , directly yielding the surface work function of the measured sample. The work function of the reference probe is taken as 5.0 eV. A spectrometer with a double monochromator (McPherson Inc., Chelmsford, U.S.A.) was used to provide illumination in the range of 2000–400 nm. A xenon lamp (250 W) was used as the light source. All the CPD spectra of MEH-PPV/Au samples were obtained after sufficient equilibration had been achieved in the dark, indicated by an essentially constant CPD. The dwell time setting was 2 s to ensure sufficient system response time.<sup>17</sup> The spectra were found to be essentially identical for dwell times of 3 and 5 s. For convenience, we distinguish the film/air interface, referred to as the “free surface,” from the film/substrate interface, which we denote by “interface.”

### III. RESULTS AND DISCUSSION

#### A. Work function and CPD spectra of MEH-PPV

Figure 1 shows the CPD spectra of three MEH-PPV films (10, 30, and 55 nm thick) deposited on Au substrates. In the dark, all the films show a CPD value of about 0.3 V. Hence, the surface work function of the MEH-PPV films is estimated to be 4.7 eV. For all the films, the CPD changes abruptly around 2.1 eV, which corresponds to the band gap of MEH-PPV.<sup>1</sup> No sub-band-gap transition is observed. For a  $\pi$ -bonding polymer with a long one-dimensional conjugated chain, the discrete  $\pi$  and  $\pi^*$  orbitals become continuous bands due to the delocalization of the  $\pi$  electrons along the conjugated chain. This formation of continuous bands results in a band structure similar to that of inorganic semiconductors.<sup>19</sup>

An inorganic semiconductor surface is distinguished by a downward (*p*-type) or upward (*n*-type) band bending. Under band-gap illumination the band bending decreases, i.e., the surface work function decreases (increases) for an *n*-type (*p*-type) semiconductor. Thus, a positive (negative) CPD change indicates a *p*-type (*n*-type) semiconductor.<sup>17</sup> Indeed, our results, shown in Fig. 1, may indicate that the film behaves as a *p*-type semiconductor with a 2.1 eV band gap.

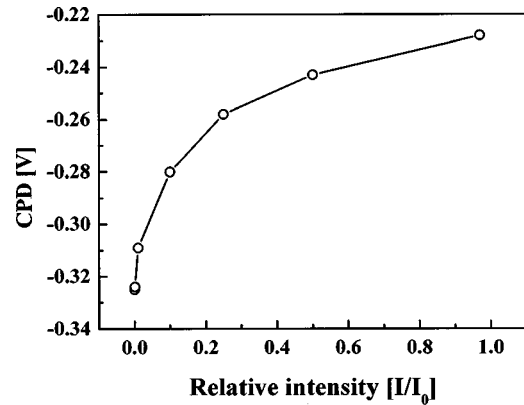


FIG. 2. CPD of a 55-nm-thick film as a function of light intensity at a wavelength of 450 nm (2.76 eV).

The analysis in a thin-film case becomes complicated due to the contribution of light absorption within the space-charge region (SCR) at the interface.<sup>20,21</sup> The substrate itself, i.e., the Au metal, has no contribution to the CPD change.

As a *p*-type semiconductor, if the MEH-PPV film showed a negative CPD change under band-gap illumination, it would indicate a strong interfacial SCR, dominating the surface photovoltage (SPV). However, in Fig. 1, we observe a positive SPV. This means that the interface does not contribute significantly to the SPV. A similar observation was reported by Moons *et al.*, who found that the depletion layer at the porphyrin/ITO interface has no significant contribution to the SPV due to a high density of recombination centers.<sup>22</sup> The work functions of the Au and film we have measured suggest that the MEH-PPV/Au interface may be accumulated rather than depleted, as would indeed be indicated by the Schottky limit. The accumulation layer at the interface does not contribute to a CPD change because of the negligible change of minority carriers at the interface.<sup>17</sup>

Furthermore, Fig. 1 shows that the SPV signal does not vary significantly with the film thickness. If the interface had a dominant influence on the measured CPD change, it would be reflected more strongly in the spectra of the thinner films, due to the more effective light absorption at the interface region. Thus, we conclude that the positive CPD change indicates a photoinduced charge separation at the free surface rather than at the interface. Thus, it shows that the MEH-PPV film is *p* type with a downward band bending at the surface.

