Tuning Schottky barrier heights by organic modification of metal-semiconductor contacts

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Abstract

The initial stage of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) adsorption on Se passivated n-type GaAs(1 0 0)-(2 × 1) surface was investigated using high-resolution soft X-ray photoemission spectroscopy (SXPS). The thickness of the film was precisely controlled using previous results of core level intensity evolution and additional valence band spectra. A very small amount of PTCDA (< 1 ML) is sufficient to induce a reduction of inhomogeneous band bending at the surface as judged from the sharpening of the core level spectra. This is interpreted in terms of preferential sticking of the organic molecules to surface defects. Thin films of PTCDA were then used as an interlayer for the electronic modification of Ag/n-GaAs(1 0 0) Schottky contacts. The electronic properties were investigated recording in situ current–voltage (IV) and capacitance–voltage (CV) characteristics. For H-plasma-treated substrates the effective barrier height decreases from 0.81 to 0.64 eV as a function of the PTCDA layer thickness (dPTCDA). In the case of the sulphur-passivated GaAs the effective barrier height first increases and then decreases, the overall range being 0.54–0.73 eV. The substrate treatment leads to a different alignment between the band edges of the GaAs and the molecular orbitals of the PTCDA, making it possible to determine the energy position of the lowest unoccupied molecular orbital (LUMO) transport level. The latter is also derived from ultraviolet photoemission spectroscopy (UPS) measurements and the investigation of the electronic structure formed upon deposition of PTCDA on differently treated n-GaAs(1 0 0) surfaces. Interface dipoles are found to form according to the electron affinities (EA) of the substrates and PTCDA films at the interfaces and, consequently, the vacuum level alignment rule does not hold. The results demonstrate that the energy offset between the conduction band minimum of n-doped inorganic semiconductors and the LUMO of organic molecular films at the interfaces can be obtained using UPS by systematically varying the EA of substrates with a known band gap. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Metal-semiconductor contacts; Schottky barriers; Organic layer modifications

1. Introduction

Organic semiconductors have attracted increasing interest owing to their potential application in various electronic and opto-electronic devices. The progress in the development of organic molecular beam deposition (OMBD) has led to monolayer-level control in the growth process of organic thin films under ultra-high vacuum (UHV) conditions [1]. One of the possible applications is the usage of organic molecules as a passivating layer of reactive semiconductor surfaces, such as Si(1 1 1)-(7 × 7) and GaAs(1 0 0) [2]. For example, a C60 monolayer on a Si(1 1 1)-(7 × 7) surface inhibits chemical
attack by water and atmospheric oxygen [2]. Moreover, it was already demonstrated that the deposition of organic molecules, in particular, perylenetetracarboxylic dianhydride (PTCDA) is useful to characterise the inorganic semiconductor surface state distribution [1].

Therefore, part I of this paper deals with a high-resolution soft X-ray photoemission spectroscopy (SXPS) study using synchrotron radiation to investigate a very thin PTCDA layer on Se-passivated GaAs(100) surfaces. The results indicate that organic molecules may also serve as very suitable probes in the photoemission studies of inorganic semiconductor surfaces.

Part II considers metal-semiconductor or Schottky contacts modified by organic interlayers. Their electronic properties are characterised by the barrier height being the difference between the edge of the respective majority-carrier band of the semiconductor and the Fermi level at the interface. The barrier heights of ideal, i.e. intimate, abrupt, homogeneous, and defect-free Schottky contacts are determined by the continuum of metal-induced gap states (MIGS) [3]. Deviations from what is predicted by the MIGS model may be attributed to secondary mechanisms like structure-related interface dipoles, interface structure, and interface defects, to name a few examples [4].

Secondary mechanisms may be used to tune the barrier height of Schottky contacts. In Pb/Si(111) contacts hydrogen was employed to decrease and increase the barrier heights of Pb contacts on n-type and p-type Si(111), respectively. The results are explained by an additional hydrogen-induced charge of positive sign on the semiconductor side of the interface [5]. Instead of hydrogen, Vilan et al. used monolayers of small molecules to modify Au/n-GaAs diodes [6]. Using a series of functional molecules whose dipole moment is varied systematically the effective barrier height is tuned by the molecular dipole moment.

Forrest et al. have used PTCDA and N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI) to modify metal/GaAs Schottky contacts [7]. Their $IV$ characteristics can be understood using the thermionic-emission-space-charge-limited transport model [8]. From their ex situ $IV$ measurements they determined barrier heights which are, in most cases, larger than what can be obtained from metal-on-GaAs contacts.

An important property of organic semiconductors like PTCDA is that the minimum energy for the formation of a pair of separated free electron and hole, i.e. the transport gap $E_{\text{trans}} = E_{\text{LUMO,trans}} - E_{\text{HOMO,trans}}$, is found to be considerably larger than the optical one involving exciton formation. The transport gap can be determined from the energy separation of the centre of mass of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level recorded by photoemission and inverse photoemission spectroscopy, respectively, and subtracting from this value the vibrational contribution and the difference between bulk and surface polarization [9].

