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Abstract

The surface sensitivity of soft x-ray photoelectron spectroscopy is exploited to probe the structural, electronic and chemical properties of an organic/inorganic semiconductor interface. Thin films of tin–phthalocyanine (SnPc) are deposited on a GaAs(001)-1 × 6 surface, prepared by argon ion bombardment. Core level photoemission spectra are analysed to follow the evolution of the interface with SnPc coverage. The results indicate that the interface is largely chemically inert, while the overlayer growth mode is closer to Stranski–Krastanov. Valence spectra show the same molecular features throughout the coverage range. The valence band offset and the interface dipole of this heterojunction are 0.45 and -0.37 eV respectively. The interface dipole may have its origin in the difference in electron affinity of the organic and inorganic semiconductors.

1. Introduction

Thin films of organic semiconductors are increasingly being employed in electronic and optoelectronic devices [1, 2]. The variability of organic molecules can be exploited to change the properties of an inorganic interface. A thin organic film can influence the properties of the interface, e.g. the operating voltage of devices such as the GaAs Schottky diode [3, 4]. The properties of such organic/inorganic semiconductor interfaces are of general interest.

One prominent type of organic molecule is the metal phthalocyanine family. These are semiconducting and thermally stable. Also it is easy to form thin films by organic molecular beam deposition (OMBD). Ordered overlayers can be formed even in the absence

of good lattice matching with the inorganic substrate [5–11], which can be explained by the weakness of molecule–substrate interactions and hence the dominance of molecule–molecule over molecule–substrate interaction. These molecules are planar and thus the π-bonds establish a delocalized electron density above and below the plane of the molecules. The interaction of the delocalized π-bonds of each molecule defines the electronic and optical properties of the film.

There is a question whether such planar molecules lie flat on the surface. This is known to be the case for phthalocyanines on various III–V surfaces (e.g. on the In-terminated (001) and (111) surfaces of InSb and InAs [6]). On disordered and rough surfaces CuPc molecules stand away from the surface [12]. Also a coverage-dependent orientation has been observed on InSb(111), where the molecules show an orientation away from the normal in the thicker film [11]. That issue is not directly addressed in this work.

The system studied here is that of tin–phthalocyanine films (SnPc) deposited on a GaAs(001)-1 $\times$ 6 surface, prepared by argon ion bombardment (AIB). Soft x-ray photoelectron spectroscopy (SXPS) provides a comprehensive monitor of the developing interface by probing both the chemical bonding and the resultant energetics (e.g. band offsets) of the interface. The results are compared with those of this molecule on other GaAs(001) surface types, as well as with the general scheme of organic/inorganic semiconductor interfaces [13].

2. Experimental details

The n-type GaAs(001) surface (Freiberger Compound Materials) was prepared by AIB (beam energy 500 eV, pressure 7×10^{-5} mbar and sample current 2.5 μA). After annealing at 500 °C, a 1$\times$6 low-energy electron diffraction (LEED) pattern was observed. The organic semiconductor thin films were deposited by OMBD using a Knudsen-type cell. Stable evaporation rates of 1 Å min^{-1} were obtained at pressures $<1 \times 10^{-9}$ mbar. The deposition rate was monitored using a quartz microbalance, assuming unity sticking factor. A 3 Å deposit is a nominal monolayer but such systems can be inaccurate by a factor of 2 in absolute terms.

The photoemission experiments were performed using soft x-ray photons at beamline 4.1 at the Synchrotron Radiation Source, (Daresbury Laboratories, UK) storage ring. Photoelectrons were collected using a hemispherical electron energy analyser (Scienta). A base pressure of 5×10^{-10} mbar was maintained during the photoemission measurements. All spectra were recorded at a photon energy of 105 eV. The Fermi level was referenced to that of a tantalum plate in contact with the sample.