We have also examined the CPD spectrum of a MEH-PPV/Al structure. Contrary to the Au substrate, we observe here a *negative* CPD change under band-gap illumination. This indicates a strong SCR at the MEH-PPV/Al interface (as opposed to the Au interface, which is accumulated), induced by the lower work function of Al (4.3 eV) and dominating the CPD signal. Therefore, the CPD spectrum of an organic thin film may depend on the metal substrate. Hence, caution should be exercised when the type of conductivity is to be inferred from the polarity of the CPD change.

Figure 2 shows the CPD in a 55-nm-thick film as a function of light intensity at an incident light wavelength of 450

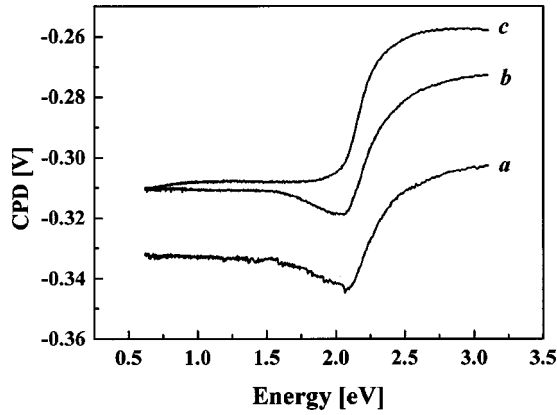


FIG. 3. CPD spectra of two samples deposited at low spin rates [a,  $1.2 \times 10^3$  rpm, b,  $1.0 \times 10^3$  rpm, and c, a reference sample deposited at  $2.0 \times 10^3$  rpm taken from Fig. 1 (55 nm thick)].

nm (2.76 eV). The SPV intensity increases (up to 0.1 eV) with increasing light intensity but no saturation is reached. Therefore, the MEH-PPV film has at least 0.1 eV surface band bending and a  $4.8 (= 4.7 + 0.1)$  eV bulk work function. Taking into account the measured surface work function of MEH-PPV, its electron affinity, and its band gap further supports the conclusion that MEH-PPV has a *p*-type conductivity. The work function of 4.9 eV measured on our Au substrate suggests that the film/Au interface is accumulated, with an upward band bending of about 0.1 eV.

Using a Mott-Schottky plot ( $C^2$  versus  $V$ ), Savenije *et al.* calculated an acceptor impurity concentration of  $9 \times 10^{17} \text{ cm}^{-3}$  for MEH-PPV.<sup>12</sup> Assuming a similar impurity concentration in our film and applying the depletion model, which expresses the depletion width as<sup>23</sup>  $d = \sqrt{2\epsilon\epsilon_0 V / eN_D}$  [where  $\epsilon$  is the relative dielectric constant of MEH-PPV film (taken as  $\epsilon = 3$ ),  $\epsilon_0$  is the free-space dielectric permittivity,  $V$  is the surface band bending,  $e$  is the electronic charge, and  $N_D$  is the impurity concentration], we estimate the MEH-PPV depletion layer to be at least 6 nm deep.

The films discussed above were obtained with spin rates above  $2.0 \times 10^3$  rpm and do not show any sub-band-gap features. Figure 3 shows the CPD spectra of two samples deposited at low spin rates [a at  $1.2 \times 10^3$  rpm and b at  $1.0 \times 10^3$  rpm; c is a reference sample deposited at  $2.0 \times 10^3$  rpm taken from Fig. 1 (55 nm thick)]. A spectral feature is observed at 1.6 eV in these films. Using atomic force microscopy, we found that the surface of the two films were rougher than that deposited at  $2.0 \times 10^3$  rpm. This may indicate that the observed feature is induced by surface roughness. Since SPS is sensitive to carrier formation and separation rather than to light scattering or reflection at rough surfaces, we may conclude that the feature is associated with a surface state transition. The polarity of the CPD change indicates that this transition is due to photoexcitation of electrons from an occupied surface acceptor state to the conduction band of the MEH-PPV. The transition energy locates the gap state at 0.5 eV above the valence-band edge. This suggests that good film morphology is important to reduce defect concentration, which may affect device performance.

