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Copper Phthalocyanine on InSb(111)A – interface bonding, growth mode and energy band alignment

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Abstract

The growth of the organic semiconductor CuPc on the InSb(111)A surface at 300 K has been studied using Photoelectron Spectroscopy. Core level emission data obtained using low energy synchrotron radiation reveal that the interface is abrupt with very weak bonding between the InSb surface atoms and the adsorbed molecules. The coverage-dependence of the substrate and overlayer core level peak intensities follows the prediction of a uniform growth mode at high growth rates, but the organic film follows a Stranski-Krastanov growth mode at lower growth rates. C1s and N1s photoelectron emission data obtained with Mg K α radiation confirm that the CuPc molecules are intact within the layer, and shake-up satellites associated with benzene and pyrrole C and N peaks provide an insight into the energy and spatial distribution of the highest occupied and lowest unoccupied molecular orbitals. Photoelectron emission from the occupied bonding states of the CuPc and the valence band states of InSb provides the band offset for the filled states and the overall energy band profile for this organic-inorganic heterojunction. The presence of an interface dipole at the interface disproves a simple band alignment based on the vacuum level; the energy bands have a nested arrangement where both band edges in the InSb lie within the HOMO-LUMO gap of the CuPc.

1. Introduction

The semiconducting properties of metal phthalocyanines have been known and studied for many years [1], and they are now widely used in organic optoelectronic devices. For example, CuPc acts as contacting and protecting material for both the hole and electron transport layers in organic LEDs [2]. Phthalocyanines have also been used as the light-sensitive material in organic solar cells [3], and organic thin films have been used to decrease the operating voltage of high-frequency III-V Schottky diodes [4]. These applications depend crucially on the conductivity of the organic molecular material, on photon absorption/emission and on charge transport across semiconductor-semiconductor and semiconductor-metal interfaces. These in turn are dependent on intermolecular and interlayer bonding, molecular structure and interface energetics (i.e. energy band alignment and band bending). In spite of the widespread use of these materials, many of the fundamental processes are poorly understood, and there is a considerable theoretical and experimental effort currently underway to address each of the key issues. Photoelectron Emission Spectroscopy (PES) has been shown to be a powerful probe of both interface bonding and energetics at specific interfaces and is most usefully applied in-situ to monitor the development of the interface as an organic thin film is grown on a known substrate surface (usually an inorganic semiconductor, glass or metal) or on another organic material in a multilayer system. In some cases, the technique can also provide structural information, but this is usually obtained from a complementary technique such as low energy electron diffraction (LEED) applied in parallel.

The properties of the interface and the organic film for many systems have been found to be sensitive to both the substrate surface preparation and the growth conditions. For example, the orientation of phthalocyanine molecules is dependent on the substrate order, with a flat-lying geometry on ordered substrates and a more upright geometry on disordered substrates [5]. The energy band profile of organic-inorganic interfaces is also very sensitive to the preparation of

the surface, as illustrated by the very different band offsets for phthalocyanines on clean and S-terminated GaAs(001) surfaces [6,7]. Ordered growth of weakly-bonded molecular films on III-V semiconductors often requires passivation of the surface [8], but this is not the case for In-containing materials such as InSb and InAs. CuPc has been shown to form ordered layers on both the (111) and (001) surfaces of InSb [9] and the CuPc/InSb(111) heterojunction has therefore been chosen in the present PES study as a model organic-inorganic interface.

2. Experimental

The photon sources used to probe the evolving organic/inorganic interfaces were a laboratory-based Mg K α source (for X-ray Photoelectron Spectroscopy (XPS)) and synchrotron radiation at the Berlin electron storage ring, BESSY (for Soft X-ray Photoelectron Spectroscopy (SXPS)). Photoemitted electrons were collected in both cases by hemispherical electron energy analysers in ultrahigh vacuum (UHV). The InSb(111)A surfaces were prepared by several cycles of Ar ion sputtering and annealing in UHV. Low energy (500 eV) Ar ions were incident at an angle of 45° to the surface, with the InSb kept at a temperature of 250°C. Following the sputtering stages, a final heating to 400°C was needed to achieve a 2×2 reconstructed surface. The chemical composition of the surface was monitored by core level XPS and SXPS and its structure by LEED. The organic semiconductor CuPc (Aldrich Ltd) was purified by repeated evaporation/condensation cycles in vacuo and the purified material was thermally evaporated from a Knudsen cell at temperatures of around 400°C to produce thin films on the InSb surface. The thickness of the organic layers was estimated by a quartz crystal oscillator placed close to the sample. Core and valence level XPS and SXPS data were collected during the growth of the organic film to monitor the bonding, morphology and energetics. The InSb was kept at room temperature throughout.