Here, PTCDA was used as an interlayer for the modification of Ag/n-GaAs(100) Schottky contacts. The electronic transport properties, in particular the barrier heights, were investigated using in situ current–voltage ($IV$) and capacitance–voltage ($CV$) measurements as a function of thickness $d_{\text{PTCDA}}$. Two differently treated GaAs substrates were used, first H-plasma-treated, and secondly S-passivated surfaces. Chalcogen passivation of GaAs(100) reduces the number of chemically active sites on the surface and improves the structural properties of PTCDA films [10,11].

For a complete description of device characteristics, a thorough understanding of the electronic structure at organic/inorganic as well as metal/organic interfaces is essential. Therefore, part III deals with an ultraviolet photoemission spectroscopy (UPS) study of the energy level alignment at the organic/inorganic semiconductor interface.

A number of studies were systematically performed on the energy level alignment at metal/organic interfaces using UPS [12,13]. Concerning metal/organic interfaces there are three fundamental issues that have long been debated: (1) Hole and electron barriers which depend on the position of the HOMO and LUMO with respect to the metal Fermi level ($E_F$). For the determination of the LUMO energy position ($E_{\text{LUMO}}$), so far, mostly the optical gap of the organic molecular films is employed, which is based on the formation of a Frenkel exciton with the electron and hole on
the same molecule upon photon absorption. However, it is known that the energy level for the electron transport in organic semiconductors is different from $E_{LUMO}$ as obtained from the optical gap [9]. Due to localisation and polarisation phenomena dominating the physics of charged excitation and transport in organic semiconductors, the difference between the optical and transport gap is in the order of $\sim 1\text{eV}$ [9]. Thus, modelling the carrier injection using the optical gap could result in dramatic failure. (2) The vacuum level alignment rule in which case the interface barrier heights can simply be calculated from the ionisation potential (IP) and electron affinities (EA) values of the organic molecules and $E_F$ of the metal. Concerning this point, a conclusion that in general the vacuum levels do not align at metal–organic interfaces seems to have been reached [9,12,13]. However, reasons for the occurrence of an interface dipole are still under discussion. (3) The “band bending”-like electrostatic energy shift in the organic layer. Such shift is observed in many metal/organic systems [14]. This shift is in most cases confined from a monolayer regime up to only a few nanometers, which cannot be accounted for using the conventional band bending theory of inorganic semiconductors.

For organic/inorganic semiconductor interfaces, however, no systematic study was performed on the energy level alignment and all the questions mentioned above remain unsolved. The energy level alignment for interfaces of PTCDA on GaAs$(1\ 0\ 0)$ and copper-phthalocyanine (CuPc) and $N',N'$-diphenyl-$N,N'$-bis(1-naphthyl)-1,1'-biphenyl-4,4''-diamine (NPD) on InP$(1\ 1\ 0)$ were reported by Hirose et al. [15] and Chasse et al. [16], respectively. In all cases the vacuum level alignment rule does not hold.

Here, UPS studies of PTCDA deposition on differently treated GaAs$(1\ 0\ 0)$ surfaces are presented. The IP of the substrate surfaces ($I_{Ps}$) was systematically varied from $(5.23 \pm 0.10), (5.55 \pm 5.92 \pm 0.10)$ to $(6.40 \pm 0.10)\text{eV}$ for GaAs$(1\ 0\ 0)$-$c(4 \times 4)$, wet chemically S-passivated GaAs$(1\ 0\ 0)$, and Se-passivated GaAs$(1\ 0\ 0)$-$c(2 \times 1)$ surfaces, respectively. The interface dipole formed upon PTCDA deposition onto these surfaces is found to depend on the relative energy position of the conduction band minimum (CBM) of the substrates ($E_{CBM}$) with respect to the LUMO of PTCDA ($E_{LUMO}$).

2. Experimental

For part I considering the interaction of PTCDA molecules with a GaAs surface homoepitaxially grown n-type GaAs$(1\ 0\ 0)$ layers (Si doped, $n = 1 \times 10^{18}\text{cm}^{-3}$) were used as substrates. They were covered by thick amorphous As layers to prevent contamination and oxidation during transportation. Samples were transferred into an UHV chamber and decapped by gentle annealing up to 380°C. The Se modification of GaAs$(1\ 0\ 0)$ was performed by thermal decomposition of SnSe$_2$ from a Knudsen cell at 340°C. During the Se treatment, the sample was kept at 400°C, which leads to a sharp $(2 \times 1)$ LEED pattern in agreement with the reconstruction observed previously [17–20]. Onto this modified surface PTCDA was deposited with thicknesses controlled by a quartz microbalance located in the vicinity of the sample. After each modification step, photoelectron spectra were taken using photon energies of 60 eV for Ga 3d, 79 eV for As 3d, 95 eV for Se 3d, and 26 eV for the valence band spectra. The measurements were performed in an UHV chamber at the base pressure $1 \times 10^{-8}\text{Pa}$ with an ADES 400 electron spectrometer equipped with Knudsen cells for Se and PTCDA deposition and aligned to the TGM2 monochromator at the synchrotron radiation source BESSY. The overall resolution (light + electrons) was measured to be $300\text{meV}$ at 60 eV photon energy.