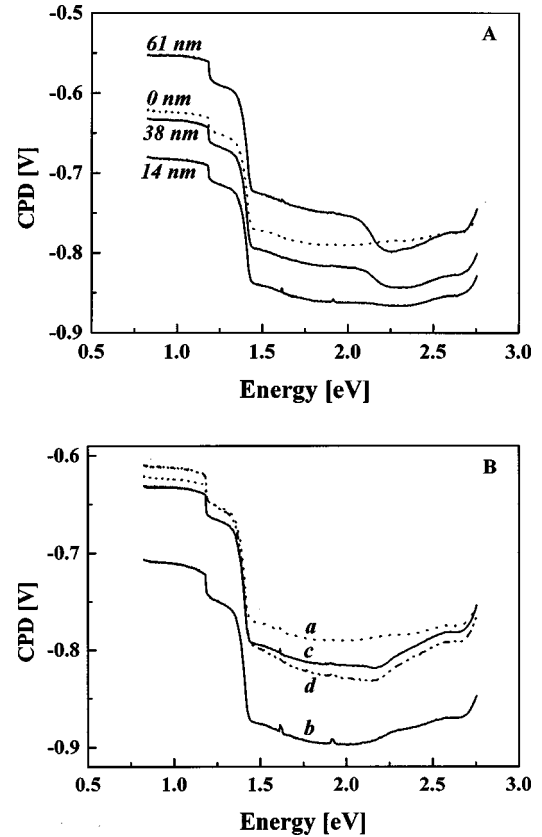


FIG. 4. (a) CPD spectra of a bare GaAs(111) and three MEH-PPV/GaAs heterostructures of different film thicknesses. The small shift at 1.2 eV is due to a filter change. (b) CPD spectra of the same samples before heat treatment. The curves marked a, b, c and d correspond to film thickness of 0, 14, 38, and 61 nm of (a), respectively.

### B. Photoinduced electron transfer at MEH-PPV/GaAs interfaces

Figure 4(a) shows the CPD spectra of a bare GaAs and three MEH-PPV/GaAs structures with different film thicknesses. The bare GaAs shows an abrupt transition at around 1.42 eV, which is the GaAs band-to-band transition (the small shift at 1.2 eV is due to a filter change). No feature is noted above the band-gap transition. The GaAs band-gap transition is consistently observed in the MEH-PPV/GaAs structures and, in addition, another transition is observed at 2.1 eV (especially for thicker films), corresponding to the MEH-PPV band gap. The polarity of this CPD change is negative while it is positive if the MEH-PPV is deposited on Au. This means that the film interface plays a dominant role in this case, as in the Al case. The photoinduced  $\pi$ - $\pi^*$  transition lowers the surface work function of the system, i.e., increases the film interface potential and positive charge. Hence, it can be concluded that the electrons photoexcited in the  $\pi$ - $\pi^*$  transition may be injected into the GaAs substrate. This is supported by the photoinduced charge transfer indicated by the CPD slope change at the same position as the MEH-PPV band-to-band transition. Since no other new tran

sition, i.e., electronic state, is observed, we conclude that photoexcited MEH-PPV electrons are injected into the GaAs substrate without any chemical reaction between the two materials.

Figure 4(b) shows the CPD spectra of the same group of samples measured 3 h after the spin coating and before the heat treatment mentioned in the previous section. The curves marked *a*, *b*, *c*, and *d* correspond to film thickness of 0, 14, 38, and 61 nm of Fig. 4(a), respectively. The photoinduced charge transfer is weaker as compared to the heat-treated structures. This may be related to residual solvent molecules in the film that may obstruct efficient electron transport and injection into the GaAs substrate.

