

# Interactions at tetraphenyl-porphyrin/InP interfaces observed by surface photovoltage spectroscopy

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Received 3 October 2007; received in revised form 1 November 2007; accepted 1 November 2007

Available online 13 November 2007

## Abstract

Illumination induced charge separation processes at tetraphenyl-porphyrin (H<sub>2</sub>TPP)/InP interfaces are characterized. The results indicate that upon illumination an electronic transition takes place between the organic highest occupied molecular orbital (HOMO) and the InP conduction band. A 70 meV blue shift in the characteristic modulated surface photovoltage spectrum of a 50 nm H<sub>2</sub>TPP film was observed when n-InP substrate was used. Such blue shift was not observed when Au, SnO<sub>2</sub>:F or p-InP substrates were used. The shift may suggest a presence of an ordered interfacial sub-layer in an almost lying orientation, due to chemical or physical interactions at the interface. The results indicate that the Fermi level is unpinned at the interface. An exciton diffusion barrier in close proximity to the H<sub>2</sub>TPP/n-InP interface has been demonstrated. © 2007 Elsevier B.V. All rights reserved.

PACS : 73.20.-r; 73.50.Pz; 73.40.-c; 73.61.P

Keywords: Surface photovoltage; Interfaces; Tetraphenyl-porphyrin; InP; Charge separation

## 1. Introduction

Due to their increased technological importance, the electronic structures at interfaces with conducting organic layers are intensively studied [1,2]. Recent studies have reported that the electronic structure at interfaces of organic layer with metals, other organic layers and native oxidized substrates are changed from vacuum level alignment to Fermi level pinning [3]. The latter corresponds to creation of an interface dipole due to charge transfer across the interface sufficient to shift the organic layer polaronic level to the substrate Fermi level. The pinning can occur once the negative (positive) polaronic level is larger (smaller) than the Fermi level of the substrate [4,5]. More mechanisms, such as chemical interactions at the interface and other polarizations effects [6,7], e.g., changes in the molecules orientation within the layer [8], affect the electronic structure. Furthermore, when inorganic semiconducting substrates are used, chemical interactions can create new surface states or change the position and density of occupied surface states of the substrate [9].

Commonly, interface interactions are elaborated from changes in a characteristic photoemission spectrum. The ultraviolet photoemission [10] in ultra-high vacuum (UHV) and photoluminescence [11] spectra are widely investigated. Interface properties can also be studied by characterizing the light induced charge separation mechanisms in interfaces with organic materials [12]. Diffusing excitons dissociate at the interface and preferential escape of one type of charge carriers takes place, resulting in a measurable surface photovoltage (SPV) [13]. In addition to light absorption, both the exciton diffusion length and transport properties are important for proper analysis. Additional charge separation mechanisms may take place at organic layer interfaces and should be considered. Internal photoemission, due to light absorption at Au substrate, has been demonstrated [14]. For metal oxide substrates, illumination induced charging, in which the substrate surface states are involved, is assumed and used to explain SPV observations [15]. The outcome is an illumination induced permanent charging. By using modulated SPV techniques, the charge separation processes can be identified. A slow back diffusion process limits the modulated SPV signal that originates from charge transfer between the substrate and the organic layer [16].

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Surface photovoltage spectroscopy (SPS) can also be performed using a Kelvin probe (KP) which is a quasi-static measurement and very sensitive to the permanent charging effects of the organic layer [14,15]. Yet, quasi-static SPS using KP is a well-established experimental technique to investigate the electronic structure of inorganic semiconductors surfaces [13]. For interfaces with organic layer and inorganic semiconductors, charge separation processes within the substrate should be correctly separated from charging effects and related excitons dissociation process within the organic layer. Such separation is better achieved using complementary measurements, combining KP and modulated SPV techniques.

In this work, SPV techniques are implemented to characterize possible chemical or physical interactions at tetraphenyl-porphyrin ( $H_2TPP$ )/InP interfaces.  $H_2TPP$  is a synthetic porphyrin derivative with several absorption bands in the visible range, the Soret band is at about 2.9 eV, the Q bands are at 2.4, 2.2, 2.1, and 1.9 eV [11,17]. SPS using KP is useful for characterizing changes in the substrate electronic structure after deposition of  $H_2TPP$  layer, i.e., the “InP side” of the interface. Modulated SPV measurements using the capacitor arrangement [18] are better suited to characterize exciton dissociation processes at the interface, i.e., the “ $H_2TPP$  side” of the interface. The results are compared to modulated SPV data obtained for  $H_2TPP/Au$  and  $SnO_2:F$  (denoted by FTO) interfaces and to measured absorption spectrum.