In order to get a precise thickness control, two successive PTCDA deposition series on the Se-passivated GaAs$(1\ 0\ 0)$ surface were performed under identical conditions. First, PTCDA was grown with increasing thicknesses up to an equivalent thickness of 40 ML (1 ML corresponds to 0.321 nm, which is the distance between the molecular planes in a PTCDA crystal and assuming flat lying molecules). The intensity evolution of Ga 3d and As 3d bulk emission components with respect to the nominally deposited coverage indicates a Stranski–Krastanov-like growth mode.
i.e. the formation of 1 ML followed by island formation. From the exponential attenuation in the monolayer region the deposition rate was estimated to be \( \sim 2 \text{ML/min} \). PTCDA was then deposited onto another Se-passivated GaAs(100) surface in the sub-monolayer regime. From the intensity attenuation (0.13 of the initial intensity) the coverage of this second sample corresponds to \( \sim 0.3 \text{ML} \).

For the electrical transport characterization (part II) tellurium-doped n-GaAs(100) with a doping concentration of \( N_D = 2 \times 10^{17} \text{cm}^{-3} \) (Freiberger compound materials) served as a substrate. Two different substrate treatments were used to prepare passivated or non-passivated GaAs(100) surfaces. In both treatments the substrates were first degreased in aceton, ethanol, and finally deionised in water using an ultrasonic bath. To prepare non-passivated but nearly oxide-free surfaces, the substrate surfaces were etched in HCl for 30 s. The samples were then attached to a copper holder with an In–Ga alloy. After transfer into the UHV chamber (base pressure \( \sim 10^{-8} \text{Pa} \)) the samples were annealed for 30 min up to a temperature of 300°C. This leads to the formation of an InGaAs alloy on the backside of the sample resulting in a low series resistance of \( < 20 \Omega \) [22,23]. During the last 5 min of the annealing a hydrogen plasma treatment was carried out at a hydrogen pressure of \( 3 \times 10^{-1} \text{Pa} \). Atomic hydrogen reacts with arsenic and gallium oxides to form volatile compounds thus removing residual oxides [24–26].

Sulphur passivation was obtained by a wet chemical etching procedure under atmospheric conditions [27]. This etching procedure consists of a sequence of three steps. After cleaning as above the GaAs was dipped into a solution consisting of a 3:1 mixture of CCl\(_4\) and S\(_2\)Cl\(_2\) for 10 s. In the last step the substrate was rinsed successively in CCl\(_4\), acetone, ethanol and deionised water for 5 s each. After this treatment the substrate was transferred into a UHV system and annealed at 430°C. This procedure leads to a well ordered \((2 \times 1)\) reconstructed surface as revealed by low energy electron diffraction (LEED) [17].

OMBD growth of PTCDA layers was performed at room temperature. The deposition rates were between 0.3 and 0.8 nm/min and the thickness of the organic layer was again controlled by a quartz crystal microbalance. Silver contacts with an area of \( 2.1 \times 10^{-7} \text{m}^2 \) were evaporated through a shadow mask with a deposition rate of 7 nm/min. All \( IV \) and \( CV \) characteristics were recorded at room temperature (RT) in situ using a HP semiconductor test system.

Finally, the UPS measurements were carried out either using synchrotron radiation or a He discharge lamp for excitation. The overall resolution was measured to be better than 0.2 eV. For the determination of the sample work function, a sample bias of \( -9 \text{V} \) was given to allow the observation of the secondary electron onset position. Here, it should be mentioned that the Se–GaAs(100) surface shows a sharp \((2 \times 1)\) LEED pattern while the surfaces for wet chemically etched S-GaAs(100) vary from a \((1 \times 1)\) to a weak \((2 \times 1)\) reconstruction.

3. Results and discussion

3.1. Part I: interaction of PTCDA molecules with GaAs surfaces

Fig. 1 presents valence band spectra for the Se-passivated surface (a), after subsequent deposition of (b) 1 ML PTCDA, and (c) 40 ML PTCDA. 1 ML PTCDA deposition induces a clear change in the spectra even though there are still features of the substrate present (Fig. 1(a)). In the spectra corresponding to 40 ML PTCDA (Fig. 1(c)), four features of \( p \) occupied molecular orbitals (1,2,3,4) and two of \( s \) orbitals (5,6) of PTCDA are clearly seen, indicating emission from the PTCDA molecule itself. This is in good agreement with previous work [15]. The valence band spectrum for the 0.3 ML (Fig. 1(d)) reveals a line shape intermediate between that of the Se-passivated surface (Fig. 1(a)) and that of 1 ML PTCDA (Fig. 1(b)), thus corroborating the sub-monolayer PTCDA coverage.