3. Results and discussion

3.1. The InSb(111)A surface

The chemical and structural integrity of the InSb(111)A surface was confirmed by monitoring the substrate XPS core level lineshapes and the diffraction pattern in LEED as the oxidised surface layer was sequentially removed by Ar ion sputter/anneal cycles. A satisfactory surface is obtained when the C1s and O1s peaks are at the limit of detection of the technique and the substrate core level peaks (Sb3d, In3d, Sb4d and In4d) are indicative of pure InSb. The binding energies of In and Sb electron levels in InSb are lower than in the oxide film and this results in well-separated XPS emission peaks as shown for the Sb3d level in Fig. 1a. The two distinct doublets correspond to emission from the substrate InSb and, at 2.7 eV lower kinetic energy (higher binding energy), from the surface oxide layer. Following the sputter/anneal cycles, all traces of the oxide are removed, leaving only the substrate InSb doublet (Fig. 1b). The absence of further components confirms that the stoichiometry of the substrate remains intact. The In3d photoelectron emission data (not shown) confirm the complete removal of the surface oxide.

The clean surfaces of III-V semiconductors are known to undergo significant surface reconstruction and in many cases this leads to significantly different binding energies for the surface atoms compared to the sub-surface bulk atoms. This ability to identify the surface species provides a way of identifying local bonding when the surface is modified by, for example, the adsorption of organic molecules. Strongly-bonded adsorbates can change the electron binding energies in surface atoms, in principle identifying their adsorption site. Conversely, weakly-bonded or physisorbed molecules can be identified by the absence of changes in the surface core level electron binding energies. However, it is not always possible to distinguish between surface and bulk atom contributions to XPS data due to the limitations of surface sensitivity and energy resolution. This can be overcome by using synchrotron

radiation with a photon energy low enough to ensure emission of electrons close to the minimum of the electron escape depth curve (for surface sensitivity) but high enough to photoexcite electrons from the shallower substrate 4d core levels.

The photoelectron emission spectra for the In4d and Sb4d core levels in InSb are shown in Figs 2 and 3 respectively for the clean (111)A surface and for that surface completely covered by a thin film of CuPc. The data have been normalised to equal height for clarity but have not been otherwise modified. The fitting procedure was governed by the principle of using the least number of peaks with physically sensible fit parameters, and in this way it was found that the In4d data of Fig. 2 required a minimum of four peaks while the Sb4d data of Fig. 3 required only two. The spin-orbit splitting for these two core levels (1.25 eV for the Sb4d, and 0.86 eV for the In4d) is larger than the peak broadening, and so the split peaks are well-resolved in the SXPS data. The data were therefore fitted using double peaks linked by the expected relative intensity ratio predicted for these spin-orbit split pairs. Since the intrinsic broadening and experimental broadening have similar values, Voigt functions were used to model the data, and a least-squares minimisation resulted in the fitted curves shown as the solid lines through the data points in Figs 2 and 3. The residuals are shown beneath each curve, and these reflect the quality of the fitted curves.

The most commonly accepted model for the InSb(111)A surface is the In vacancy buckling model [10] where the In-deficient surface layer atoms are sp_2 bonded with the sub-surface Sb atoms to form a new surface layer with filled s-type dangling bonds on the Sb atoms and empty p_z dangling bonds on the In atoms. The two doublet components necessary to fit the In4d data (Fig 2a) are separated by 0.25 eV and this is consistent with this model as proposed in previous studies, where the lower kinetic energy contribution is derived from the surface In atoms [11]. Although the surface Sb atoms are also predicted in the model to have a different bonding environment to the bulk atoms, only a single doublet is necessary to fit the Sb4d data

of Fig 3. This is a common observation for the anion core levels in the reconstructed (111)A surface of other III-V semiconductors (GaAs [12], InAs [11]) where a similar model has been proposed. Surface core level shifts are a complex combination of competing contributions and it is possible in this case that these are nearly balanced.