## 2. Experimental

Organic  $H_2TPP$  layers were evaporated at the same time on n-type ( $2.5 \times 10^{16} \text{ cm}^{-3}$ ) and p-type ( $5.7 \times 10^{16} \text{ cm}^{-3}$ ) InP (1 0 0) substrates and on glass substrates coated with a thin Ti adhesion layer and a 100-nm-thick Au. For absorption measurements,  $H_2TPP$  layer was evaporated on bare glass substrates. The substrates were cleaned ultrasonically in acetone and *iso*-propanol and dried in  $N_2$  before evaporation in high vacuum at room temperature. The deposition rate of the  $H_2TPP$  layers (5,10,15,20-tetraphenyl-21H, 23H-porphine, by Sigma Aldrich Inc.) was controlled by using a quartz thickness monitor and set to about  $1 \text{ \AA/s}$ . 50 nm was a standard thickness of the  $H_2TPP$  layers. The samples were stored in vacuum or nitrogen ambient after evaporation and between measurements. SPV spectra were excited with a halogen lamp and a quartz prism monochromator. SPV measurements were carried out in vacuum, air, nitrogen and at increased humidity (3 mbar  $H_2O$ ) atmospheres. Dynamic SPV measurements were carried out using 8 Hz chopped illumination, in which the modulation of the slow negative charges is minimized [16]. The in-phase PV signal was detected by a lock-in amplifier. Quasi static SPS measurements were carried out using Kelvin probe (KP). The KP is a semi-transparent 2.5 mm diameter gold mesh, which vibrates at frequency of about 166 Hz using a piezo-electric crystal, with sensitivity of less than 1 mV. The probe is manufactured by Besocke Delta Phi Electronic (Jülich, Germany). Some chemical composition analysis was done using X-ray photoelectron spectroscopy (XPS). The measurements were performed under ultra-high vacuum conditions

(base pressure below  $3 \times 10^{-10}$  Torr) using 5600 Multi-Technique (AES/XPS) System (PHI, USA). The samples were irradiated with an Al  $K\alpha$  monochromatic source (1486.6 eV). Spherical capacitor analyzer using the slit aperture with a diameter of 800  $\mu\text{m}$  analyzed the generated electrons.

## 3. Results and discussion

### 3.1. Surface state occupation changes

Changes in the InP substrate surface electronic structure induced by  $H_2TPP$  deposition were best seen when a p-type substrate was used. Any transitions, related to surface states, were below the noise level when n-InP substrates were used. The spectra of a bare p-InP and a 50 nm  $H_2TPP/p$ -InP samples taken at  $-60^\circ\text{C}$  are shown in Fig. 1. Low temperature SPV measurements are expected to have higher sensitivity to surface charge redistribution. At lower temperatures, lattice phonons are suppressed and thermally induced charge carrier concentration is reduced, thus the influence of the light induced charges is enhanced. For p-type semiconductor downward (upward) slope changes are related to illumination induced surface state depopulation (population) i.e., acceptor-like (i.e., donor-like). Once a surface state is depopulated (populated), the net charge separation causes a decrease (increase) in the work function. This means a negative (positive) contact potential difference (CPD) change relative to the work function of the Au probe. These concepts were used to detect previously reported surface transitions at Zn doped p-InP (1 0 0) [19,20] in the spectrum of the bare p-InP. Starting from low energy, depopulation of the  $S_2$  state at  $E_c - 0.79 \text{ eV}$  and the  $A_1$  state at  $E_c - 1.24 \text{ eV}$  and population of the  $D_1$  state at  $E_v + 1.04 \text{ eV}$  are clearly observed in the spectrum. The SPV signal due to depopulation of  $S_1$  state at  $E_c - 1.12 \text{ eV}$  is small and hardly seen in the spectrum. The  $A_1$  and  $D_1$  states are attributed to existence of excess P and adsorbed O at the surface, respectively, the  $S_1$  and  $S_2$  states are attributed to existence

