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Self-ordering of metal-free phthalocyanine on InAs(100) and InSb(100)

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Abstract

The adsorption and surface ordering of metal-free phthalocyanine (H_2PC) on InAs(100)$(4 \times 2)/c(8 \times 2)$ and InSb(100) $c(8 \times 2)$ is investigated using scanning tunnelling microscopy (STM) and synchrotron based photoelectron spectroscopy. The two systems show structural similarities; at submonolayer coverage the preferred adsorption site of H_2PC is on top of the In rows, and above 1 monolayer and after thermal treatment the first molecular layer is ordered in a densely packed '×3' structure observed with both low energy electron diffraction and STM.

The electronic properties and the surface bonds of the two systems are quite different: the InAs–H_2PC interface is semiconducting after room temperature adsorption but becomes metallic upon thermal treatment whereas InSb(100)–H_2PC is semiconducting at all preparations. These differences are reflected in pronounced differences in the C 1s line shape between the two systems. N 1s core level spectra from both surfaces reveal deprotonation of the molecules, i.e. the central hydrogen atoms are lost upon thermal treatment.

1. Introduction

The field of molecular electronics is growing steadily and organic–inorganic semiconductor junctions are under current investigation due to their usefulness in applications such as photovoltaics [1–3], field effect transistors [4], organic light emitting diodes (OLED) [5, 6] and dye-sensitized solar cells [7, 8]. Phthalocyanines are a class of organic macromolecules that display interesting properties; they show thermal and chemical stability along with a suitable energy gap for photonic excitations by visible light. In this context they are used as sensitizers in solar cells [9–11] or as hole transport layers in OLEDs [6].

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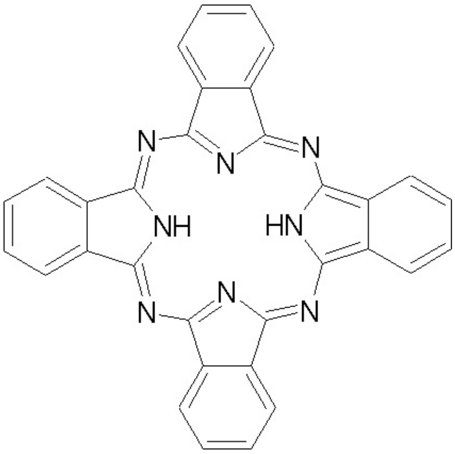

Figure 1. A schematic diagram of the H_2PC molecule.

The phthalocyanines are composed of four isoindole groups, each consisting of a pyrrole group coupled to a benzene ring. These four isoindole groups are in turn connected via bridging nitrogens to form a ring-like structure (a schematic diagram is shown in figure 1). This leaves a void in the centre of the molecule which can be populated with a metal ion (such as Cu, Ru, Zn, Sn or Pb), a compound (such as a titanyl group (TiO)) or two hydrogen atoms to form a metal-free phthalocyanine (H_2PC). H_2PC is a planar molecule, roughly 15 Å in square, whose highest occupied molecular orbital (HOMO) is made up from the delocalized π-electrons and the lowest unoccupied molecular orbital (LUMO) is an excited state of these [12, 13] and is considered to be a model system for phthalocyanines.

In technical applications the characteristics of interfaces are of vital importance for the performance of a device. Ordering and abruptness at interfaces play key roles in electronic transport properties. The choice of substrate (lattice parameter and presence of reactive dangling bonds) and method of preparation are therefore important factors to be considered. One attractive system with substrate dimensions of the order of the molecular size is the (100) surfaces of InAs and InSb. These surfaces show a $(4 \times 2)/c(8 \times 2)$ reconstruction which consists of In rows in the [110] direction [14–20], spaced 18.3 Å (InSb) and 17.1 Å (InAs) apart, which are thus potential templates for the ordered growth of PCs. It has been shown that ordered structures of PCs can be achieved without prior passivation of the surface; PbPC forms ordered one-dimensional chains on the InSb(100) surface [21, 22], while CuPC forms an adlayer with a (3×3) periodicity on the same surface [23, 24] and a $(\sqrt{10} \times \sqrt{10})$ R $\pm$ 18.4° structure on InAs(100) [24, 25]. Ordered layers of H_2PC and CuPC have also been achieved on InSb(111)A and InAs(111)A where a $(\sqrt{12} \times \sqrt{12})$ R30° reconstruction is found for the first monolayer (ML) on both surfaces [25, 26]. GaAs and Si both need to be passivated [24, 27–30] to allow ordered growth, whereas on Sb-terminated GaSb no ordered overlayers were observed [24]. Previously, H_2PC has also been investigated on InSb(100) where (3×3) and $(\sqrt{10} \times \sqrt{10})$ R $\pm$ 18.4° structures were found using low energy electron diffraction (LEED) [23], on InAs(100), where no ordered growth of H_2PC was reported [23], and in thick films on conductive glass (ITO) [12, 31].

In this paper we investigate the initial interface formation of H_2PC on InSb(100) $c(8 \times 2)$ and InAs(100) $(4 \times 2)/c(8 \times 2)$, as to date no thorough investigation invoking scanning tunnelling microscopy (STM) and photoelectron spectroscopy (PES) to determine the adsorption and ordering on an atomic level has been done. We find ordered first layers on both substrates. Our photoemission results reveal an abrupt H_2PC/InSb interface where the organic layer preserves its molecular character, whereas H_2PC/InAs instead form a reactive interface that strongly perturbs the molecular electronic structure, resulting in a finite density of states at the Fermi level.

2. Experimental details

InAs(100) and InSb(100) samples were cut from wafers supplied by Wafer Tech. Ltd, UK. The wafers were oriented to $\pm 0.1^\circ$ off the (100) plane and both wafers were n-type; InAs was doped with S (4.4×10^{16} cm^{-3}) and InSb with Te (2.3–3.6 $\times 10^{15}$ cm^{-3}). In order to prepare a well defined surface, the samples were Ar^+ sputtered for several cycles with subsequent annealing to about 670–720 K. This treatment resulted in large terraces (up to several hundred nm wide) on both substrates. In LEED, InSb(100) displayed a $c(8 \times 2)$ pattern while InAs(100) showed a $(4 \times 2)/c(8 \times 2)$ pattern.

A resistively heated quartz crucible in a home built Knudsen-type evaporation cell was used for phthalocyanine deposition. The temperature during evaporation was $\sim$500 K, measured with a thermocouple attached to the outside of the quartz crucible. The H_2PC, $>99\%$ pure, is home made and was supplied by Dr N Papageorgiou. The powdered phthalocyanine was used after a thorough outgassing for several hours in front of a quadrupole mass spectrometer until no contaminants (mainly water) could be detected. During evaporation, the cell was positioned a few centimetres from the sample; the pressure in the chamber was below 5×10^{-9} mbar.

Determination of the evaporation-rate was done by counting the number of adsorbed molecules in a large number of STM images. Full coverage, i.e. a tightly packed layer of molecules, is thus defined as 1 ML. This gives a deposition rate of $\sim$1 ML min^{-1} for both InSb and InAs. There is of course some uncertainty in this estimation as the molecules are mobile on the surface and the distribution of the molecules is not perfectly homogeneous, but the values were reproducible from several preparations. The depositions in the photoemission experiments were estimated from the STM calibration, and also checked by monitoring the intensity from the substrate core levels and comparing with an exponential attenuation model.

The STM chamber is equipped with an Omicron VT-STM, a LEED as well as sample cleaning facilities (Ar sputter and sample heating) along with the phthalocyanine source. All STM images presented here are recorded in constant current mode and at room temperature, using a negative tip bias and thus probing empty states.