The photoelectron core level spectra were curve fitted assuming Voigt profiles—a Lorentzian convolved with a Gaussian line shape—and using a non-linear least squares fitting routine. While the
Lorentzian shape is the natural broadening due to the finite lifetime of the core hole, the Gaussian broadening accounts for the instrumental resolution and also for any broadening due to disorder and potential variations across the surface [28]. The latter in particular occur as a result of defects on the surface and related inhomogeneous band bending.

During curve fitting, the Lorentzian linewidth, spin–orbit splitting, and branching ratio were kept fixed at values providing satisfactory results over an entire series of spectra. These parameters are presented in Table 1. The peak intensity, position, and Gaussian linewidth were variable. All binding energies are given for the d_{5/2} components of the spin–orbit split core levels relative to the Fermi level.

The Se 3d core level spectra for the second sample are shown in Fig. 2. The best fit for the spectra was obtained using two components.

Pashley et al. proposed a structural model for the Se-passivated GaAs(100) surface on the basis of STM, XPS results, and the electron counting rule [17]. Assuming this structural model, Se1 component at a binding energy of 55.3 eV is assigned to the emission from the Se atoms in a topmost Se dimer layer while Se2 corresponds to those in a Ga$_2$Se$_3$-like environment between a second Ga layer and a fourth Ga layer with vacancies. The Se2 component is shifted by 0.93 eV towards lower binding energy. This assignment is in good agreement with previous results [18,19], electronegativity considerations, and also stronger reactivity of the Se1 atoms upon subsequent metal deposition. PTCDA deposition onto the Se-passivated surface does not induce any dramatic

**Table 1**

<table>
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<tr>
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<th>Ga 3d</th>
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<tr>
<td>Lorentzian width/eV</td>
<td>0.1</td>
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<tr>
<td>Branching ratio</td>
<td>1.58</td>
</tr>
<tr>
<td>Spin–orbit splitting/eV</td>
<td>0.48</td>
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**Fig. 1.** Valence band spectra of the PTCDA on Se-passivated GaAs(100) for (a) Se-passivated GaAs(100), after deposition of (b) 1 ML PTCDA and (c) 40 ML PTCDA. The uppermost spectrum (d) represents 0.3 ML PTCDA on Se–GaAs.

**Fig. 2.** Se 3d core level spectra (a) before and (b) after the deposition of 0.3 ML PTCDA on Se-passivated GaAs(100) surface.
change in the line shape of the Se 3d core level spectra, strongly indicating the absence of any chemical reaction of the PTCDA molecules with Se atoms. However, a more subtle change is apparent, namely the shoulders at both sides of the peak become clearer (see arrows in Fig. 2(b)). The curve fitting underlines this result more clearly. While the relative peak positions between the two components remain constant within an error of 10 meV, the Gaussian broadening of the spectra changes from 0.87 to 0.78 eV by 90 meV. It should be pointed out that this decrease in Gaussian broadening was repeatedly observed upon PTCDA deposition onto Se-passivated GaAs(100) surfaces. Moreover, a very similar behaviour is found for the S core level spectra during PTCDA deposition onto S2Cl2 wet chemically etched GaAs(100). At higher PTCDA coverage the Gaussian broadening remains constant.

From the previous STM study [17,29], it is known that a very well-ordered Se terminated (2×1) surface is produced by Se deposition and subsequent annealing. They found that there are virtually no islands on any of the GaAs terraces in the STM image. However, there are still two types of defects on the surface observed: a few small holes simply from missing dimers and many more small bright features. The density of these bright features is approximately 10^{12} cm\(^{-2}\) in the image, which matches the density of dopant atoms on the surface at a doping concentration of 3–6×10^{18} cm\(^{-3}\) used in their study. Our samples were treated in slightly different conditions. However, a sharp (2×1) LEED pattern was observed, confirming that the surface is also well reconstructed. At the doping level used in our experiments (n = 1×10^{18} cm\(^{-3}\)), the number of dopant atoms on the surface would also be \(\sim 10^{12} \text{ cm}^{-2}\) among \(6 \times 10^{14} \text{ cm}^{-2}\) surface atoms. This means that there is approximately one dopant atom in 300 surface unit cells. It is also well known that the PTCDA molecules preferentially adsorb on defect sites due to an enhanced interaction [1,15]. Certainly, 0.3 ML PTCDA are sufficient to cover all defect sites induced by dopant atoms. Indeed no more change is observed in the Gaussian broadening upon further PTCDA deposition. Hence, the sharpening of the core level spectra being indicative of a removal of inhomogeneous pinning is attributed to the preferential adsorption of PTCDA on the defect sites.