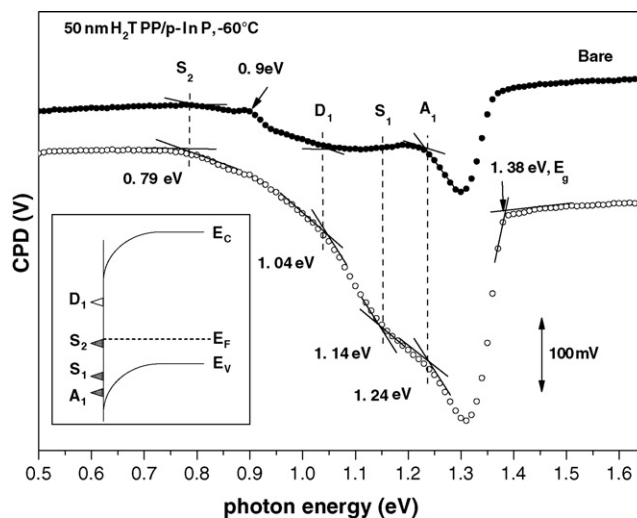


Fig. 1. CPD spectra of bare p-InP and p-InP/ $H_2TPP$  at  $-60^\circ\text{C}$ . (Inset) Schematics of the InP surface states distribution.

of some Fe. The origin of the slope change at 0.9 eV is unclear and assumed to be an artifact or simply a relaxation process of excess charge carriers. The energy positions of the surface states are schematically demonstrated in the inset of Fig. 1.

At a glance, no new transitions are generally observed in the spectrum of H<sub>2</sub>TPP/p-InP at  $-60^{\circ}\text{C}$ . The A<sub>1</sub> and S<sub>2</sub> surface states clearly are detected, at 1.04 eV (D<sub>1</sub>) and 1.14 eV (S<sub>1</sub>) a change in the slope is observed but the polarity of the change is opposite to that in the spectrum of bare p-InP. For example, at 1.04 eV (D<sub>1</sub>) a negative instead of a positive slope change is detected. This may indicate that electrons are transferred from an occupied state at  $E_c - 1.04$  eV to the conduction band.

The ionization energy of p-InP is about 5.8 eV [21] and therefore, the S<sub>1</sub> and S<sub>2</sub> states at about 5.6 and 5.2 eV are both in relatively close proximity to the H<sub>2</sub>TPP HOMO level at about 5.4 eV. [22] The increased negative slope change at 1.04 eV is most likely related to transition from the HOMO level to the conduction band. The signature of the D<sub>1</sub> state in the spectrum is the small positive slope change in the overall signal at about 1.14 eV, in which the relative contribution of the transition from the filled states is reduced. The possibility of about 100 meV red shift in S<sub>1</sub> and/or S<sub>2</sub> transitions, due to chemical interactions (molecular orbital coupling) with the HOMO level, cannot be excluded as well. The possibility of a blue shift in the D<sub>1</sub> transition should also be considered but it is unlikely. The strength of the interaction between the molecules and the semiconductor surface states decreases when the energy difference between the interacting levels increases. [9] Electron transfer from the HOMO to the D<sub>1</sub> state has to overcome a barrier of about 0.6 eV, the expected outcome is a red shift in the transition spectral signature. [9] The large energy difference between D<sub>1</sub> and the LUMO level (more than 1 eV) reduces significantly any orbital coupling between the two.

Since H<sub>2</sub>TPP was evaporated on naturally oxidized InP substrate, the H<sub>2</sub>TPP molecules are expected to be physically rather than chemically adsorbed. Only small portions of the molecules are expected to form a chemical bond, covalent in nature, at the H<sub>2</sub>TPP/InP interface. Large changes, if at all, in the energy position of the surface states are not expected. The experimental observation supports the weak interaction assumption. From the agreement between the expected HOMO level energy [22] and the energy difference, assumed from the CPD spectrum, between the HOMO and conduction band it can be concluded that within the measurement resolution no interface dipole is seen. Furthermore, the HOMO level is located at about 0.3 eV below the Fermi level at the InP surface of a similar substrate [19] and the Fermi level of the H<sub>2</sub>TPP is located at about 0.6–0.8 eV above the HOMO level according to the results obtained for H<sub>2</sub>TPP/Au heterostructure [19]. Therefore, the Fermi levels are not perfectly aligned at the interface, i.e., weak interaction.

Existence of gas atoms in the layer may alter the InP surface electronic structure as well. Surface states of similar InP substrates were found to be affected by various components within an overlayer of organic polymer [23]. The A<sub>1</sub> surface state was found to be suppressed in the presence of sulfur or fluorine while D<sub>1</sub> state is suppressed by existence of N atoms in

the film [23]. Chemical analysis using XPS showed no presence of P and negligible concentrations of S in the layer. Bonded nitrogen, but not free atoms, exist in the H<sub>2</sub>TPP molecule and are not likely to affect the D<sub>1</sub> state transition.