The photoelectron spectroscopy experiments were performed at beam line I511 at MAX-lab in Sweden. I511 is an undulator-based beam line equipped with a Scienta SES-200 hemispherical electron analyser, rotatable around the axis of the photon beam. The photon energy ranges from 100 to 1200 eV. In connection with the photoemission chamber is a preparation chamber equipped with LEED, mass spectrometer, sample cleaning possibilities (heating and Ar^+ sputter) and the evaporation cell. Details of the I511 set-up are presented in [32]. The core level spectra were recorded at room temperature, in normal emission and grazing incidence (approximately 80° off-normal) of the photons. The resolution of the photoelectron (PE) spectra was better than 170 meV for N 1s, 100 meV for C 1s and $\sim$30 meV for In 4d, As 3d, Sb 4d and valence band spectra. All spectra were normalized to the background (for the core level spectra at the low binding energy side of the peak and for the valence band spectra at the high binding energy side of the spectrum). The Fermi level, measured on a Ta foil in electric contact with the sample, was used as a binding energy reference. The core levels were analysed by a curve fitting procedure using Voigt functions and a Shirley background.

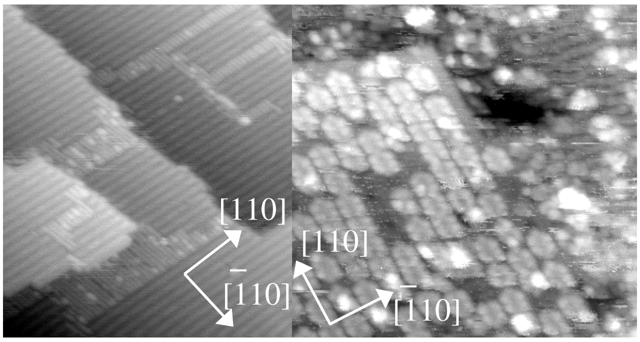

Figure 2. Empty state STM images from the InSb(100) surface: (a) a 485 × 560 $Å^2$ empty state image bias −2.0 V and 49 pA, showing the clean $c(8 \times 2)$ reconstructed surface with small patches of the antimony-rich (1 × 3) phase and (b) imaged directly after deposition of nearly 1 ML of H_2PC, at −3.0 V, 78 pA and 230 × 225 $Å^2$ large. The adsorbed molecules are aligned along the [110] direction, i.e. they prefer the In rows and not the Sb-rich domain as it shows a significantly lower coverage.

3. Results and discussion

3.1. Scanning tunnelling microscopy

InSb(100) can simultaneously host two different surface reconstructions after sputtering and annealing, the relative surface coverage depends on the annealing temperature. In addition to the indium-rich $c(8 \times 2)$ reconstruction, a Sb-rich (1 × 3) phase also exist [16]. The situation is depicted in figure 2(a), which is a 485 × 560 $Å^2$ empty states STM image (−2.0 V, 49 pA). The In rows of the $c(8 \times 2)$ reconstruction are parallel with the [110] direction whereas the lines of (1 × 3) reconstruction follow the [$\bar{1}$10] direction.

Figure 2(b) is an empty states image, 230 × 225 $Å^2$ (−3.0 V, 78 pA), recorded immediately after deposition of H_2PC. Molecules are depicted as four readily distinguishable protrusions, each representing one isoindole group. The molecules align along the substrate In rows, and they all have the same orientation with respect to the underlying substrate. Note that the scan direction is rotated by almost 90° compared to figure 2(a). The upper right corner of the image is a Sb-rich domain. The H_2PC coverage is substantially lower here than on the In-rows, clearly indicating the preferred adsorption site. This observation agrees with a previous report [24] where ordered growth was not observed on antimony-rich GaSb(100) 1 × 3, $c(2 \times 6)$ and InSb(100) $c(4 \times 4)$ surfaces.

On the (1 × 3) surfaces one may explain the lack of order or low adsorption by a lattice mismatch between substrate and molecule. This explanation does not hold on $c(4 \times 4)$ and a more plausible picture is that the electronic structure on the Sb-rich phase prevents efficient charge rearrangement for bonding and/or rearrangement of the substrate atoms. The Sb-rich InSb(100) surface structures are terminated by Sb dimers [33, 34] with filled lone pairs. Furthermore, Sb cap layers are used to protect MBE-grown heterostructures [35], and can be expected to have a low chemical activity.

STM images from annealed submonolayer (∼1/3 ML) covered InSb(100) $c(8 \times 2)$ surface are shown in figure 3. InSb was annealed to 450 K in figures 3(a) and (b) and to 575 K in figure 3(c). Depending on the tunnelling bias, molecules as well as the substrate change their appearance. At −1.86 V (in figure 3(a)) the molecules are nicely pictured as a four leaf clover with two lobes on each side of the indium rows. At this tunnel bias the substrate is

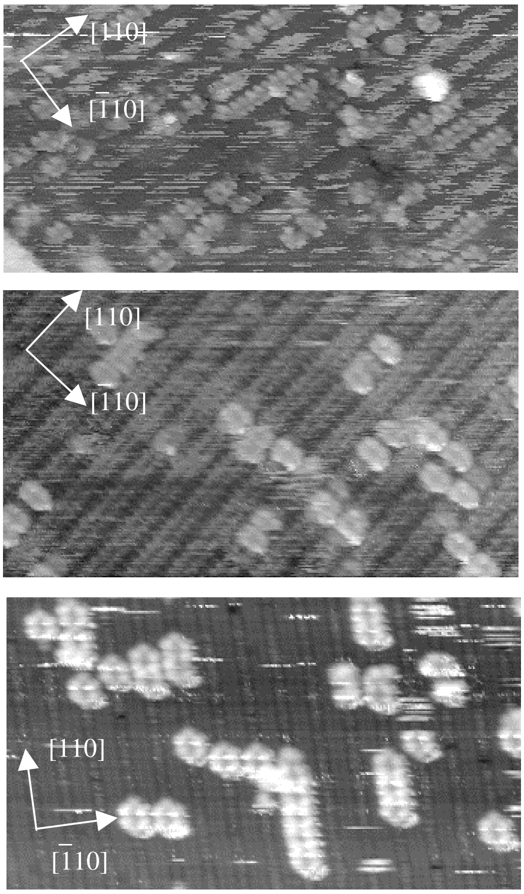

Figure 3. STM images of InSb(100)-$c(8 \times 2)$ dosed with H_2PC and after thermal treatment. The coverage is $\sim 1/3$ ML. In (a) the image size is 325×170 Å^2 with tunnelling conditions -1.86 V, 1.0 nA and the sample is annealed to ~450 K. The image size is 375×205 Å^2 in (b), imaged at -2.36 V, 0.16 nA also after annealing to ~450 K. In (c), the image is 290×170 Å^2 in size with bias -3.0 V and current 0.30 nA and after annealing to ~575 K.

not well resolved and appears streaky. In figure 3(b), at -2.36 V, the molecules appear ring-shaped with the isoindole groups barely distinguishable. At this bias the indium rows appear double, due to a higher density of states on the atoms adjacent to the indium rows, as previously reported [16, 17]. In figure 3(c), at -3.0 V, the molecules appear as hexagons from the well resolved isoindole groups and an additional protrusion just outside the molecular structure along the indium rows. The substrate is again imaged with protruding In-rows separated by double rows of antimony.