3.2. Interface and molecular bonding

During the growth of the CuPc film, there is remarkably little change in the lineshape of any substrate core level peak, including the surface-sensitive In4d and Sb4d spectra obtained in SXPS measurements (Figs 2,3). All core level emission peak intensities are however attenuated by CuPc adsorption at room temperature. Both In4d and Sb4d core level lineshapes are largely unchanged as the CuPc film grows, and the spectra for the CuPc-covered surface can be fitted with the clean surface parameters apart from a slightly increased gaussian broadening term for the In4d spectra (Fig 2b) and a slightly decreased gaussian broadening for the Sb4d spectra (Fig 3b). The unchanging In4d surface/bulk intensity ratio in particular is an indication of the absence of strong molecule-surface bonding – the InSb surface appears to be intact under a complete coverage by the CuPc film, and the interface is abrupt at the atomic level. The corresponding CuPc / InSb(001) interface is similarly inert and abrupt [6].

The bonding within the molecular overlayer is revealed in the C1s and N1s core level emission spectra obtained with a higher photon energy in XPS studies (Figs 4, 5). Due to the reduced surface sensitivity and photon flux, it is not possible to extract unambiguous lineshape information at sub-ML coverages, but the data obtained for thin films (~nm coverage) suggest that the CuPc molecules within the films are intact.

The carbon C1s spectrum (Fig. 4) appears similar to previously published data [13,14] and is composed of a minimum of four peaks. The two most intense peaks correspond to carbon atoms in the outer benzene rings and the inner pyrrole group. The other two peaks are

generated by shake-up processes associated with each of the main excitations. Only one main peak is evident in the corresponding N1s spectrum (Fig 5) although this again has an associated shake-up satellite at lower kinetic energy. A fitting procedure is clearly needed to extract the energy positions and relative intensities of these peaks, especially for the C1s data. Each component in the spectra of Figs 4 and 5 is shown along with the resultant fit curve, (solid line through the data points). For both spectra, the fitting parameters used are consistent with other studies on similar phthalocyanine molecules [15]. The relative positions of the C-C and C-N components in the C1s emission spectra (1.23eV) and their related shake-up satellites (1.8 eV and 2.1 eV respectively) are also consistent with these previous studies. The difference in energy shift between the two shake-up satellites suggest that different molecular orbitals may be involved in the internal transition and this in turn reflects the spatial distribution of the orbitals on the relatively large CuPc molecule. Interestingly, the shake-up energies observed are close to the lowest energy peaks in optical absorption measurements performed using spectroscopic ellipsometry on bulk CuPc. Both processes involve $\pi-\pi^*$ transitions in the molecules, but the excitation processes are very different in both the excitation energy (visible vs. x-ray photons) and the photoelectron/core hole generation in XPS.

In a theoretical study for free base phthalocyanine [16], the strongest absorption bands are assigned to $\pi-\pi^*$ excitations, and the origin of the lower absorption bands are assigned to occupied molecular π -orbitals that are located at different sites on the molecule. Although the energy shifts are not correctly predicted, this model offers a qualitative explanation for the different shakeup shifts for the C1s and N1s emission peaks.

The relative intensity of the shake-up and core level peaks is also very different for each component and this again may be linked to the spatial distribution of the molecular orbitals. The C-C shake-up peak reaches 16% of the C-C peak intensity and the C-N shake-up reaches

25% of the C-N peak intensity. This suggests that there is a higher combined density of states in the centre of the molecule than at its arms. Furthermore, since the N-C shake-up in the N1s spectra has a lower relative intensity (8%), it appears that the shake-up processes are more likely to occur near C sites than N sites. The ratio of C-N to C-C carbon atoms in the CuPc molecule is 3:1. When the total intensity of the C-C and associated shake-up peaks is compared with that for the C-N peak and its associated shake-up satellite, the ratio is close to this expected value. This adds confidence to the fitting procedure and indicates that the molecule retains its integrity during the evaporation and adsorption processes.

3.3. Structure and Morphology

LEED studies on this interface [9] have shown that the first layer of molecules is ordered, but the surfaces of thicker films did not appear to be ordered. The diffraction pattern for the ordered monolayer was interpreted as a hexagonal CuPc structure commensurate with the substrate InSb lattice where the molecules are adsorbed on specific surface sites. However, more recent STM measurements suggest that the molecules may arrange in multi-domain square lattices with point-on-line symmetry [17]. Beyond the initial ordered phase, there is evidence that the molecules within the evolving CuPc film have a preferred orientation even though LEED studies do not reveal any structural order on the growing surface. Using polarised laser radiation, Raman spectroscopy studies have suggested that the CuPc molecules are oriented away from the surface towards the normal, tending towards a bulk CuPc arrangement within the thicker films [18].