### 3.2. Changes in the barrier at the interface

In addition to surface dipole formation, change in the surface barrier, i.e., band bending (BB), can be caused by charge transfer at the interface [9]. Changes in the magnitude of the band-to-band transition in the spectra can be correlated to changes in the BB if other effects may be neglected. Changes in the surface recombination velocity (SRV) due to H<sub>2</sub>TPP deposition may be neglected. Reduced SRV can cause an increase in the SPV [13]. Since the substrate features a high trap concentration and a fast SRV [23] and since no degenerated/passivated surface states were observed in the CPD spectra, post-deposition lower SRV is not expected.

The band-to-band transition at 1.38 eV is also shown in the spectra taken at  $-60^{\circ}\text{C}$  (Fig. 1). The transition magnitude is increased by a factor of two in the spectrum of the H<sub>2</sub>TPP/p-InP sample, possibly due to increased BB. The surface barrier, i.e., surface potential, can increase due to additional positive charges, which are trapped at the surface or in the H<sub>2</sub>TPP layer in close proximity to the interface. In that case, the surface states are pushed further lower in energy relative to Fermi level in thermal equilibrium. The results do not support such predictions. Although passivation of surface states is not observed, the concentration of trapped electrons in the energy range between  $E_c - 0.8$  eV and  $E_c - 1.2$  eV of the p-InP band gap is increased. In that case, increased negative surface charges results in a decrease in the surface barrier.

Kinrot and Shapira [19] have shown that below 150 K ( $-123^{\circ}\text{C}$ ) the S<sub>2</sub> state is depopulated, in dark, due to thermodynamic changes in the Fermi level position. In relation to the increased band gap at low temperatures, a surface barrier of about 0.56 eV in thermal equilibrium was estimated. It is assumed to have little dependence on temperature. CPD spectra of the p-InP/H<sub>2</sub>TPP at  $-120$  and  $-180^{\circ}\text{C}$  are shown in Fig. 2. Once the illumination is switched on, a positive charging/negative discharging process (i.e., negative CPD change) is observed. The origin of the process is not clear; it was not detected in the spectrum of the bare p-InP at  $-100^{\circ}\text{C}$  (inset of Fig. 2). Therefore, it is presumably related to a positive charging process of the organic layer at low temperatures. This charging process makes an exact analysis of changes in S<sub>2</sub> surface state occupation a difficult task, yet a qualitative picture may be deduced. Comparison at 1 eV suggests that the SPV signal related to the S<sub>2</sub> transition is significantly reduced in the  $-180^{\circ}\text{C}$  spectrum. The CPD at 1 eV is a good comparing position for the S<sub>2</sub> state since the signal is not affected by the D<sub>1</sub> state transition. It is safe to deduce that the S<sub>2</sub> is close to being empty within the measurement resolution, similar to Kinrot and Shapira findings. Therefore, changes in the p-InP BB after H<sub>2</sub>TPP deposition, if exist, are minor.

An effective BB under illumination concept should be tested to explain the observations. Under continuous illumination, the

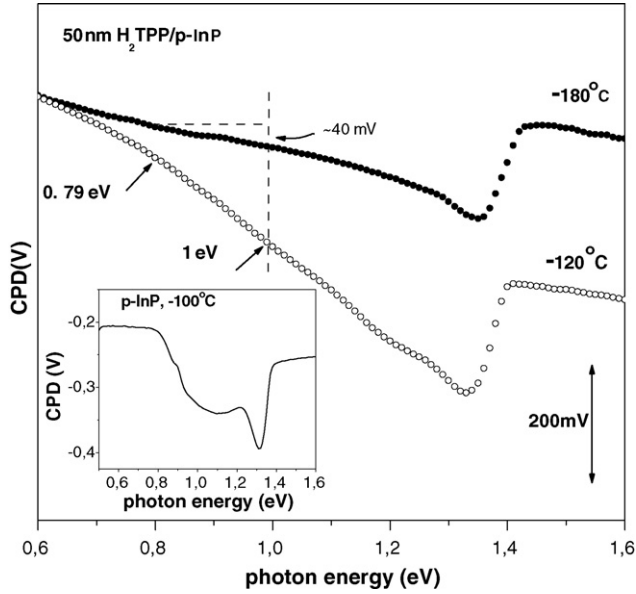


Fig. 2. CPD spectra of 50 nm H<sub>2</sub>TPP/p-InP at –120 and –180 °C. (Inset) CPD spectrum of bare p-InP at –100 °C.