Figure 4(a) is an empty state image from the InAs(100) surface after deposition of $\sim 1/6$ ML of H_2PC. Again the molecules are imaged as four separate protrusions centred over the indium rows, with two isoindole groups on each side of row. Figure 4(b), 490×240 Å^2, was recorded at -3.0 V tunnel bias and 0.30 nA, after annealing a low coverage surface ($\sim 1/6$ ML) to ~675 K. The preferred adsorption is unchanged on top of the indium rows. The molecules have a similar appearance with a hexagonal shape as for the InSb case, when imaged with the same bias. The additional features forming the hexagons are seen in the STM images of

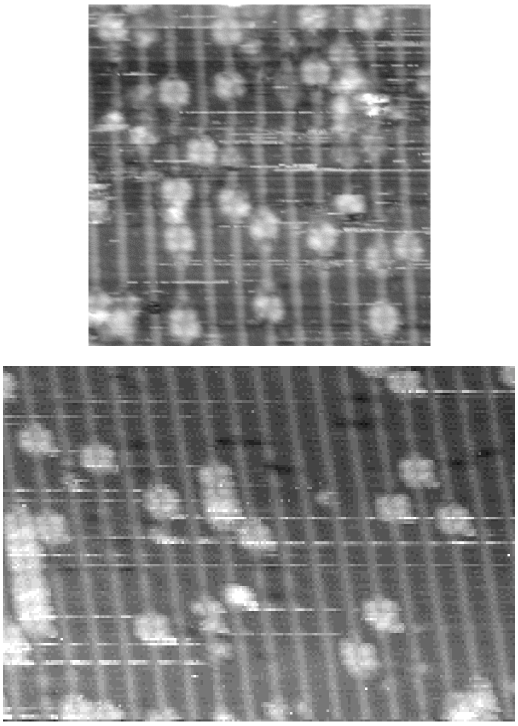

Figure 4. STM images from the InAs(100) surface after deposition of ∼1/6 ML H_2PC: (a) recorded from the surface after room temperature deposition, −3.0 V and 78 pA and (b) after annealing at 675 K. 300 × 210 $Å^2$, −3.0 V and 0.30 nA.

both the annealed and as-deposited molecules and are thus not related to the thermal treatment. They appear ∼8 Å outside the isoindole protrusion. This is much further out than what would be expected for any molecular orbital in this direction. It is much more likely to be related to an increased density of states on the neighbouring In atoms near the molecule.

An adsorption model for PbPC/InSb(100) $c(8 \times 2)$ was proposed by Angot *et al* [21], with the central Pb atom directly on top of indium in the rows. We cannot from our images state the exact adsorption position, but within the Angot model, with the molecular centre either on top of In or on bridging site, the bridging-nitrogens are located in close vicinity to indium atoms. The increased tunnel current over these sites, that gives the hexagonal shape, indicates a nitrogen–indium interaction. In the model the benzene rings are located above top layer Sb(As) and three-fold coordinated indium between the indium rows. This is supported by the STM image in figure 3(b) where molecule-related protrusions are in line with the second layer of indium double rows.

Figure 5(a) is an image from the InSb(100) surface after deposition of 2 ML H_2PC, and subsequently annealed to 575 K. Here molecules rearrange on the surface to form a closely packed first layer with small islands on top. The LEED pattern was similar to that found in [21]; a $c(8 \times 2)$ pattern from the substrate remained with two rows of additional streaks visible in the [110] direction. We adopt their notation, namely the '×3', meaning that the closely packed molecules are separated by three substrate distances along the In rows but not correlated to the neighbouring rows which would lead to a 4 × 3 pattern. The LEED pattern is hence a superposition of the two patterns, $c(8 \times 2)$ and '×3', indicating the coexistence of the

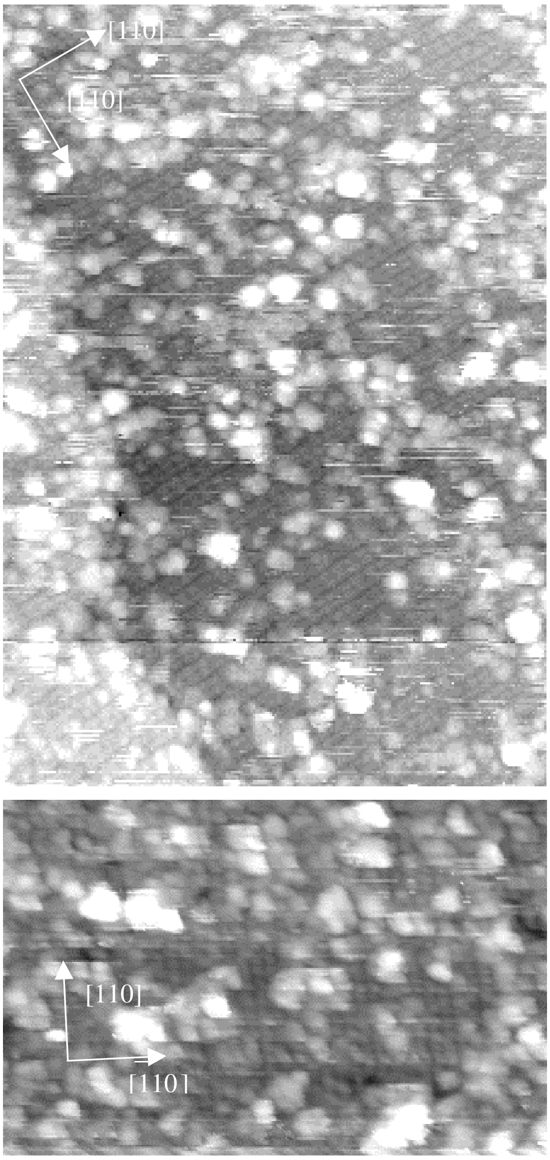

Figure 5. STM images from the InSb (left) and InAs (right) surfaces after deposition of 2 ML and subsequent annealing. InSb was annealed at ∼575 K, image size 475 × 725 Å^2 recorded at −3.0 V and 0.20 nA. InAs was annealed at 675 K, recorded at −2.0 V, 0.11 nA and sized 500 × 225 Å^2.

two structures. The original $c(8 \times 2)$ reconstruction is thus still present below the molecular layer, indicating that the interaction between substrate and adsorbate is relatively weak.

The corresponding STM image from the InAs surface is shown in figure 5(b). A 2 ML thick H_2PC film was annealed at ∼675 K. The STM image is 500 × 225 Å^2 large and the tunnel bias was −2.0 V and the current 0.11 nA. A layer of densely packed molecules can be seen underneath small islands. This surface gave a LEED pattern with the original $(4 \times 2)/c(8 \times 2)$ pattern plus extra streaks to form the '×3' pattern as previously described, indicating that the molecules form an ordered first layer.