Since the Si dopant atoms have a relatively small covalent radius (1.11 Å), they may induce local distortion of the surface. Upon PTCDA deposition on top of the dopant atoms, Si atoms may geometrically relax accompanied by charge redistribution, resulting in a more homogeneous surface.

However, charge transfer may also occur via a chemical reaction of the PTCDA with the defect sites. While the line shape of the Se 3d core level spectra does not reveal any evidence for covalent bonding between PTCDA and the Se atoms, we cannot exclude the possibility of a reaction with dopant atoms. The latter is not detectable due to the low defect density. In addition, PTCDA is a non-polar molecule due to its mirror symmetry, which annihilates local dipole moments of polar carboxylic and anhydride groups. However, electric fields induced by the local dipole moment of the side groups and the van der Waals force of the whole molecule may also influence the charge redistribution at the interface.

The influence of the organic molecules on the core level spectra of deeper lying Ga and As atom is less pronounced. The results are presented in Fig. 3. For instance, the As 3d core level spectra seem to be sharper upon PTCDA deposition as can be judged from a slightly deeper dip between the spin–orbit split components. Values derived from curve fitting for the decrease in Gaussian broadening are in the order of tens of meV. Such effect clearly requires further confirmation using higher resolution experiments. There are two dominant components found in the Ga 3d core level spectra. From angular dependent photoemission spectra [19], Ga2 is assigned to the Ga layer below Se dimer surface while Ga1 corresponds to bulk Ga atoms. Upon 0.3 ML PTCDA deposition the overall line shape of Ga 3d core level spectra hardly change. However, curve fitting results seem to indicate an increasing contribution of the subsurface Ga2 component. The initial stage of PTCDA deposition on defect sites may thus also influence subsurface Ga layers. This effect was again repeatedly observed in all samples.
3.2. Part II: Electrical characterisation of organic modified Ag/GaAs Schottky contacts

The IV characteristics of Ag contacts on both types of substrates, i.e. hydrogen plasma-treated and sulphur-passivated GaAs, as a function of \(d_{\text{PTCDA}}\) are shown in Fig. 4. The curves of the two unmodified Ag contacts may be described by thermionic emission of carriers over a barrier, i.e. by (see, for example, Ref. [30])

\[
I = A^* T^2 \exp \left( \frac{-\phi_{Bn}}{k_B T} \right) \exp \left( \frac{e_0 V_a}{n k_B T} \right) \\
\times \left[ 1 - \exp \left( \frac{-e_0 V_a}{k_B T} \right) \right].
\]  

Here \(A^*\), \(k_B\), \(e_0\), \(F\), and \(T\) are the effective Richardson constant of n-GaAs, Boltzmann’s constant, elementary charge, area of the contact, and temperature, respectively, and \(I\) is the current. For applied voltages \(V_a > 3k_B T/e_0 \approx 0.08\) eV at RT the experimental IV characteristics exhibit a linear behaviour in a semilogarithmic plot. Least square fits to these parts of the data give zero-bias barrier heights \(\phi_{Bn}\) of \((0.82 \pm 0.01)\) and \((0.59 \pm 0.01)\) eV and ideality factors \(n\) of \(1.1 \pm 0.01\) and \(1.09 \pm 0.01\) for the Ag/GaAs(100) and Ag/S–GaAs(100) contacts, respectively. The voltage drop

\[
V_R = RI
\]

across a series resistance \(R\) with contribution from the GaAs bulk, its ohmic back-contacts, and external connections results in a deviation from straight lines for high forward biases.

Fig. 4a shows the IV characteristics of Ag/PTCDA/GaAs(100) for different PTCDA layer
thickness ($d_{PTCDA}$). With increasing $d_{PTCDA}$ the current is increasing, indicating that the barrier height of the contact is effectively lowered. For reverse biases and forward biases below 0.2 V a behaviour typical for thermionic emission is observed. For $d_{PTCDA} > 5$ nm and applied voltages larger than 0.2 V the $IV$ characteristics are now influenced by the transport properties of the organic material. Transport through organic materials is governed by space charge limited currents (SCLC) which can be described by the Mott–Gurney law as

$$I = \frac{FA^* n}{d_{PTCDA}^{3/2}} V^{2/3}.$$  \hspace{1cm} (3)

Here, $d_{PTCDA}$, $V_a$, and $\mu$ are the thickness of the organic layer, voltage applied to the organic layer, and mobility of the charge carriers in the organic layer, respectively.