BB can be increased due to the light induced de-trapping processes of charges from occupied surface states/HOMO level to the conduction band of the InP and possibly other charging processes of the organic layer. Although the surface potential of p-InP attracts the excited electrons back to the surface, the outcome of such transition is an increase in the surface barrier [13]. The effective BB under illumination is higher for p-InP substrates as the de-trapping process is intensified. When analyzing the ΔCPD of the band-to-band transition, this effective BB should be addressed if other thermally related effects can be neglected. The increased BB under illumination is demonstrated in the CPD transients shown in Fig. 3. Under 1.35 eV illumination, the band-to-band transition of bare InP is fast saturating in comparison to the CPD value obtained for a 50 nm H<sub>2</sub>TPP/p-InP sample that does not saturate at room temperature even after 1000 s. The initial response to

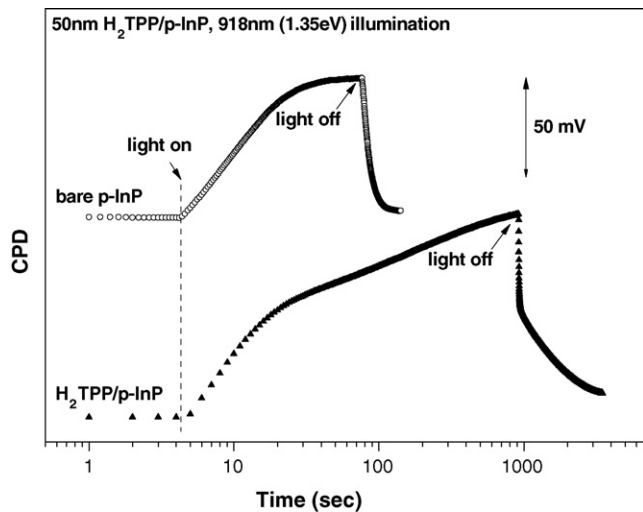


Fig. 3. CPD transients obtained for bare InP and 50 nm H<sub>2</sub>TPP/p-InP samples under 1.35 eV illumination at room temperature.

illumination is a fast increase in the CPD value due to direct band-to-band transition in the p-InP and is about the same for the two samples. Afterwards, a slowly increasing CPD transient of the H<sub>2</sub>TPP/p-InP sample is observed it indicates an increase in the surface barrier of the p-InP substrate under illumination. This is possibly due to illumination induced electron transfer from the HOMO level of H<sub>2</sub>TPP to the conduction band of p-InP. The same reasoning can be applied when analyzing the CPD transients once the illumination is turned off. The bare InP returns to thermodynamic equilibrium relatively fast in comparison with the H<sub>2</sub>TPP/p-InP sample. When chopped illumination at a relevant photon energy is used, i.e., when the relatively slow positive charging processes are reduced, the SPV signal due to the band-to-band transition should be unaffected or even reduced for the heterostructure.

### 3.3. Polarization changes

In order to detect changes in the signatures of H<sub>2</sub>TPP transitions in the modulated SPV spectrum of H<sub>2</sub>TPP/InP heterostructure, the characteristic modulated SPV spectrum of H<sub>2</sub>TPP needs to be studied in comparison to measured absorption spectrum. Fig. 4(a) shows the measured absorption spectra of a 50 nm H<sub>2</sub>TPP layer. The Soret band is at photon energy of 2.86 eV, the Q-bands ( $Q_x(0, 0)$ ,  $Q_x(0, 1)$ ,  $Q_y(0, 0)$ ,  $Q_y(0, 1)$ ), denoted  $Q_1$ – $Q_4$  for simplicity, have maximum absorption at about 1.86, 2.04, 2.19, and 2.35 eV.  $Q_1$  corresponds to the