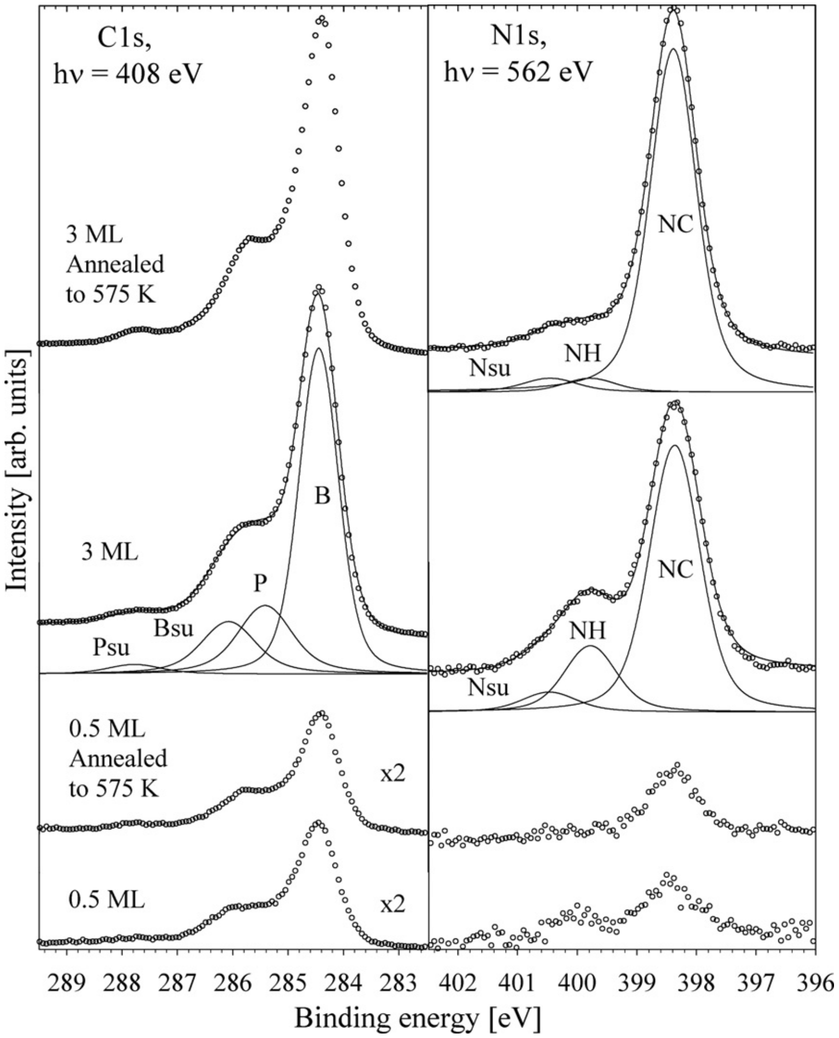

Figure 6. The H_2PC C 1s and N 1s core levels measured on InSb(100)–H_2PC with 408 and 562 eV photon energy, respectively. The C 1s core level is fitted with four components: B from the benzene type carbon atoms, P from the pyrrole type carbon atoms and B_{SU} and P_{SU} is the shake-up intensity associated with B and P, respectively. The N 1s core level is fitted with three components: NC from pyrrole and bridging nitrogen atoms, NH from the central nitrogen bonded to hydrogen and N_{SU} is the shake-up feature.

3.2. Photoelectron spectroscopy

The electronic structure and surface chemistry was studied with photoelectron spectroscopy. We begin by presenting C 1s and N 1s spectra, followed by valence band spectra and substrate core level spectra, from selected preparations as indicated in the figures.

C 1s (left) and N 1s (right) core levels from InSb(100)–H_2PC are presented in figure 6. The C 1s line shape from the 3 ML thick film closely resembles the one from bulk H_2PC (see [12, 31]). The spectrum is accordingly fitted with four components: B at 284.4 eV binding energy related to carbon atoms in the benzene ring, B_{SU} at 284.9 eV from the π–π^* shake-up related to B, P at 285.9 eV represents pyrrole carbon atoms bonded to nitrogen and finally P_{SU} at 287.9 eV is the shake-up peak related to P. The relative intensities, 77% for benzene-type carbon and 23% for pyrrole-type carbon, agree well with the expected molecular fraction. This indicates that the H_2PC multilayer preserves its molecular electronic structure. Thermal treatment to 575 K does not cause any large changes in the C 1s line profile except a narrower width that reflects an increased order at the interface, concurring with the '×3 'periodicity along the [110] direction found in LEED. The two spectra from 0.5 ML coverage (multiplied by a factor of 2) are very similar to the thicker film, which indicates a relatively weak interaction with the substrate. Again a reduction of the peak width is observed after annealing.

To fit the N 1s core level spectrum from the 3 ML film three components are used [12, 31]: NC at 398.4 eV represents nitrogen with a N–C bond in the pyrrole group and the bridging N atoms, NH at 399.8 eV originates in nitrogen with a N–H bond in the centre of the molecule and finally N_{SU}, which is due to shake-ups at 400.5 eV. The relative intensities of NH and NC are 19% and 74%, respectively. Upon thermal treatment the N–H related component is strongly reduced (only ∼20% remains of the original intensity), indicating deprotonation of the molecule. The loss in intensity in NH is gained in NC, and there is no desorption from the surface; the total N 1s signal is reduced by only 1% after annealing. A similar scenario can be seen in the spectra from 0.5 ML coverage and 3 ML coverage. The two 0.5 ML spectra in the N 1s spectra are not fitted because of poor statistics due to a weak signal, but the disappearance of the N–H related peak upon thermal treatment is clearly seen. A similar observation was done on the PbPC/InSb(100) system where Pb is found to leave the molecule and change oxidation state, from Pb^{2+} to Pb^0, upon thermal treatment [36].

Figure 7 shows the C 1s (left) and N 1s (right) core level spectra from selected preparations of H_2PC on InAs(100). The C 1s line shape for the 0.66 ML coverage is strongly perturbed by the interaction with the surface without any resolved internal structure. At 3 ML coverage the line shape is again similar to (but broader than) spectra from the bulk film and the 3 ML film on the InSb surface. This spectrum is again reproduced with four components (with the same notation as previously used for InSb): B (benzene-related) at 284.7 eV, P (pyrrole-related) at 285.7 eV and the shake-up related peaks B_{SU} at 286.3 eV and P_{SU} at 287.9 eV. The relative positions of the contributing peaks are in the InAs case the same (within 0.1 eV) as for InSb, but the widths of the peaks are larger due to the additional interface contribution. The intensity ratio between benzene and pyrrole peaks is in good agreement with the expected values, 78% and 22% respectively. The bulk like C 1s line shape in the 3 ML film indicates that only the first layer is affected by the interaction with the substrate: hence two types of molecules exist, one in contact with the substrate having an altered line shape and a second type with a bulk-like line shape. Upon thermal treatment a gradual change of the spectra from 'bulk-like' to 'interface-like' molecules occurs, and at 675 K the C 1s line shape is similar to the 0.66 ML line shape. The C 1s line shape at low coverage and after annealing is similar to what is found for phthalocyanines on more reactive surfaces such as, for example, Si(111) or Si(100) [37], and also very similar to recently published C 1s spectra from K-doped CuPC films [38], and can thus be due to a stronger interaction with the substrate and/or an electron-rich environment of the molecule. We rule out dissociation of the molecule from our STM data. The integrated C 1s intensity is reduced to 80% after annealing. From the STM measurements we observed a contraction of the overlayer into islands, which can explain this reduction. However, we cannot exclude desorption at higher annealing temperatures.

The N 1s core level spectrum for the 3 ML film also shows strong similarities with bulk or thick films [31] (the 0.66 ML coverage is omitted due to the weak signal). This spectrum is fitted with three components in correspondence with the InSb case: NC (from pyrrole and bridging nitrogen) is found at 398.4 eV, NH (central hydrogen–nitrogen bond) at 399.9 eV and