The morphology of the organic film is also an important parameter in the design of organic semiconductor structures and the intensity variation of the XPS and SXPS core level peaks can be used to determine the growth mode of the film. It is important to know, for example, if the growth is uniform (or layer-by-layer) or strongly clustered. For uniform growth, the

substrate core levels are expected to follow a simple exponential decrease in intensity, and a similar exponential expression can also be used to model the intensity increase of the overlayer core level peaks. Under certain growth conditions, such a simple exponential dependence of peak intensity on CuPc film thickness is observed, although the model requires some modification for the C1s intensity to allow for non-Pc carbon at very low coverages. This uniform growth mode is observed with the InSb substrate at 300 K and for relatively high growth rates of ~1 nm/min. At lower growth rates the film growth tends towards island formation in a Stranski-Krastanov growth mode. There is also some evidence that the clustering continues over time after the film has been grown.

Results of the modelling procedure for uniform film growth are illustrated for selected core levels in Fig 6. The normalised In3d core level peak intensities, when plotted as a function of CuPc film thickness, are seen to follow an exponential attenuation (the dashed line represents a least-squares fit to the data). The model function used for the fit yields the electron escape depth within the CuPc layer at energies corresponding to the kinetic energies of these In3d photoelectrons (around 1.45 nm at 800 eV). Also shown in Fig. 6 is the increase in C1s and N1s intensities over the same film thickness range, and again the data follow the predicted curve (shown dashed), albeit with a larger scatter. The electron mean free path at these higher energies is greater (around 1.55 nm), and these values have a rather larger associated error.

When this procedure is carried out for all available substrate and overlayer core levels, it is possible to derive the energy dependence of the mean free path, λ , over a wide range of XPS energies. The measured energy-dependence is shown in Fig 7, and a least-squares fitting to the data using the relationship $\lambda = aE^b$ [19], yields the dashed line shown. The value of b has been variously proposed to lie in the range 0.5 - 0.7 [19,20] and the measured value of 0.51 is in agreement with the lower end of these predictions [19].

3.4. Electronic states and energy band alignment

The excitation of electrons from states near the Fermi energy provides a further insight into substrate-molecule and intra-molecular bonding. In SXPS experiments, the photon energy is sufficiently large that the emission spectra reflect the density of filled valence states but sufficiently low that the cross-section for the C- and N- derived molecular orbitals are reasonable. The photoelectron emission spectra in this energy range recorded during the growth of CuPc on InSb(111)A are shown in Fig 8 (central panel). Three main features are evident for the clean InSb(111)A surface (top) consistent with the valence electronic states for this III-V semiconductor excited by an incident photon energy of 65 eV. For a relatively thick CuPc film (100 nm), there are five main features corresponding to the lowest binding energy molecular orbitals (labelled A-E in Fig 8). These molecular orbitals are evident even at sub-monolayer coverages, indicating that the surface is rapidly covered by the adsorbed CuPc molecules. There are no obvious additional features at the lowest coverages and so these data are broadly supportive of the weak interfacial bonding inferred from the core level data.

Several studies, both experimental and theoretical, have addressed the origin of the observed peaks in the photoemission spectra of many phthalocyanines and related molecules. The data of Fig 8 are consistent with an experimental study on bulk phthalocyanines where emission peaks with binding energies up to 20 eV have been observed [21]. Three peaks between 10eV and 20 eV (not shown in Fig 8) have been compared with solid benzene and these peaks were ascribed to the outer benzene rings of the phthalocyanine molecule. The lower binding energy peaks B, C, D and E, were identified as being of predominantly C2p and N2p character, while the lowest energy peak, A, was identified as a π -type molecular orbital with strong contributions from the C2p orbitals of carbon atoms situated next to nitrogen atoms on the macrocycle. Optical transitions occur near the HOMO, and so peak A is the most important in this respect. Calculated energy levels for metal phthalocyanines vary considerably [22,23] and