The $IV$ characteristics of the Ag/PTCDA/S–GaAs(100) contacts are displayed in Fig. 4b. In contrast to the behaviour of the Ag/PTCDA/GaAs(100) contacts the current first decreases as a function of $d_{PTCDA}$, while for $d_{PTCDA} \geq 12$ nm the current becomes larger compared to the unmodified contact in the reverse and the low forward bias region.

For $d_{PTCDA} < 30$ nm the flat-band barrier heights determined from $CV$ characteristics of organic modified contacts on both types of substrates are of the same value as for the unmodified contacts. The $CV$ characteristics are completely determined by the capacitance of the space-charge region in the inorganic semiconductor, which does not change upon deposition of PTCDA. For $d_{PTCDA} \geq 30$ nm SCLC affects the $IV$ characteristics and the capacitance of the organic layer starts to contribute significantly to the $CV$ characteristics.

The difference in barrier heights of the Ag/GaAs(100) and Ag/S–GaAs(100) contacts can be described by an sulphur-induced interface dipole already used for the description of the hydrogen modified Pb/Si(111) contacts. In both cases the Pauling electronegativity of the atom used for the modification ($\chi^H = 2.2$, $\chi^S = 2.58$) is larger than the electronegativities of the substrate atoms ($\chi^Si = 1.9$, $\chi^Ga = 1.81$, $\chi^As = 2.18$). Therefore, an additional charge of positive sign is induced on the semiconductor side of the interface, resulting in an increase of the ionisation energy of the clean surfaces and a reduction of the barrier heights at metal-GaAs(100) interfaces [20,31].

For the determination of the barrier heights for the organic modified Ag/GaAs(100) Schottky contacts the contribution of SCLC and series resistances to the charge transport have to be taken into account in addition to thermonic emission. The voltage drop over each contribution add up to the total applied voltage:

$$V = V_a + V_o + V_r.$$  \hspace{1cm} (4)

Inserting Eqs. (1)–(3) in Eq. (4) the experimental $IV$ curves can be fitted, using $\phi_{Bn}$, $n$, $\mu$ and $R$ as fitting parameters. For the Ag/PTCDA/GaAs(100) contacts the effective barrier height decreases as a function of $d_{PTCDA}$. For $d_{PTCDA} \geq 30$ nm when SCLC dominate the charge transport the effective barrier height remains constant.

Fig. 5 shows the resulting effective barrier heights for the two types of contacts as a function of $d_{PTCDA}$. The change in barrier height as a function of $d_{PTCDA}$ can be quantitatively explained using the energy level diagrams determined by photoemission spectroscopy shown in Fig. 6 [32]. In both cases PTCDA does not change the electronic properties of the as-prepared GaAs substrate, i.e. the band bending is constant. For the plasma-treated substrate the band bending in
GaAs is determined to be \((0.8 \pm 0.01)\) eV, which is the same as in Ag/GaAs(100) contacts. Starting with the lowest \(d_{PTCDA}\) the effective barrier height is first constant and then decreases, indicating that \(E_{LUMO,\text{trans}}\) is approximately at the same energy or below the CBM of GaAs at the interface. For Ag/PTCDA/S–GaAs contacts the barrier height initially increases for low \(d_{PTCDA}\) indicating that \(E_{LUMO,\text{trans}}\) is now above CBM. The distance \(E_{LUMO,\text{trans}}-\text{CBM}\) can be estimated by the initial increase in barrier height to be 0.15 eV. With these results the distance between \(E_{LUMO,\text{trans}}\) and the high-energy edge of the HOMO can already be estimated to be 2.55–2.8 eV.

A further increase in \(d_{PTCDA}\) results in a decrease in effective barrier height. The decrease in effective barrier height observed for both types of substrate can be explained by a strong contribution of the low dielectric constant material PTCDA (\(\varepsilon \approx 2\)) to image force lowering at the PTCDA/GaAs interface. The image force lowering can be calculated using (see Ref. [30])

\[
\Delta \phi_\text{ff} = \varepsilon_0 \left[ \frac{2 e_0^2 N_D (\phi_B - \xi - e_0 V_a - k_B T)}{(4\pi)^2 (e_b \varepsilon_0)^3} \right]^{1/4}.
\]

Here, \(\xi = 20\) meV is the position of the Fermi level with respect to the CBM in the bulk, \(e_b\) the dielectric constant of the inorganic semiconductor, and \(e_0\) the permittivity in vacuum. For Ag/GaAs(100) contacts the image force lowering amounts to 50 meV. In a very simple approach, one may substitute \(e_b\) by the dielectric constant of PTCDA. This results in an image force lowering of about 200 meV which is in good agreement with the experimentally determined decrease in barrier height of 150 meV.