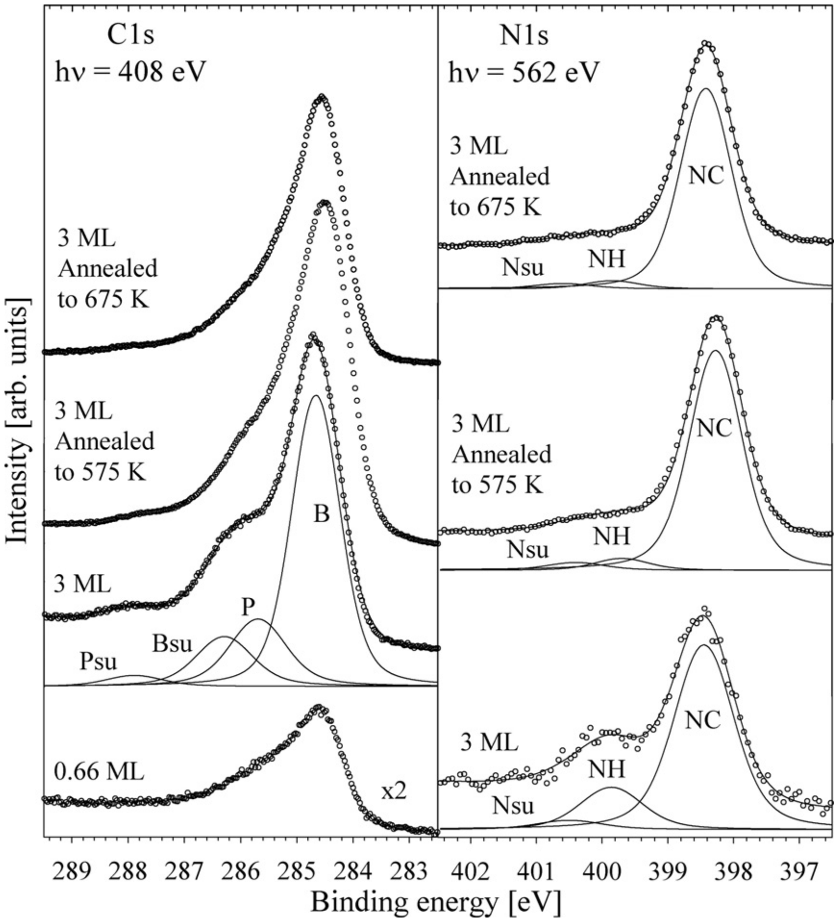

Figure 7. The H_2PC C 1s and N 1s core levels measured on InAs(100)–H_2PC with 408 and 562 eV photon energy, respectively. Following the notation defined for InSb, the four components of the C 1s core level are: B (benzene type carbon atoms), P (pyrrole type carbon atoms) and B_{SU} and P_{SU} are their shake-up intensities. The three components of the N 1s core level are: NC (pyrrole and bridging nitrogen atoms), NH (nitrogen bonded to hydrogen) and N_{SU} is the shake-up feature.

finally the shake-up related peak at 400.5 eV. These values are also in agreement with the ones found for InSb. The molecule on this surface is also deprotonated after annealing, the N 1s peak related to hydrogen (NH) is severely reduced and only 25% of the original intensity remains at 575 K. At 675 K, the NH peak is further reduced. It is worth noting that the deprotonation is not due to thermal treatment or adsorption alone but a combination of the two. This indicates that the central part of the molecule takes part in bonding to the surface.

Valence band (VB) spectra for the two systems are shown in figure 8, InSb to the left and InAs to the right. All spectra were excited by 110 eV photons. Spectra from the clean InSb(100) surface are dominated by three features: S related to surface states and B_1 and B_2 related to bulk states [39]. Upon dosing the InSb(100) surfaces with H_2PC, new features appear: they slowly grow in intensity and become clearly visible at 1 ML and the intensity of the surface states S decrease in intensity as expected due to the presence of the adsorbate. At 3 ML, and after annealing, the spectra are instead dominated by the three new features (H-1–

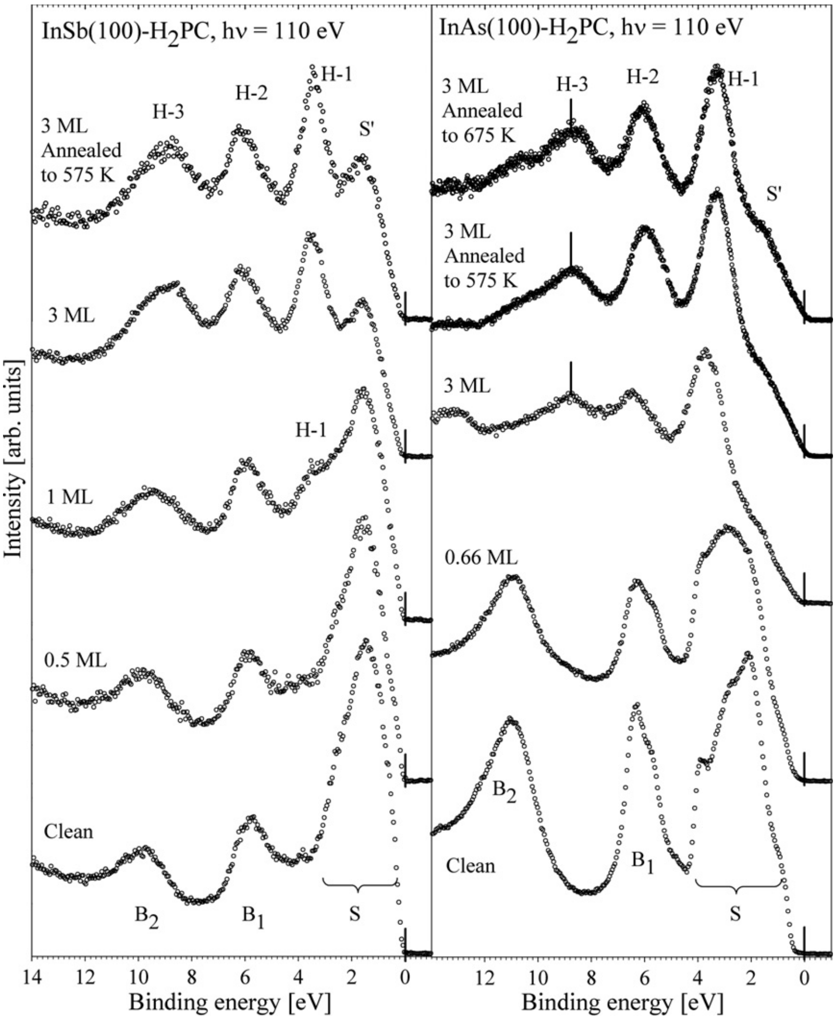

Figure 8. Valence band spectra on both surfaces are measured at 110 eV photon energy. Surface related states (S) and bulk states (B_1 and B_2) dominate the clean InSb and InAs. Upon adsorption a VB characteristic of H_2PC develops, dominated by the features H-1–H-3.

H-3), corresponding to the molecular levels HOMO-1, HOMO-2 and HOMO-3, respectively, as determined by comparison with previous experimental spectra and calculations [12, 40, 41]. The position of the HOMO on InSb(100) is located roughly at 2.7 eV above the main line (H-1) coming from the molecule [40] (the intensity is low and is thus not seen due to the scaling and the high intensity from substrate emission), inferring that the position of the HOMO is about 0.8 eV below the Fermi level. This places S′ between the HOMO and H-1, and hence is most likely coming from substrate emission. This is not surprising keeping in mind the very strong emission from this state on the pristine surface and the apparently relatively weak interaction between the substrate and the organic overlayer. With the HOMO 0.8 eV below the Fermi level and a HOMO–LUMO gap of 2.2 eV [12] the LUMO is located 1.2 eV into the conduction band (CB). Furthermore, the Fermi level is located just above the valence band maximum (VBM) on the clean surface. The VBM shifts slightly away from the Fermi level at the highest coverage, thus corresponding to a slight downward band bending, and the interface retains its semiconducting character at all coverages and thermal treatments.