Interface charge transfer at MEH-PPV/semiconductor interfaces is commonly explained by the following model.<sup>9,10</sup> The different electron affinities and ionization potentials provide a driving force for dissociating the excitons photo-generated at the interface. Each exciton yields an electron that is swept into the substrate and a hole left in the film. In the case of a very thin film with a molecular thickness, the layer may be treated as a special case of a surface state and this model may be valid. When the film is sufficiently thick to show the characteristics of a space-charge region, it has to be considered as a second phase and this simple model may no longer be valid due to the existence of interfacial fields. Based on the Fermi level positions in the two materials and on the Schottky model of this system, we can safely assume that these fields exist in the dark. In Fig. 1, even the thinnest MEH-PPV film (10 nm thick) shows the SCR effect on the CPD values under illumination. Therefore, we must consider the actual interface band structure and its role in the interface charge-transfer process.

Figure 5(a) shows the band structures of isolated MEH-PPV (Ref. 11) and GaAs.<sup>18</sup> According to our measurements, GaAs has a surface work function of 4.4 eV, i.e., 0.11 eV higher than the bulk value. However, the measured CPD change is over 160 meV. Thus, surface band bending alone cannot account for the observed CPD change. This difference may be explained, however, by a dipole at the GaAs surface. Figure 5(b) shows the interfacial band structure after the contact is made. Due to the difference in work functions between MEH-PPV and GaAs, an interface field is formed directed from the GaAs to the MEH-PPV. Figure 5(c) depicts the photoinduced interfacial charge-transfer model and the changes of surface work function and level positions (marked by primes). The photoinduced hole-electron pairs are separated under the interfacial field and the electrons move toward the interface. Due to the lower energy position of the minimum of the GaAs conduction band, the electrons are injected into it. In Figs. 5(a) and 5(b), the band bending of the GaAs substrate is considered unchanged before and after contact, because according to our CPD measurements the GaAs substrate is not substantially influenced by the MEH-PPV coverage, indicating Fermi level pinning of the GaAs surface. In the three samples studied, the signal of the electron transfer increases with increasing film thickness [see Fig. 4(a)]. Since the film diffusion length is about 20 nm,<sup>12</sup> more photogenerated electrons are expected to be injected

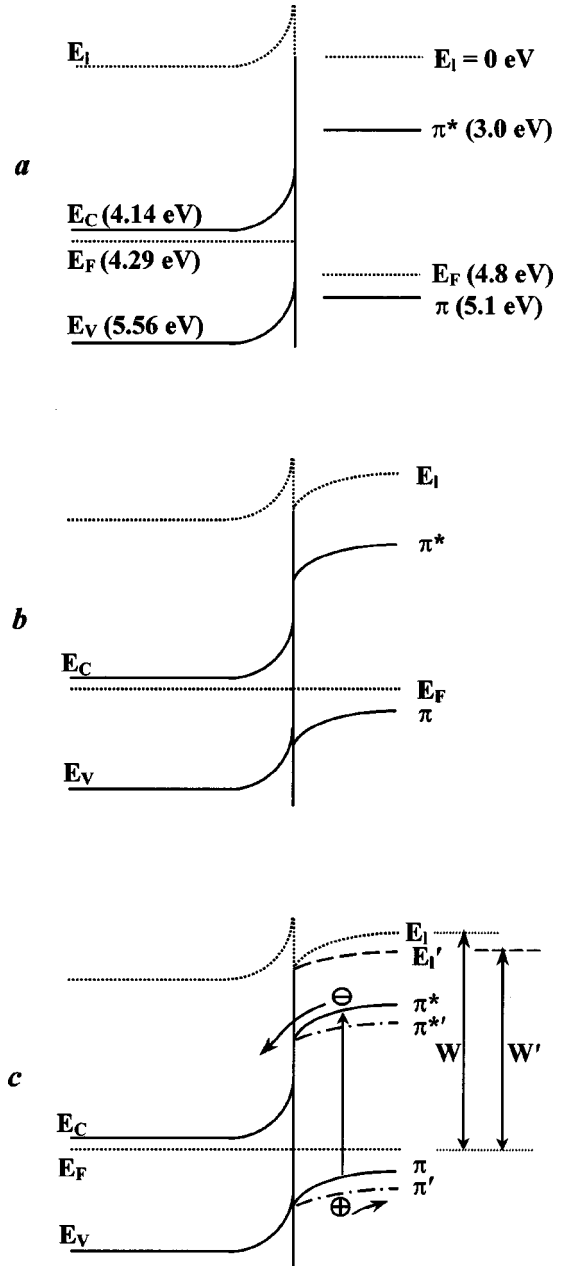


FIG. 5. Interfacial band structure of the MEH-PPV/GaAs heterostructure (a) before contact, (b) after contact, and (c) under band-gap illumination [photoinduced charge-transfer model and changes of surface work function and level positions (prime) are depicted].

from our thicker MEH-PPV films. Increasing the film thickness may also improve the film coverage of the substrate.