3.3. Part III: energy level alignment at PTCDA/GaAs interfaces

Fig. 7 presents an example of UP spectra using a binding energy scale for the clean Se–GaAs(100) surface and after subsequent stepwise deposition of a 12 nm PTCDA film on the surface. The left and right panels show the onset of the low-kinetic (high binding) energy secondary electron peak and the valence band structures, respectively. \(IP_s\) is obtained by subtracting the total width of the valence band spectra from the photon energy, i.e. \(IP_s = h\nu - (E^F_{\text{cutoff}} - E^F_{\text{VBM}})\). Here, \(E^F_{\text{cutoff}}\) and \(E^F_{\text{VBM}}\) represent the energy positions of the secondary electron onset and the VBM of the substrate surfaces relative to \(E_F\), respectively. \(IP_{PTCDA}\) was obtained by replacing \(E^F_{\text{VBM}}\) by the low-binding energy edge of HOMO \((E^F_{\text{HOMO}})\) in the previous equation. The shifts in \(E^F_{\text{cutoff}}\) upon PTCDA deposition can be interpreted as interface dipoles while the energy barrier for hole transport is obtained by \(E^F_{\text{VBM}} - E^F_{\text{HOMO}}\).

The only energy positions that are not directly obtained from the measured UP spectra are \(E_{CBM}\) of the substrates and \(E_{LUMO}\) of the PTCDA films. In order to determine \(E_{CBM}\) it is reasonable to use the optical gap (1.42 eV) because of the low polarisation energies and high carrier screening efficiency leading to exciton binding energies of a
few meV [9]. This optical gap of GaAs(1 0 0) does not change upon different surface treatment since the modification is confined within a few atomic layers. On the other hand, $E_{LUMO}$ of the PTCDA film is not well known. The difference between the optical and transport HOMO–LUMO gap of PTCDA films were proposed by Hill et al. using UPS and inverse photoemission [9]. This value amounts to $\sim 0.6$ eV. The accuracy of this value, however, is limited by a rather poor resolution of inverse PS.

Fig. 8 shows the energy level alignment obtained from UP spectra between PTCDA films and GaAs(100) surfaces with different $I_{PS}$. For simplicity the band bending of the substrates is omitted, so that the energy level corresponding to the substrates represents that of the substrate surfaces. It can be seen that the different surface treatment varies $I_{PS}$ of the GaAs(100) surfaces. The measured $I_{PS}$ ranges from $(5.23 \pm 0.10)$ eV for the GaAs(100)-c(4×4), $(5.55 \sim 5.92 \pm 0.10)$ eV for S–GaAs(100) to $(6.40 \pm 0.10)$ eV for the Se–GaAs(100) surfaces. The $I_{PS}$ of the GaAs(100)-c(4×4) surface agrees well with the value of 5.29 eV reported previously [33]. It is known that the passivation of GaAs(100) surfaces by S or Se atoms terminates the chemically active sites, leading to the formation of S–Ga or Se–Ga surface dipoles with S or Se atoms on the surfaces, and thus inducing the change in $I_{PS}$. It should be noted that the scatter of $I_{PS}$ observed for S–GaAs(100) surfaces can be correlated with the development of the VB structures. A slightly different temperature ramp rate and pressure increase during annealing appears to strongly affect the degree of the related surface reconstruction.

On these surfaces PTCDA was evaporated in a stepwise manner. The energy levels of the PTCDA films were obtained using the UP spectra of thin (4–12 nm) PTCDA films in order to prevent any influence due to sample charging. The energy position corresponding to the centre of the PTCDA HOMO in UP spectra for each sample does not appear to change during the stepwise deposition despite the fact that it is difficult to evaluate the energy shift below a PTCDA thickness of 1 nm due to the screening by the VB features of the substrates. The measured $I_{PTCDA}$ fluctuates slightly from 6.56 to 6.67 eV, probably due to slight variations in surface morphologies and molecular orientation [13]. However, the values are still within the error of the measurements ($\pm 0.1$ eV). $E_{F}^{HOMO}$ is found to be in the range of 1.85–2.04 eV, showing a weak dependence on $I_{PS}$. This indicates that the ability of $E_{F}$ to move within the HOMO–LUMO gap is low. A pinning of the Fermi level was also observed for PTCDA/metal interfaces [13].

The shaded region in Fig. 8 shows the possible energy position range for the PTCDA LUMO,
with the low limit being drawn using the optical HOMO–LUMO gap value of PTCDA (2.2 eV) obtained by the energy position of the first peak in the optical absorption spectra of PTCDA films. The upper limit is obtained considering an energy difference of 0.6 eV between the optical and transport HOMO–LUMO gap of PTCDA [9]. A strong correlation is found between the interface dipole and the relative energy position between \( \Delta E_{\text{LUMO}} \) and \( E_{\text{CBM}} \), respectively, the EA of the PTCDA film (\( E_A^{\text{PTCD}} \)) and substrates (\( E_A \)). \( E_{\text{HOMO}} \) is always located well below \( E_{\text{VBM}} \). At the PTCDA/GaAs(1 0 0)-c(4 \times 4) interface where a positive interface dipole is formed, \( E_{\text{LUMO}} \) is located below \( E_{\text{CBM}} \). The situation is reversed when a negative dipole is formed, as in the case of the PTCDA/Se–GaAs(1 0 0) interface. Consequently, the interface dipole formed at the PTCDA/S–GaAs(1 0 0) interface varies from positive to negative depending on \( I_P \) (or \( E_A \)). It can therefore be deduced that the formation of the interface dipole at PTCDA/GaAs(100) interfaces is possibly driven by the difference in \( E_A \) and \( E_A^{\text{PTCD}} \) and that in general the vacuum level alignment rule is not applicable for those interfaces.