Valence band spectra from InAs(100) are also dominated by three groups of features (the same notation is chosen due to the similarity of the VB): S originating in several surface states and B_1 and B_2 originating in bulk emission [20, 42, 43]. At the 0.66 ML coverage the states related to emission from H_2PC emerge (H-1) and surface states (S) decrease. The bulk related emission is reduced in intensity but preserves its line shape. For the as-deposited 3 ML thick film clear molecular states appear. They are, as previously, denoted H-1, H-2, and H-3. Even though C 1s indicates substantial interaction after thermal treatment, the VB retains the molecular character. The position of the HOMO on the as-deposited 3 ML film is estimated as above, assuming a 2.7 eV HOMO-1 to HOMO separation to be located 0.9 eV below the Fermi level giving a LUMO position 0.9 eV above the CBM (conduction band minimum). After thermal treatment H-3 remains fixed but H-1 and H-2 are shifted to a lower binding energy by about 0.4 eV. HOMO and LUMO accordingly shift upwards as well. H-1 and H-2 have a mixed C 2p and N 2p lone pair origin [40, 41]. We relate the observed shift to a change in the nitrogen atoms in the molecule due to rehybridization with the substrate. There is also a finite intensity at the Fermi level after annealing the 3 ML film; thus the interface is metallic.

Substrate core level spectra were recorded using 110 eV photon energy for all preparations. In figure 9 we present In 4d and Sb 4d spectra from the H_2PC/InSb(100) system and in figure 10 we present In 4d and As 3d spectra from the H_2PC/InAs(100) system. Indium 4d spectra from clean $c(8 \times 2)$ reconstructed InSb(100) were fitted with three separate components: B for bulk, S1 shifted 0.25 eV to lower binding energy has been assigned to In in the rows and S2 shifted 0.23 eV to higher binding energy is due to emission from other surface indium [44, 45]. The currently accepted structure model contains a collection of indium in different bonding geometries [14] that may give rise to many different shifted components in the spectrum. However, these shifts are apparently much smaller than the different broadening mechanisms in the spectra and can thus not be separately resolved. Deposition of 0.5 ML of H_2PC does not alter the line shape within our precision. Annealing the same surface may have a slight effect on the energy balance between the two surface peaks, but this is not a strong effect. Deposition of 3 ML H_2PC reduces the intensity on the low binding energy side, which is regained after annealing. The conclusion from this set of spectra must simply be that there is very little change in the In 4d spectra and that indium is not influenced by the adsorption. The bulk component shifts by $\sim$35 meV to higher binding energy between the clean and the annealed 3 ML film. This corresponds to a downward band bending induced by the adsorption, in agreement with the previously observed shift of the VBM to higher binding energy.

Sb 4d spectra are fitted with two components on the clean surface and an additional shifted component at high H_2PC coverage. Very little has been done on this surface and the interpretation of spectra is not well established. In a previous analysis of this surface, three components were used [44]. We applied the same fit but the energy shifts and relative intensities depend strongly on the selected fit parameters and we judge the two-component fit to be more reliable. The components are related to bulk (B) and surface atoms (S). The surface shift is 0.27 eV to lower binding energy. Low coverage adsorption of H_2PC reduces the surface intensity but does not alter the surface shift. The same is valid also after annealing this surface, in agreement with the results for In 4d. At 3 ML coverage the surface shifted component is reduced to 35% of the total intensity in the spectrum. In addition there is a new shifted component on the high binding energy side. The shift is 0.32 eV and the relative intensity is 4% before annealing and 7.5% after annealing. Thus only a small portion of the surface antimony atoms are affected by the H_2PC adsorption. The bulk component shifts by $\sim$50 meV

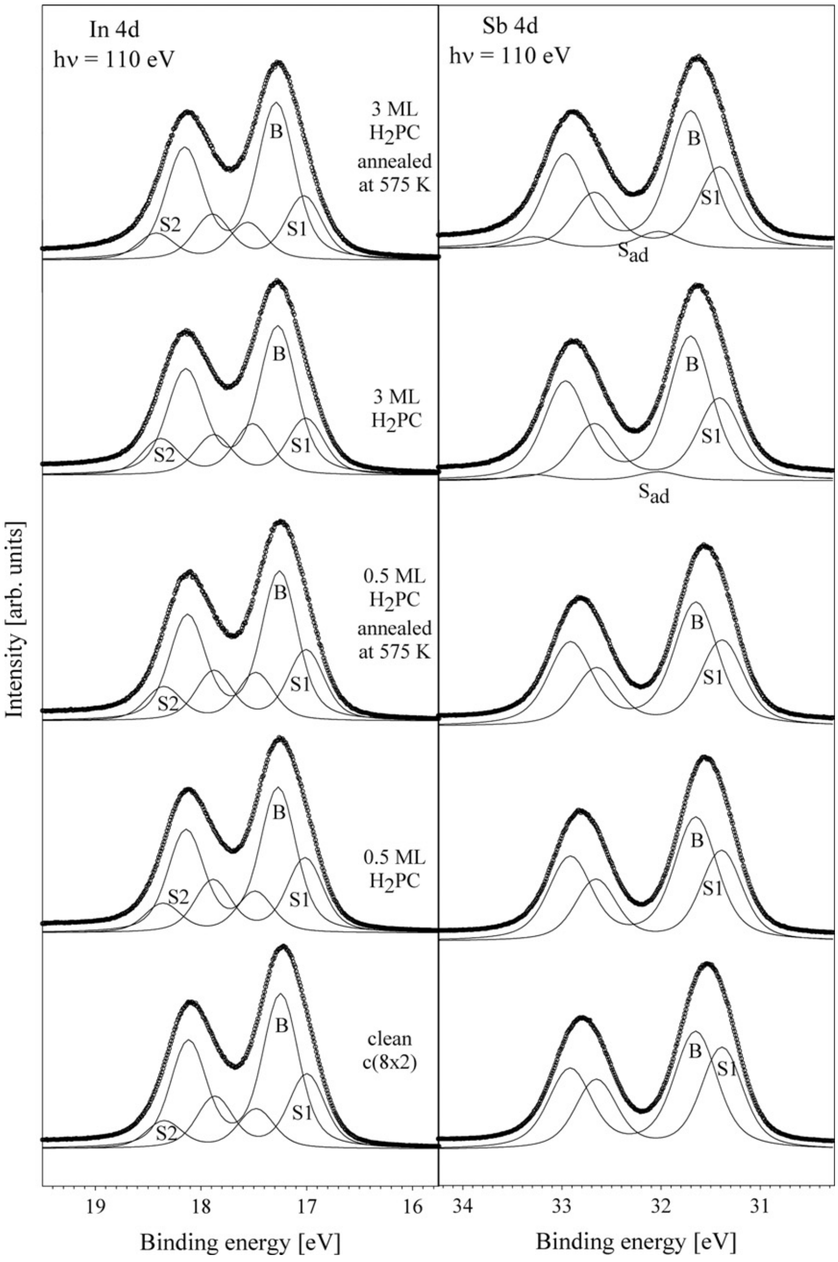

Figure 9. Indium 4d and Sb 4d core level spectra from InSb(100)/H_2PC using 110 eV photon energy. Indium 4d spectra were fitted with three components using a 0.87 eV spin–orbit split (SO), branching ratio (Br) 1.47, Gaussian width (W_G) 0.33 eV and Lorentzian width (W_L) 0.175 eV. Sb 4d was fitted with a bulk component, a surface component and one adsorbate-induced component. The fit parameters were SO = 1.26 eV, Br = 1.4–1.45, $W_G = 0.30$ eV and $W_L = 0.22$ eV.

to higher binding energy between the clean and 3 ML annealed film. This is in agreement with the downward band bending discussed above. The shifts observed are indeed small, of the limit of the experimental resolution, and should not be over-interpreted.