Figure 4(a) shows that there is a positive slope change at a photon energy of about 2.25 eV. This change is more pronounced for the 61-nm-thick film, but is totally absent in the bare GaAs. This change is probably indicative of the change in absorption depth of the incident light with wavelength. At shorter wavelengths, light absorption is more efficient at the free surface. This results in a dominant contribution of the surface (rather than the interface) CPD change, which is positive due to the *p*-type conductivity of MEH-PPV.



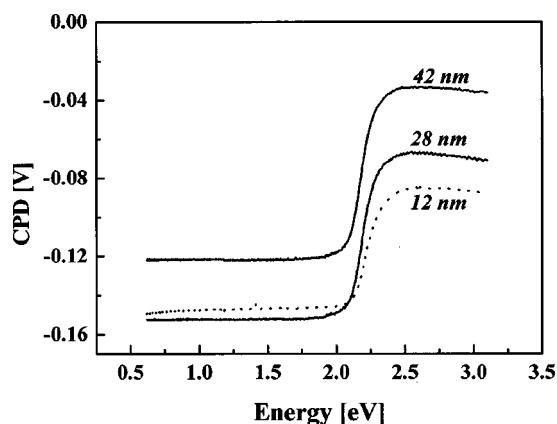


FIG. 6. CPD spectra of MEH-PPV/Au for three films of different thickness coated using a CB solution of 1% weight/volume.

### C. The influence of solvent on the charge transfer

Recently, to reconcile several contradictory reports on various film coating conditions, Nguyen *et al.* have suggested that the photophysical properties of MEH-PPV films depend on the solvent choice for the solution from which the film is coated, i.e., memory of the chain state in the solution may be preserved through the coating process and survive in the film.<sup>24,25</sup> In a THF (nonaromatic solvent) solution, MEH-PPV chains coil tightly to maximize their side-group interactions with the solvent and minimize their backbone exposure to it. In a CB (aromatic solvent) solution, however, MEH-PPV chains are rigid and open so as to have their aromatic backbone sufficiently exposed due to the preferential interaction of the aromatic backbone with the solvent. The effect of the former solvent intends to make MEH-PPV chains isolated from each other, while the effect of the latter is favorable for  $\pi$ -electron coupling of ground-state or excited MEH-PPV chains.

For experimental verification of this concept, we have also studied MEH-PPV/Au and MEH-PPV/GaAs heterostructures coated from CB solutions of 1% weight/volume (the same concentration as the THF solutions). Figure 6 shows the CPD spectra of three different MEH-PPV/Au heterostructures. Showing the influence of chain configuration on the film electronic structure, the surface work function of MEH-PPV films coated from CB solution is higher than those made using THF solution by about 0.15 eV. Figure 7 displays the CPD spectra of three different MEH-PPV/GaAs heterostructures, coated using CB solution. It is surprising and interesting to observe that only the 50-nm-thick film shows a weak negative slope change at the band-to-band transition of MEH-PPV, while the 17- and 35-nm-thick films do not. To exclude the influence of possible remnant CB solvent (CB is heavier than THF), the MEH-PPV/GaAs sample with 35-nm-thick film was heat-treated at 55 °C for another 12 h, but the photoinduced charge-transfer effect was still absent. Therefore, in comparison with films coated using THF solution, MEH-PPV coated using CB solution has a weaker photointeraction with GaAs.