3. Results and discussion

Figures 1–3 show As 3d, Ga 3d and Sn 4d core level spectra, respectively, for the clean surface and for five sequential deposits of SnPc. These spectra were fitted with a sum of Voigt functions and a background calculated with a Shirley-plus-polynomial model [14]. Spin–orbit splittings of 0.69, 0.44 and 1.05 eV [15, 16] were used for the As 3d, Ga 3d and Sn 4d respectively. The original data are shown by small circles, the dotted curves show the individual components and the solid curve gives the total contribution of the components. Spectra were fitted using a minimum number of components and a minimum number of parameters were allowed to vary. Final fitting parameters are shown in table 1.

The As 3d spectra are fitted with two components: the main component is assigned to the bulk (As-B) and the smaller component, shifted by 0.56 eV towards lower binding energy, is assigned to the surface (As-S). After the first deposition of SnPc, a shift of 0.11 eV towards lower binding energy is observed for the emission envelope, along with a broadening
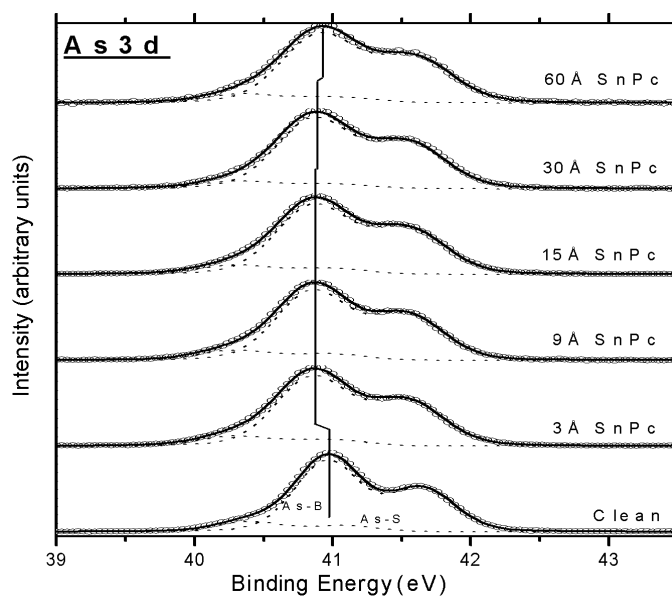
Figure 1. As 3d core level photoelectron emission spectra for the clean GaAs(001)-1 × 6 surface and for different coverages of SnPc. The small circles represent the measured data and the dotted curves represent the fitted components; one component is assigned to the bulk (As-B) and the other, shifted towards lower binding energy, to the surface (As-S). The solid curves represent the sum of the fitted components. All spectra are normalized to unity for better comparison. The photon energy is 105 eV.