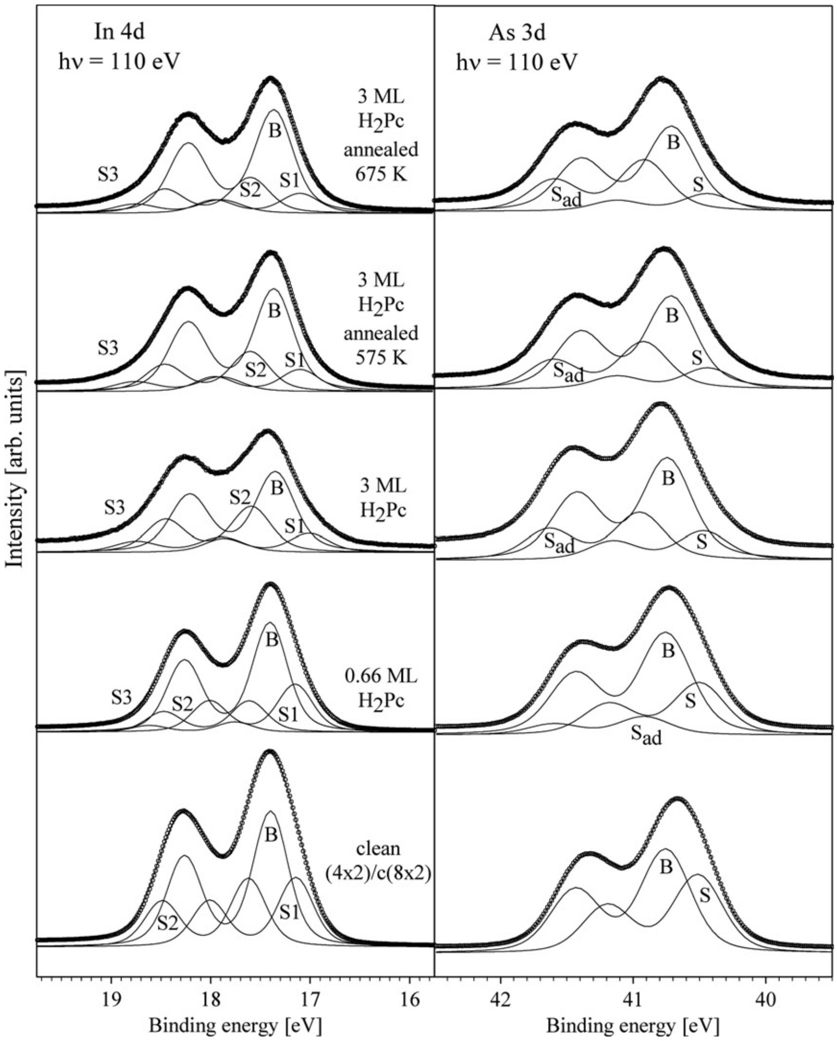

Figure 10. Indium 4d and As 3d core level spectra from InAs(100)/H_2PC using 110 eV photon energy. Indium 4d spectra were fitted with three components using a 0.87 eV spin–orbit split (SO), branching ratio (Br) 1.47, Gaussian width (W_G) 0.33 eV and Lorentzian width (W_L) 0.175 eV. As 3d was fitted with a bulk component, a surface component and one adsorbate-induced component. The fit parameters were SO = 0.68 eV, Br = 1.55–1.62, $W_G = 0.32$ eV and $W_L = 0.20$ eV.

The InSb–H_2PC is an abrupt interface with van der Waals type interaction between the film and the substrate. This is evidenced by the C 1s core level, which keeps a molecular line profile at all coverages; the VB spectra also have a clear molecular character at 3 ML coverage and the STM images show individual molecules at a coverage of both less and more than 1 ML. H_2PC adsorption induces a weak downward band bending at the surface, and the system remains semiconducting at all preparations.

The InAs(100)–H_2PC system displayed a different C 1s line profile from InSb(100)–H_2PC and is also metallic. The In 4d and As 3d core level spectra reflect these differences. In figure 10 we present In 4d and As 3d spectra from the selected preparations. The In 4d spectrum from the clean surface was fitted with three components in agreement with previous reports [20]. The bulk peak (B) dominates the spectrum with one surface shifted component on each side; S1 at 0.25 eV lower binding energy and S2 at 0.22 eV higher binding energy. They are identified similar to InSb with S1 representing In in indium rows, and S2 representing other surface indium. Deposition of 0.66 ML H_2PC reduces S2 and introduces S3 shifted 0.54 eV to higher binding energy from the bulk peak. At 3 ML coverage S3 contributes 10% of the total intensity, while S1 is reduced from 25% on the clean surface to 11% on this surface. The bulk peak is also reduced, whereas S2 actually has a stronger relative intensity than on the clean surface. This can only be explained by the presence of a new indium species at this coverage. Upon annealing S2 gradually loses intensity while the total intensity recovers. The bulk peak shifts 40 meV to lower binding energy, thus corresponding to an adsorbate-induced upward band bending at the surface.

Arsenic 3d spectra are numerically fitted with only two components, in agreement with [20], and also similar to the InSb(100) surface. The surface shift is 0.24 eV to lower binding energy, and the relative surface intensity is 42%. 0.66 ML H_2PC adsorption reduces this intensity to 30% and introduces a new peak on the high binding energy side, S_{ad}, at 0.21 eV from the bulk line. The S_{ad} intensity steadily increases with coverage up to 33% of the total intensity. Simultaneously, S is reduced to only 11%. Thus there is a large population of As atoms involved in the bond to the adsorbate.

The bonding of the molecule to the substrate in the flat lying mode goes mainly through the π system of the outer benzene rings, but also the central part is obviously affected by the presence of the substrate. The surface–nitrogen interaction is indicated by the deprotonation of the molecule and also by the hexagonal shape of the molecule at certain tunnelling biases. This effect is similar for the two surfaces. The larger difference is seen in the C 1s core level, the chemical shifts in the As 3d and In 4d from the InAs surface and from the strong shift of the molecular orbitals upon annealing.

The C 1s line shape on InAs–H_2PC is very similar to previous results from Si [37] and also K-doped CuPC films [38]. The main interaction with Si is through the dangling bonds with the π-system, whereas in the case of K-doped films it was proposed that K binds to the bridging-nitrogens. In these two cases the molecule is perturbed through different channels, but with the same resulting C 1s line shape. The C 1s main peak has its physical origin in the benzene carbons, which are located between the surface indium rows. The largest effect was seen on the As 3d core level where the chemically shifted component contributed 33% of the total intensity. This implies that As is the primary interaction channel. However, surface As are surrounded by indium both in the top layer as well as below. Thus, surface indium can also be expected to take part in bonding the molecule, or at least be affected by the bond to arsenic, which indeed is reflected by the changed In 4d line shape.

The difference between InAs and InSb is somewhat intriguing, but there are a few potential explanations. The basic geometry is expected to be same except for the smaller lattice parameter of InAs. This does have an effect on the detailed atomic coordinates on the surface, since the strain on the surface indium will be different in the two cases. This can also be seen from the x-ray diffraction study by Kumpf *et al* [14, 46], where for example indium in the rows relaxes in towards the surface on InSb whereas this effect is not seen on InAs. These changes are accompanied by charge redistribution that naturally affects the surface bond. Another possible reason for the observed differences can be found in the electronic structure on the clean surfaces. It is known from many studies that almost all InAs surfaces (except well cleaved (110) and (111)B surfaces) form charge accumulation layers at the free surface [20, 39, 42, 43, 45, 47]. This is not seen on InSb at room temperature. The presence of this accumulation layer may well affect a surface reaction [48].

4. Conclusion

Our results provide a picture of an abrupt interface in the case of InSb–H_2PC with a weak interaction between adsorbate and substrate; the C 1s core level and the VB spectra retain their molecular nature even after thermal treatment and the interface is semiconducting. The deprotonation as evidenced in the N 1s spectrum appears not to affect the molecule significantly; it maintains its molecular character.