Factors that inhibit efficient MEH-PPV/semiconductor photoinduced charge transfer have been discussed previously.<sup>9,10</sup> However, to the best of our knowledge, the

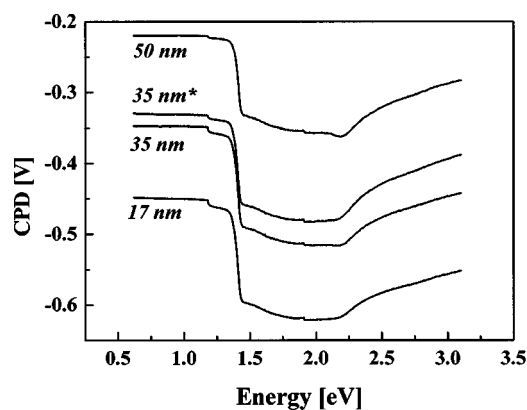


FIG. 7. CPD spectra of three MEH-PPV/GaAs heterostructures of different film thicknesses coated using a CB solution. The sample marked \* was heat-treated at 55 °C for another 12 h. The small shift at 1.2 eV is due to a filter change.

influence of the solvent choice on the charge-transfer efficiency has never been reported. Two possible factors may account for the lower charge-transfer efficiency of the films coated using CB solution. Both these factors arise from the film configuration due to the effect of the solvent.

The first is the interchain species effect. Due to the ease of MEH-PPV chain interaction, photogenerated intrachain excitons can be delocalized across the neighboring chains. This means that, before the photogenerated intrachain exciton is dissociated into an electron and a hole by the interface field, it delocalizes into an interchain exciton with lower energy. Thus, the rate of efficient electron injection should be greatly reduced. Ginger and Greenham<sup>9</sup> have found that, although the energy match (the difference in electron affinities) is satisfied for photoinduced charge transfer, the photoluminescence efficiency of DHeO-CN-PPV remains largely unaffected in a DHeO-CN-PPV/CdSe nanocrystal mixture. This indicates that the photoinduced electron transfer from DHeO-CN-PPV to CdSe nanocrystals is not efficient. One of the possibilities mentioned in that paper is that, due to the small interchain space in the cyano-substituted polymer with symmetric alkoxy side chains, the photogenerated intrachain exciton may be delocalized across the chains and form interchain species, decreasing efficient exciton dissociation and electron transfer at the interface.

The second factor is the possible interface barrier formed by the 2'-ethyl-hexyloxy at the interface. In the films coated using CB solution, the MEH-PPV chains tend to arrange with a small interchain spacing. Therefore, when MEH-PPV is deposited onto a GaAs surface, which is hydrophobic, its 2'-ethyl-hexyloxy side chain probably makes direct contact with the GaAs surface, allowing easier chain interaction. Thus, an interface barrier created by the side chains may prevent efficient charge transfer. Ginger and Greenham have also suggested that the dihexyloxy chains on both sides of DHeO-CN-PPV prevent the CdSe nanocrystals from sufficient access to the conjugated backbone to allow charge transfer to occur,<sup>9</sup> while Greenham *et al.* have found that an 11 Å alkyl barrier can effectively inhibit electron transfer from MEH-PPV to CdS nanocrystals.<sup>10</sup>

Therefore, in the design of photovoltaic devices utilizing the photosensitization effect, the energy match is only a necessary condition for efficient performance. The microscopic configuration of the sensitizer layer determined by the film coating conditions and its molecular structure must also be considered for an efficient dynamic process.

#### IV. SUMMARY

In this work, we have studied the photoinduced charge separation and transfer processes of MEH-PPV/Au and MEH-PPV/*n*-GaAs(111) heterostructures, using surface photovoltage spectroscopy. When spin coated using tetrahydrofuran solution, MEH-PPV film on Au substrate has a surface work function of about 4.7 eV. The photoinduced charge separation is dominated by the surface rather than the interface and shows the *p*-type conductivity of the film, which has a band gap of 2.1 eV. An acceptor surface state 0.5 eV above the valence-band minimum has been found in films coated at low spinning rates, probably arising from

surface roughness. The MEH-PPV/GaAs heterostructure shows efficient photoinduced electron transfer to the GaAs substrate. In comparison, using chlorobenzene as an alternative solvent, the MEH-PPV film increases its surface work function by about 0.15 eV and photoinduced electron transfer from the film to the GaAs substrate becomes weaker. This may be attributed to the interchain species effect and/or the spacer role of 2'-ethyl-hexyloxy. This result suggests that the microscopic configuration of the film determined by the deposition parameters is crucial for efficient device operation.

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