Figure 2. Ga 3d core level photoelectron emission spectra for the clean GaAs (001)-1 ×6 surface and for different coverages of SnPc. The small circles represent the measured data and the dotted curves represent the fitted components; one component is assigned to the bulk (Ga-B) and the two others, shifted towards lower and higher binding energy, to the surface (Ga-S1 and Ga-S2, respectively). The solid curves represent the sum of the fitted components. All spectra are normalized to unity for better comparison. The photon energy is 105 eV.
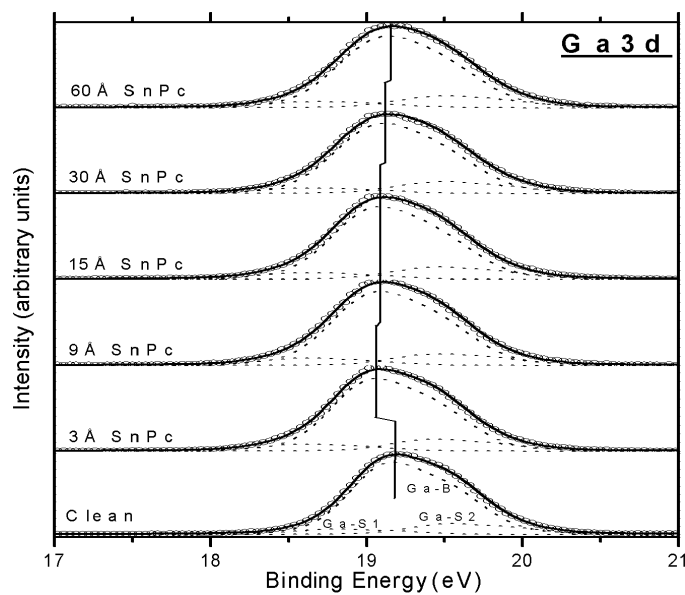
Figure 3. Sn 4d core level photoelectron emission spectra for different coverages of SnPc. The small circles represent the measured data and the dotted curves represent the fitted components; one component is assigned to the bulk (Sn-B) and the other, shifted towards higher binding energy, is unassigned (Sn-U). The solid curves represent the sum of the fitted components. All spectra are normalized to unity for better comparison. The photon energy is 105 eV.
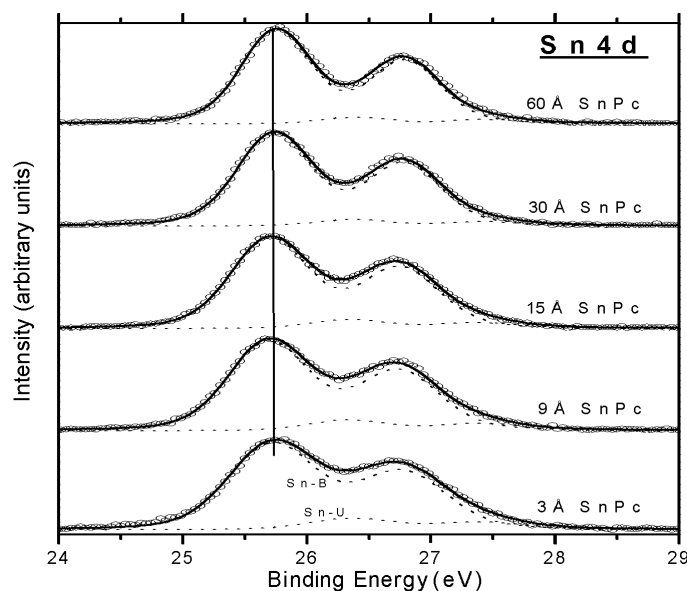
Table 1. Core level fitting parameters. (SOS: Spin orbit splitting, BE: binding energy, SCLC: surface core level components.)

		SOS (eV)	Branching ratio	Gaussian	Lorentzian	Bulk BE position (eV)	BE shift of SCLC (eV)
Ga 3d	Clean	0.44	0.6	0.48	0.13	19.11	−0.38/+0.35
	3 Å SnPc	0.44	0.6	0.50	0.13	19.00	−0.46/+0.38
	9 Å SnPc	0.44	0.6	0.54	0.13	19.01	−0.47/+0.37
	15 Å SnPc	0.44	0.6	0.54	0.13	19.01	−0.46/+0.38
	30 Å SnPc	0.44	0.6	0.55	0.13	19.03	−0.46/+0.38
	60 Å SnPc	0.44	0.6	0.56	0.13	19.05	−0.46/+0.37
As 3d	Clean	0.69	0.6	0.51	0.1	40.96	−0.56
	3 Å SnPc	0.69	0.64	0.56	0.11	40.85	−0.56
	9 Å SnPc	0.69	0.64	0.56	0.11	40.85	−0.56
	15 Å SnPc	0.69	0.64	0.58	0.11	40.85	−0.56
	30 Å SnPc	0.69	0.64	0.58	0.11	40.86	−0.55
	60 Å SnPc	0.69	0.64	0.59	0.11	40.90	−0.56
Sn 4d	3 Å SnPc	1.05	0.67	0.73	0.2	25.72	+0.64
	9 Å SnPc	1.05	0.67	0.66	0.2	25.69	+0.64
	15 Å SnPc	1.05	0.67	0.64	0.2	25.70	+0.64
	30 Å SnPc	1.05	0.67	0.60	0.2	25.73	+0.64
	60 Å SnPc	1.05	0.67	0.56	0.2	25.75	+0.64

of the main peak. This broadening slightly increases upon further depositions. The position of the surface component and its relative intensity do not change with respect to the bulk peak throughout the depositions.