The situation is different in the case of InAs–H_2PC: the molecule is also deprotonated on this surface, as seen in N 1s spectra. At sub-ML coverage, the C 1s line shape is strongly perturbed by the bond to the surface, whereas at 3 ML coverage the line shape is 'molecular'. After annealing the thicker film the C 1s is again affected by the surface interaction. Valence band spectra indicate a substantial interaction as the molecular states (HOMO-1 and HOMO-2) shift towards lower binding energy upon thermal annealing. In addition, the surface becomes metallic after annealing the thicker film.

STM images reveal adsorption geometry and ordering on the surface. The arrangement of the molecules at room-temperature deposition, as well as after thermal treatment, is selective; the molecules align along the In rows and both InSb–H_2PC and InAs–H_2PC are indeed self-ordering. For higher coverage, and after thermal treatment, interface molecules form a densely packed first ML with islands of aggregated molecules on top.

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References

[1] Yang F, Shtein M and Forrest S R 2005 *Nat. Mater.* **4** 37

[2] Suemori K, Miyata T, Yokoyama M and Hiramoto M 2005 *Appl. Phys. Lett.* **86** 063509

[3] Darwish S, El Zawawi I K and Riad A S 2005 *Thin Solid Films* **485** 182

[4] Zeis R, Siegrist T and Kloc Ch 2005 *Appl. Phys. Lett.* **86** 022103

[5] Tang C W and VanSlyke S A 1987 *Appl. Phys. Lett.* **51** 913

[6] Blochwitz J, Pfeiffer M, Fritz T and Leo K 2001 *Appl. Phys. Lett.* **73** 729

[7] O'Regan B and Grätzel M 1991 *Nature* **353** 37

[8] Grätzel M 2001 *Nature* **414** 338

[9] Nazeeruddin Md K, Humphry-Baker R, Grätzel M, Wöhrle D, Schnurpfeil G, Schneider G, Hirth A and Trombach N 1999 *J. Porphyr. Phthalocyanines* **3** 230

[10] Nazeeruddin Md K, Humphry-Baker R, Grätzel M and Murrer B A 1998 *Chem. Commun.* 719

[11] He J, Hagfeldt A, Lindquist S-E, Grennberg H, Korodi F, Sun L and Åkermark B 2001 *Langmuir* **17** 2743

[12] Alfredsson Y *et al* 2005 *J. Chem. Phys.* **122** 214723

[13] Orti E and Brédas J-L 1992 *J. Am. Chem. Soc.* **114** 8669

[14] Kumpf C *et al* 2001 *Phys. Rev. Lett.* **86** 3586

[15] Kolodziej J J, Such B and Szymonski M 2003 *Phys. Rev. Lett.* **90** 226101

[16] Varekamp P R, Björkqvist M, Göthelid M and Karlsson U O 1996 *Surf. Sci.* **350** L221

[17] MacConville C F, Jones T S, Leibsle F M, Driver S M, Noakes T C Q, Schweitzer M O and Richardson N V 1994 *Phys. Rev.* B **50** 14965

[18] John P, Miller T and Chiang T-C 1989 *Phys. Rev.* B **39** 1730

[19] Kendrick C, LeLay G and Kahn A 1996 *Phys. Rev.* B **54** 17877

[20] De Padova P, Perfetti P, Quaresima C, Richter C, Zerrouki M, Heckmann O, Ilakovac V and Hricovini K 2003 *Appl. Surf. Sci.* **212/213** 10

[21] Angot T, Salomon E, Papageorgiou N and Layet J-M 2004 *Surf. Sci.* **572** 59
[22] Papageorgiou N, Salomon E, Angot T, Layet J-M, Giovanelli L and LeLay G 2004 *Prog. Surf. Sci.* **77** 139
[23] Yim S and Jones T S 2002 *Surf. Sci.* **521** 151
[24] Cox J J, Bayliss S M and Jones T S 1999 *Surf. Sci.* **433–435** 152
[25] Cox J J, Bayliss S M and Jones T S 1999 *Surf. Sci.* **425** 326
[26] Yim S, Jones T S, Chen Q and Richardson N V 2004 *Phys. Rev.* B **69** 235402
[27] Evans D A *et al* 2003 *Appl. Surf. Sci.* **212/213** 417
[28] Yamamoto H, Tada H, Kawaguchi T and Koma A 1994 *Appl. Phys. Lett.* **64** 2099
[29] Nakamura M, Morita Y, Mori Y, Ishitani A and Tokumoto H 1996 *J. Vac. Sci. Technol.* B **14** 1109
[30] Kanai M, Kawai T, Motai K, Wang X D, Hashizume T and Sakura T 1995 *Surf. Sci.* **329** L619
[31] Brena B, Luo Y, Nyberg M, Carniato S, Nilson K, Alfredsson Y, Åhlund J, Mårtensson N, Siegbahn H and Puglia C 2004 *Phys. Rev.* B **70** 195214
[32] Denecke R, Väterlein P, Bässler M, Wassdahl N, Butorin S, Nilsson A, Rubensson J-E, Nordgren J, Mårtensson N and Nyholm R 1999 *J. Electron Spectrosc. Relat. Phenom.* **101–103** 971
[33] McConville C F, Jones T S, Leibsle F M, Driver S M, Noakes T C Q, Schweitzer M O and Richardson N V 1994 *Phys. Rev.* B **50** 14965
[34] Jones N, Norris C, Nicklin C L, Steadman P, Taylor J S G, Johnson A D and McConville C F 1998 *Surf. Sci.* **398** 105
[35] Clark S A, Cairns J W, Wilks S P, Williams R H, Johnson A D and Whitehouse C R 1995 *Surf. Sci.* **336** 193
[36] Giovanelli L, von Schenck H, Sinner-Hettenbach M, Papageorgiou N, Göthelid M and LeLay G 2001 *Surf. Sci.* **486** 55
[37] Dufour G, Poncey C, Rochet F, Roulet H, Sacchi M, De Santis M and De Crescenzi M 1994 *Surf. Sci.* **319** 251
[38] Molodtsova O V, Aristov V Yu, Zhilin V M, Vyalikh D V and Knupfer M 2006 *J. Physique* IV **132** 201
[39] Olsson L Ö, Khazmi Y O, Kanski J, Ilver L, Nilsson P O, Håkansson M C and Karlsson U O 1995 *Surf. Sci.* **331–333** 1176
[40] Tegeler E, Iwan M and Koch E-E 1981 *J. Electron Spectrosc. Relat. Phenom.* **22** 297
[41] Orti E and Bredas J L 1992 *J. Am. Chem. Soc.* **114** 8669
[42] Håkansson M C, Johansson L S O, Andersson C B M, Karlsson U O, Olsson L Ö, Kanski J, Ilver L and Nilsson P O 1997 *Surf. Sci.* **374** 73
[43] De Padova P, Perfetti P, Quaresima C, Richter C, Heckmann O, Zerrouki M, Johnson R L and Hricovini K 2003 *Surf. Sci.* **532–535** 837
[44] Varekamp P, Håkansson M C, Kanski J, Shuh D K, Björkqvist M, Göthelid M, Simpson W C, Karlsson U O and Yarmoff J A 1996 *Phys. Rev.* B **54** 2101
[45] De Padova P *et al* 2001 *Surf. Sci.* **482–485** 587
[46] Kumpf C *et al* 2001 *Phys. Rev.* B **64** 075307
[47] Olsson L Ö, Andersson C B M, Håkansson M C, Kanski J, Ilver L and Karlsson U O 1996 *Phys. Rev. Lett.* **76** 3626
Aristov V Yu, Le Lay G, Zhilin V M and Soukiassian P 1999 *Phys. Rev.* B **60** 7752
[48] Szamota-Leandersson K, Göthelid M and Karlsson U O 2003 *Appl. Surf. Sci.* **212/213** 589