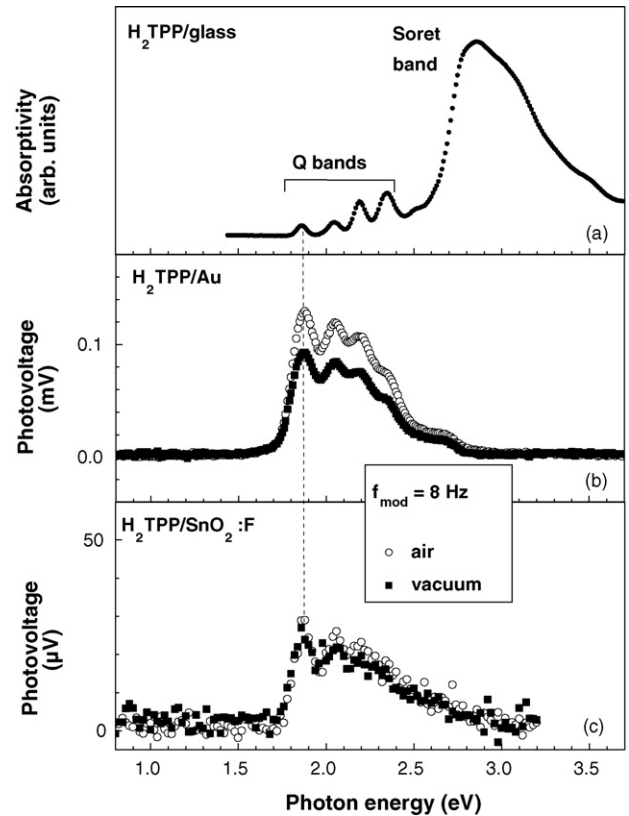


Fig. 4. (a) Absorption spectrum of a 50 nm thick H<sub>2</sub>TPP layer, (b) modulated SPV spectra of 50 nm H<sub>2</sub>TPP/Au in high vacuum and in air and (c) modulated SPV spectra of 50 nm H<sub>2</sub>TPP/SnO<sub>2</sub>:F in high vacuum and in air.

HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) optical band gap.

The modulated SPV spectra in vacuum and in air of a 50 nm  $H_2$ TPP/Au and 50 nm  $H_2$ TPP/FTO samples are presented in Fig. 4(b) and (c). The spectra were taken in vacuum and in air in order to increase the absorption of oxygen within the layer. While nitrogen and humidity have been shown to have little influence on the modulated SPV signal [16], oxygen is an electron acceptor [24], and the  $H_2$ TPP layer is negatively charged due to oxygen adsorption. The oxygen-induced internal potential distribution supports the escape of positive charges from the interface [16]. For both spectra, the SPV signal is positive and therefore positive charges are mainly modulated, i.e., holes escape from the interface. While the  $Q$  bands are observed, the more absorptive Soret band is hardly seen. Due to the increased Soret band absorption, the layer acts as a band-pass filter and less light reaches the interface. Therefore, the charge is separated at the internal interface. The weak SPV signature of the Soret band transition suggests also a short exciton diffusion length, much shorter than the layer thickness. Bulk excitons recombine before reaching the interface. Indeed, although the excitons diffusion length in organic layers is largely unknown, it is estimated to be in the order of a few nanometers at most [25].

A lower SPV signal is obtained when a FTO substrate is used (Fig. 4(c)) that can be explained by increased recombination of excitons at the  $H_2$ TPP/FTO interface. Possibly, the allowed states at the FTO surface act as recombination centers for excitons. Looking at the signature of  $H_2$ TPP transitions, the characteristic peaks of the  $Q_2$ ,  $Q_3$  and  $Q_4$  levels in the SPV spectra are in good agreement with the absorption peaks. The amplitude of SPV signal increased slightly in air ambience whereas the shape of the spectra remained unchanged.

Fig. 5(b) shows the modulated SPV spectra of the bare p-InP substrate and 50 nm  $H_2$ TPP/p-InP samples in comparison to the measured absorption spectrum (Fig. 5(a)). The maximum signal of the band gap related SPV, negative as expected for p-type inorganic semiconductor [13], is seen at 1.35 eV with increased SPV signal compared to the spectrum of the heterostructure sample. The reduction in the SPV signal may suggest a corresponding reduction in the InP band bending as discussed previously.

The spectra of the  $H_2$ TPP/p-InP sample are identical in vacuum and in air. The organic transitions are observed as positive SPV signals and the characteristic peaks of the  $Q$  bands are at the same photon energies as for the corresponding peaks in the absorption spectrum. The Soret band can be observed as well; the transition onset is at about 2.7 eV. Fig. 6(a) shows again the SPV spectra of p-InP. The spectrum of the bare p-InP can serve as a baseline for calculating the fraction of the absorbed light (without taking into account the reflectivity spectrum). The result is given in Fig. 6(b). It suggests that the  $H_2$ TPP acts as a simple band-pass filter on top of p-InP. Therefore, the  $H_2$ TPP layer does not participate actively in the modulation of separated charge on p-InP substrates. However, the situation is completely different for n-InP (Fig. 5(c)). In this case, a strong difference is observed between the SPV spectra