The Ga 3d spectra are fitted with three components: the main component is assigned to the bulk (Ga-B) and the two smaller components are assigned to the surface; the Ga-S1 component is shifted by -0.38 eV (i.e. towards lower binding energy) and the Ga-S2 component is shifted by $+0.35$ eV (i.e. towards higher binding energy). As observed for the As 3d core level, the Ga 3d emission envelope shifts by 0.11 eV towards lower binding energy after the first deposition of SnPc. A broadening of the same order accumulates throughout the deposition range. The position and the relative intensity of the surface component Ga-S2 remain constant upon deposition with respect to the bulk. By contrast, after the *first* deposition of SnPc the position of the surface Ga-S1 has increased to -0.46 eV. The position and the relative intensity of this feature remain unchanged for further deposition. The relative intensity ratio of the S1:S2 components is approximately 1:2.

The Sn 4d spectra are fitted with two components: the main component is attributed to the 'bulk' phthalocyanine (Sn-B); the second component shifted by 0.64 eV towards higher binding energy is unassigned (Sn-U). With increasing coverage the spectra sharpen and no shift of these components is observed. The relative intensity of the higher binding energy component with respect to the bulk decreases as the thickness of the film increases, suggesting that this component is associated with the interface. However, a shift of similar magnitude is observed upon deliberate beam damage of this molecule and therefore the origin of this component cannot be uniquely established [17].

The core level fitting affords three areas of discussion. The first area is the clean surface. The spectra are free of gross satellite structures, such as surface oxides or metallic gallium. The components of the fits presented here are very similar to those of Larive *et al* [15] but these components have not been assigned within any model structure. It is not the intention of this paper to attempt such a definitive assignment. Rather, we wish only to comment on how possible model assignments compare with the data. The 1 × 6 surface is sometimes described in the literature as 2 × 6 and a general structure involves missing As dimers. For example, Biegelsen *et al* [18] have proposed a model consisting of two As dimers and four missing As dimers stacked along the ×6 direction. The net effect is that a 2 × 6 cell has four As dimer-atoms and four Ga dimer-atoms in the next layer (described as a trench); moreover, the four As dimer-atoms are bonded to six Ga atoms, of which four have non-bulk environments. This model is not wholly consistent with the fitting: the single As-S component is assigned to As dimer-atoms while the Ga-S1 and Ga-S2 components are assigned to either of the four Ga dimer-atoms and the four non-bulk Ga atoms beneath the As dimers. We have no *a priori* argument for which is which; moreover, the ratio of 1:1 is discouraging. A potentially better assignment derives from the model of Chizhov *et al* [19] which retains the trench but suggests a more complicated arrangement between the trenches; in this structure the Ga dimer-atom to Ga non-bulk atom ratio is closer to the fit ratio of 1:2, which would suggest that Ga-S1 is to be associated with the Ga dimer-atoms in the trench.