At thermal equilibrium, the number of electrons and holes that are transported across the interfaces should be equal. Due to the difference in EA and IP between substrate surfaces and PTCDA films, each electron and hole transported undergoes an energy loss or gain. The net energy loss, therefore, depends on the electron and hole concentration that is transported across the interface and the energy difference of \( E_A \) – \( E_A^{\text{PTCD}} \) and \( I_P – I_P^{\text{PTCD}} \). The interface dipole is formed in order to compensate the net energy loss. In the case of PTCDA films on n-GaAs(100) surfaces, it is expected that the number of electrons transported across the interface is much higher than that of holes and, therefore, \( E_A – E_A^{\text{PTCD}} \) can be proposed to be the determining driving force for the interface dipole formation.

In Fig. 9 the interface dipole is presented as a function of \( E_A \). It can be seen that the interface dipole formed at PTCDA/GaAs(1 0 0) interfaces is linearly dependent on \( E_A \). Using a linear fit, the interface dipole is found to be zero at \( E_A = (4.12 \pm 0.10) \text{ eV} \). This value also represents \( E_A^{\text{PTCD}} \) assuming that the formation of the interface dipole is driven by the difference in \( E_A \) and \( E_A^{\text{PTCD}} \). Using \( E_A^{\text{PTCD}} = (4.12 \pm 0.10) \text{ eV} \), the energy offset between \( E_{\text{CBM}} \) and \( E_{\text{LUMO}} \) at the interfaces can be estimated to be \(-0.17 \pm 0.10 \) eV for PTCDA/GaAs(100)-c(4 x 4), \( 0.05 \sim 0.08 \pm 0.10 \) eV for PTCDA/S–GaAs(100), and \( 0.27 \pm 0.10 \) eV for PTCDA/Se–GaAs(100) interfaces. In addition, assuming that the energy level of the PTCDA films extends up to the interfaces without energy shifts we can
estimate the HOMO–LUMO gap to be in the range of 2.44–2.55 eV. This value is larger than the optical gap of PTCDA but still smaller than the transport HOMO–LUMO gap proposed by Hill et al. [9].

4. Conclusions

Soft X-ray photoemission spectra after deposition of a very small amount of PTCDA molecules (\(<1\) ML) onto the Se-passivated GaAs(1 0 0) (2 \(\times\) 1) surface were presented in part I. We interpret the change in core level spectra as an effect resulting from preferential adsorption of PTCDA on defect sites, thus inducing a reduction of inhomogeneous pinning of the surface. Our results also demonstrate the usefulness of PTCDA as a probe for defect studies using photoemission. Most probably, this finding can be further exploited utilising higher resolution photoemission experiments at third generation synchrotron sources.

The barrier heights of Ag contacts modified by PTCDA and grown on two differently treated GaAs(100) substrates were investigated by in situ \(IV\) and \(CV\) measurements. Using the effect of substrate treatment and organic layer thickness the effective barrier height can be tuned between 0.54 and 0.81 eV. Here, the decrease in barrier height is explained by an increase in image force lowering due to the presence of PTCDA. In addition, the position of the LUMO transport level with respect to the high-energy edge of the HOMO can be estimated to be in the range of 2.55–2.8 eV.

The energy level alignment formed at interfaces between PTCDA and differently treated n-GaAs(100) surfaces was obtained using UPS. Depending on the substrate treatment, \(IP_s\) of the GaAs surfaces varies from (5.23 \(\pm\) 0.10) to (6.40 \(\pm\) 0.10) eV. An interface dipole is found to form according to the difference \(EAS - EAPTCD\) at the interfaces and the vacuum level alignment rule is not valid for such interfaces. The electron affinity for PTCDA which was obtained at zero interface dipole from a linear fit of the interface dipole vs. \(EAS\) is (4.12 \(\pm\) 0.10) eV and, using this value, the energy offset between \(E_{CBM}\) and \(E_{LUMO}\) at the interfaces was estimated. The value for the HOMO–LUMO gap is in agreement with the lower limit estimated from the electrical measurements.

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References

[31] Zahn DRT, Kampen TU, Hohenecker St, Braun W. Vacuum 2000;57:139.