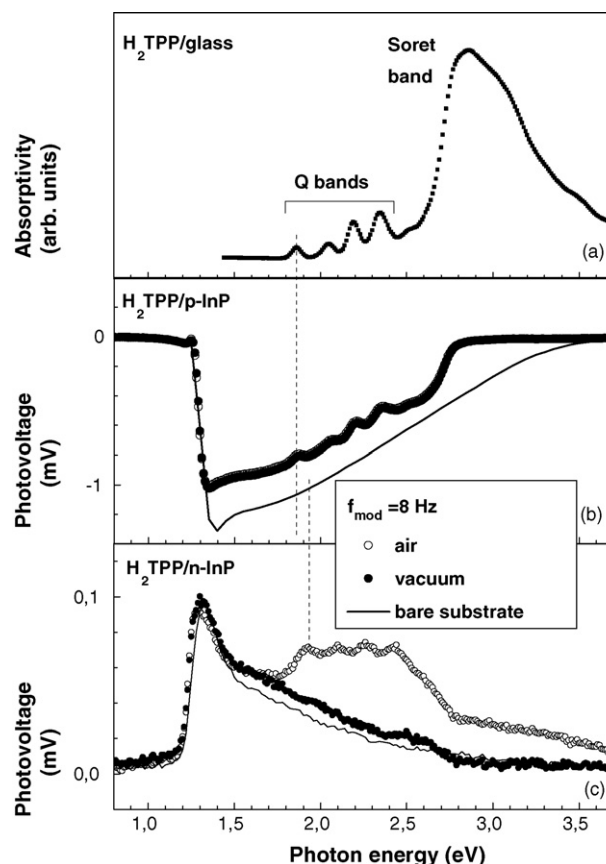


Fig. 5. (a) Absorption spectrum of a 50 nm thick  $H_2$ TPP layer, (b) modulated SPV spectra of p-InP/50 nm  $H_2$ TPP in high vacuum and in air in comparison to the bare p-InP spectrum, inset: enlargement of the InP sub band gap energy range and (c) modulated SPV spectra of n-InP/50 nm  $H_2$ TPP in high vacuum and in air in comparison to the bare n-InP spectrum, the  $H_2$ TPP transitions are 70 meV blue shifted.

measured in vacuum and measured in air. Under vacuum, the transitions of the  $Q$ -bands are hardly detected while the S-band acts as a strong band pass filter as for p-InP. In air, the band bending remains unchanged but a dominant signature of the

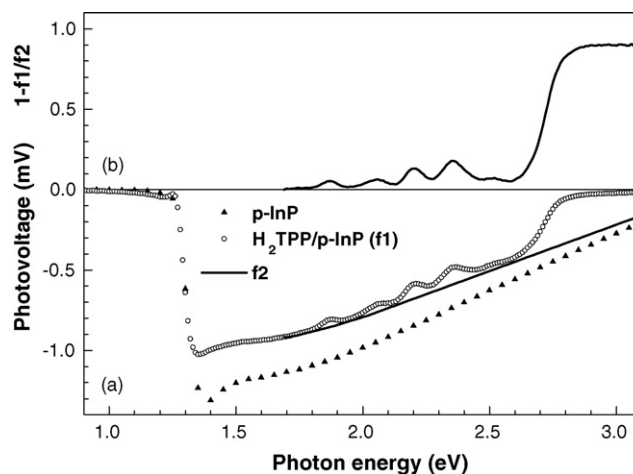


Fig. 6. Photovoltage spectra of p-InP (bare and coated with  $H_2$ TPP) (a). Function  $f_2$  corresponds to the spectrum of bare p-InP multiplied with 0.8 and serves as a baseline for the  $1 - f_1/f_2$  spectrum (b).

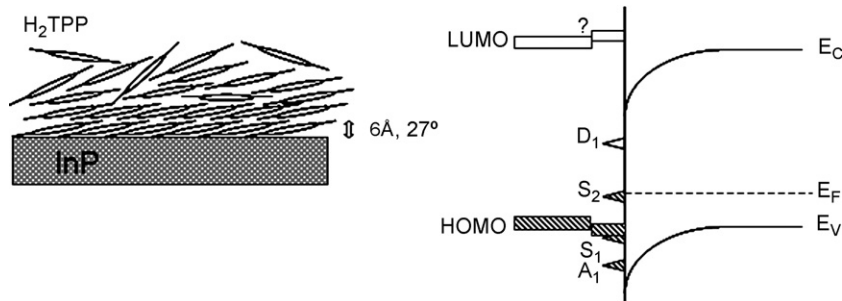


Fig. 7. Schematics of (right) a possible molecular arrangement on InP substrate, the first inter layers of molecules are ordered in almost lying orientation and (left) the interface electronic structure.

Q-band transitions appears while the positive charge is separated towards the external surface.