The second area of discussion of core level spectra is the effect of the first deposit of SnPc. The overall shift of Ga and As envelopes to lower binding energy can be attributed to an initial reduction in band bending of 0.11 eV (this parameter enters into the calculation of interface energetics below, but only via the final deposit value of 0.06 eV). The other effect of the first deposit is the change in relative binding energy of the Ga-S1 component. This suggests that the SnPc overlayer interacts, albeit weakly, with the Ga dimers of the Chizov model; indeed, the 'interaction' could simply be a change in relaxation of the core hole. Assuming the model is correct, these molecules would reside in the trenches formed by the missing dimers. Indeed, the SnPc molecule would fit comfortably into this trench. However, the data are also subject to other interpretations. Overall, there is no evidence in this spectroscopy of strong interaction between the molecule and the substrate.
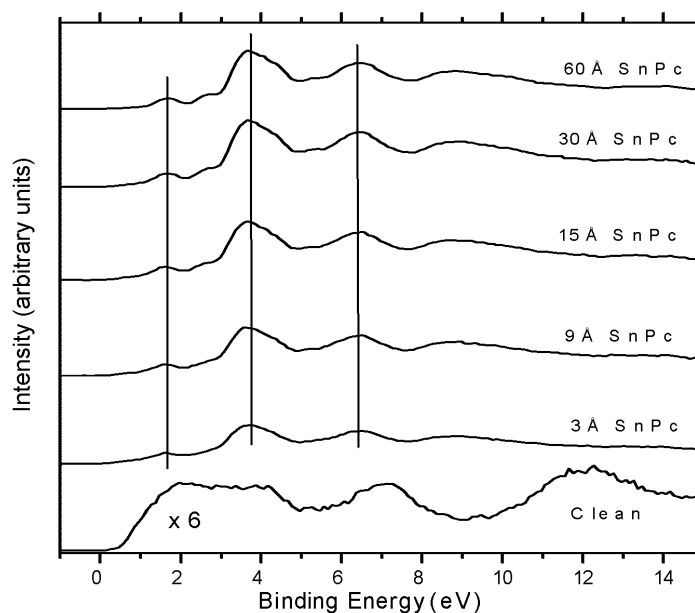
Figure 4. Valence band photoelectron emission spectra for the clean GaAs(001)-1 × 6 surface (multiplied six times) and with different coverages of SnPc. Spectra are normalized to the incident photon flux. The photon energy is 105 eV.

The third area of discussion of core level spectra concerns the nature of the adlayer. From the intensity–decay profiles of the Ga 3d and As 3d envelopes it is clear that the growth mode is not layer-by-layer. Upon the first deposit of 3 Å, the intensity of substrate emission is reduced to about 20%; thereafter, the reduction is considerably slower. The natural explanation is islanding. Moreover, the strong reduction in substrate emission by the first deposit seems to indicate that this deposit is more than one monolayer, which connects with the discussion above about the fraction of a monolayer that might prefer to reside in the trench. Overall, the growth mode is closer to Stranski–Krastanov. Evidence that the growth mode is dependent on both growth rate and post-deposition time has been presented for CuPc on InSb(111) surfaces [20]. The data suggest that a near edge x-ray absorption fine structure (NEXAFS) study of this system would be useful.

Photoemission spectra of the valence band of the clean surface and after successive depositions of SnPc are shown in figure 4. The spectrum for the clean surface is multiplied six times for comparison. The Fermi level is pinned below mid-gap on the clean surface. The valence band maximum of the clean surface as determined by the extrapolation of the valence band emission is 0.46 ± 0.04 eV below E_F; the ionization energy of the clean surface (the distance from the valence band maximum to the vacuum level) is 4.58 eV.

After the first deposition, the orbital features of the organic molecule are already very clear. The only discernible change with coverage is a small narrowing of features. The highest occupied molecular orbital (HOMO) edge as determined by extrapolation is 0.97 ± 0.04 eV below E_F. In order to determine the interface band offset, it is necessary to know the position of the GaAs valence band maximum at the interface. This is assumed to be the value at the clean surface (0.46 eV) plus the amount by which the band bending is reduced in the final coverage (0.06 eV), i.e. a value of 0.52 eV. The interface band offset (the separation of the valence band maximum and the HOMO edge) is therefore $0.97 - 0.52 = 0.45 \pm 0.08$ eV.
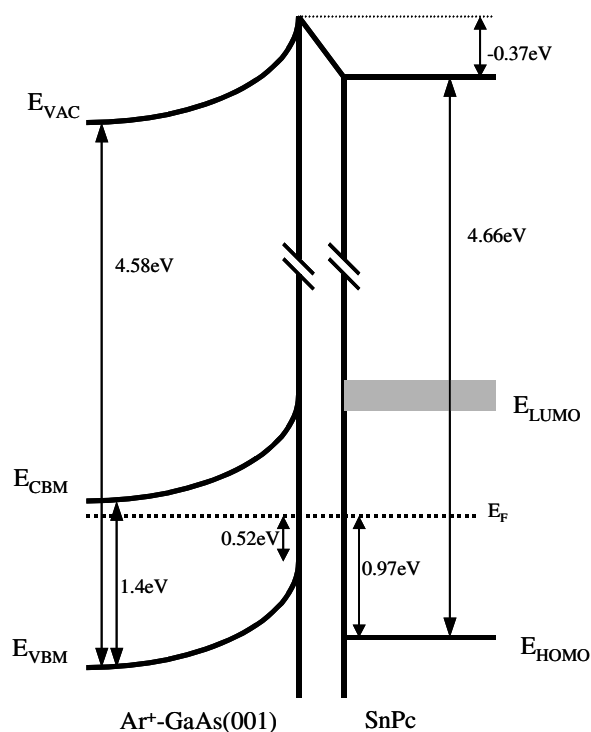
Figure 5. Energy band alignment of the SnPc–GaAs(001)-1 × 6 heterojunction. The upper and lower limits of the hatched region marked LUMO are derived from the transport and optical gaps respectively.