Modulated charge separation in the H<sub>2</sub>TPP layer appears due to dissociation of excitons at the H<sub>2</sub>TPP/InP interface and preferential escape of excess electrons or holes. Usually, the holes escape is easier [16]. The disappearance of modulated charge separation in H<sub>2</sub>TPP layers deposited on p-InP can be explained by the high concentration of holes in the H<sub>2</sub>TPP film transferred from the substrate. In this case, excess electrons recombine quickly and the excess hole concentration does not change significantly. For H<sub>2</sub>TPP deposited on n-InP substrates, excess holes recombine rapidly with electrons and modulated charge separation in H<sub>2</sub>TPP cannot be observed for samples under vacuum condition. Recombination becomes slower in air ambience since electrons are mainly trapped by oxygen. In addition, adsorbed oxygen in the organic layer increases the driving force of dissociated holes to escape from the interface [24]. Therefore, the concentration of excess holes escaping from the internal interface can be modulated.

If looking more carefully the peak positions related to the Q-bands are blue-shifted by 0.07 eV for n-InP/H<sub>2</sub>TPP deposited in air. The blue-shift originates from a region of the H<sub>2</sub>TPP layer very close to the internal interface since the exciton diffusion length is very small (no modulated signal with active participation of the Soret band transition). The blue shifts can be explained by an increased ordered thin H<sub>2</sub>TPP layer in close proximity to the interface. In relation to solid-state physics, the atomic order and orientation in the lattice determines the electronic structure of the close-packed material. Recent studies, using UPS, showed the possibility of a reduction in the HOMO–Fermi level gap few molecular layers away from the interface [8]. Such spontaneous polarization effects may take place if the Fermi level is unpinned at the interface, which has been indeed deduced in this work from SPS data of the H<sub>2</sub>TPP/p-InP sample. Possible explanations are chemical interaction at the interface and/or changes in the layer molecular orientation [6]. A solid conclusion regarding the specific interaction at the interface cannot be reached based on our results. If the blue shift in the spectra and spontaneous polarization effects indeed correlate, our results indicate an increased HOMO–LUMO gap in addition to changes in the position of HOMO level energy. Regarding practical devices, since only dissociated excitons,

generated in this interface layer, are modulated, a diffusion barrier for excitons in the H<sub>2</sub>TPP exists and better be avoided.

Choudhury et al. [11] characterized Langmuir–Blodgett films of H<sub>2</sub>TPP molecules that were connected to the substrate by side chains of various lengths. Their results showed a linear behavior between the measured areas per molecule and shifts in the absorption spectra. A packed layer, i.e., arrangement in which the molecules are perpendicular to the substrate and the area per molecule is reduced, is reflected in red shifted absorption spectrum. Accordingly, for a blue shift of about 70 meV in the Soret band energy gap, an area per molecule of about 120 Å<sup>2</sup> can be calculated. In a perfect lying arrangement, an area per molecule of 155–160 Å<sup>2</sup> is expected [26]. Therefore, since the H<sub>2</sub>TPP molecule is perfectly symmetric it can be easily shown that the thickness of one molecular layer is approximately 6 Å if the molecules are perfectly arranged at an angle of 27° (with respect to the n-InP surface). In summary, Fig. 7 schematically demonstrates a possible molecular arrangement and the related electronic structure when a p-InP substrate is used. The exact energy position of the HOMO and the LUMO within the H<sub>2</sub>TPP film cannot be deduced from the results.

#### 4. Conclusions

Illumination induced charge separation processes at H<sub>2</sub>TPP/InP interfaces have been characterized. The results indicate a weak interaction between H<sub>2</sub>TPP molecules and surface states of p-InP substrate. Charging processes due to transition of electrons from the HOMO level of H<sub>2</sub>TPP to the conduction band may take place. No indication of interface dipole formation at the H<sub>2</sub>TPP/InP interface was found. The experimental observation suggests unpinning of the Fermi level at the H<sub>2</sub>TPP interfaces with native oxide on InP substrates. Shifts, if observed, of the organic transition signatures in modulated SPV spectra can be correlated to changes in the orientation of the H<sub>2</sub>TPP molecules at the InP substrate interface. An ultra-thin interlayer, at which the molecules assume an almost lying orientation, was deduced. This interlayer may act as a diffusion barrier for excitons. Modulated SPV spectra may be detected when H<sub>2</sub>TPP is measured on n-InP substrates in air. Due to ambient-induced internal potential redistribution, dissociated holes can escape from the interface before recombining with excess charge carriers.

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