The ionization energy of the 60 Å layer deposit is 4.66 eV, whereas that of the clean GaAs substrate is 4.58 eV. Assuming the latter is unchanged by the adsorption, these values together with the interface band offset determined above imply an interface dipole of -0.37 ± 0.08 eV. The interface energetics are illustrated in figure 5. The existence of an interface dipole indicates that the vacuum alignment rule does not apply. In a recent study of perylenetetracarboxylic dianhydride (PTCDA) on various GaAs surfaces, Zahn *et al* [21] have noted that the driving force for such dipoles seems to be the difference in electron affinity. This approach focuses on the relative position of the GaAs conduction band edge at the interface (E_{CBM}) and the lowest unoccupied molecular orbital (LUMO) of the organic. The electron affinity of the GaAs substrate is closely approximated by subtracting the bandgap of 1.42 eV from the measured ionization potential; the electron affinity of the organic is less tractable. Subtracting the optical gap of 1.7 eV from the measured ionization potential yields the lower bound of the hatched region in figure 5. However, it is estimated that the transport gap is some 0.6 eV larger than the optical gap and this results in the upper bound of the hatched region. As shown in figure 5, E_{CBM} at the interface lies within this hatched region, which suggests that electron affinity difference may indeed determine the interface dipole of this system [22]. However, a more systematic study of organic/inorganic interface energetics is required to consolidate this observation into a general rule.

4. Conclusions

The first conclusion is that the interaction between the organic adlayer and the GaAs(001)-1 × 6 surface is very weak. The overall envelopes of substrate emission exhibit small shifts which can

be attributed to reduced band bending. Deposition-induced broadening of substrate core level features is of the same order, which can be attributed to inhomogeneous band bending. The additional small shift of the low binding energy Ga-S1 component may reflect some interaction with the first molecular layer but again this seems weak. These changes apart, the lineshapes of the As 3d and the Ga 3d core level spectra remain very similar throughout the coverage range; the valence spectra of the various deposits exhibit the same molecular features.

Secondly, the growth mode is not layer-by-layer, but is closer to Stranski–Krastanov; this might also reflect a coverage-dependent reorientation; clearly a structural technique such as NEXAFS would be useful in this regard.

Thirdly, the energetics of the interface have been established; there is a significant valence band offset of 0.45 ± 0.08 eV and an interface dipole of -0.37 ± 0.08 eV. The vacuum alignment rule does not stand for this organic/inorganic semiconductor heterojunction, confirming previous studies [4, 21, 23]. The interface dipole is broadly consistent with the difference in electron affinity of the organic and inorganic semiconductors.

Finally, an attempt to relate the results of surface/interface core level shifts to an initial adsorption geometry is, at best, indicative, being dependent both on relatively small experimental effects and considerable assumptions about the nature of the 1×6 surface. A scanning tunnelling microscopy (STM) study of the SnPc/GaAs(001)-1×6 system is planned.

Acknowledgments

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