can hence only provide only a rough guide to the character of the CuPc molecular orbitals. The role of the Cu 3d and 4s states is also unclear in these studies. The metal valence states can however be identified in the SXPS data using two independent approaches. The energy-dependence of the photo-ionisation cross-section for the Cu3d states is very different from the outer C and N states and so the relative intensity of Cu3d features in the valence band spectra will vary significantly with changing photon energy. Peak C is found to increase relative to peaks B, D, and E as the photon energy is increased and hence this is identified as containing a significant contribution from the Cu3d states. The second approach has been to compare the valence band spectra of phthalocyanines containing different central metal atoms (CuPc and SnPc [24]). Peaks B, D and E are well-matched but peak C is significantly larger for CuPc. There is also some evidence of an increased intensity in the vicinity of the smaller peak, A. The binding energies of these copper features correspond to those of Cu3d and Cu4s in metallic Cu; this has some resonance with one theoretical study on molecular CuPc [23] and similar values have been reported for Cu orbitals in porphyrazine compounds [25].

The final, and very important, piece of information that can be extracted from PES data for the evolution of these organic-inorganic heterojunctions, is the energy band profile. Since the filled electronic states are directly measured, the valence band offset emerges readily. The highest occupied states are shown in detail in the right-hand panel of Fig 8 for the clean InSb surface (top) through to the surface of a thick CuPc film (bottom). Also shown is the system Fermi level, E_f . Due to the width of the peaks and the limited energy resolution, the value taken for the valence band edge requires careful consideration. In this study, the valence band edge is taken as the extrapolation of the leading edge of the peaks on to the extrapolated background. The band edge of CuPc is clearly further from the Fermi level than that of InSb and this suggests a significant band offset for this junction. The true valence band offset is obtained from the measured offset by including any additional band-bending shifts. In this

case, there are no shifts in either of the substrate core level peaks or in any of the valence band peaks and hence there is no band-bending on either side of the interface as the CuPc layer is grown. The measured band offset is thus the true offset and has a value of (0.80 ± 0.14) eV. This value is similar to that reported for CuPc / InSb(001) heterojunction [6].

In order to complete the energy band profile, the ionisation energies of the InSb and CuPc are required, and these can be directly determined if the low energy onset of the electron distribution curve is recorded along with the high energy valence band edge. These are shown in the left hand panel of Fig 8 for a range of CuPc coverage over which the onset changes. A negative bias was applied to the sample during these measurements in order to overcome the mismatch between analyser and sample work function and reduced analyser sensitivity at low energies. The ionisation energies measured for various InSb surfaces were found to vary between 4.79 eV and 4.94 eV with the clean InSb(111)A surface at the lower end. These are in agreement with previously reported values [26,27]. The measured ionisation energy for CuPc (5.35 eV) is slightly higher than reported elsewhere [28,29]; a small variation is likely since there is a considerable variation in morphology and molecular structure for CuPc films grown on different substrate under different growth conditions. The measured ionisation energies and band offset can then be combined to construct the energy band diagram for this hybrid heterojunction as shown in Fig 9. The vacuum levels are not aligned at the interface and this means that there is a dipole potential at the interface, with a value of (0.24 ± 0.14) eV. Interface dipoles are commonly inferred for a range of interfaces involving organic semiconductors. For certain metal-organic interfaces (e.g. PTCDA, Alq₃ [30], α -NPD, H₂TPP, H₂T(4-Py) [31]), the interface dipole scales with the metal work function, although the slope varies from 0.2 (for Alq₃) to 1 (PTCDA). However, for other interfaces (e.g. CBP [30]), no work function dependence is observed. The work function dependence has been explained in terms of a polarisation of the first layer of organic molecules by the image potential at the

surface [31] but this is likely to be modified if the molecule-substrate bonding is very different. For CuPc interfaces with inorganic semiconductors, there appears to be little dependence of interface potential on work function or ionisation energy when the interface bonding is weak (e.g. for CuPc/S:GaAs(001) the interface dipole is around -0.3 eV [32]). However, the interface dipole at the CuPc/ITO interface, where there is chemical interaction, is very different (0.1 eV [33]).

The only unknown in the energy band profile is the position of the CuPc LUMO relative to the HOMO. This is shown as a shaded area in Fig 8, located at approximately the position predicted by the optical gap of CuPc (or the core level shake-up energies). However, it is known that the optical gap can be as much as 1 eV different to the transport gap in organic semiconductors due to the localised nature of the Frenkel exciton formed by optical excitation, and so other techniques (such as Inverse Photoelectron Spectroscopy) are needed to determine the true position of the LUMO. Nevertheless, since the transport gap is larger than the optical gap, the general profile of the CuPc/InSb interface will be unchanged – it is a nested interface with a barrier for both electrons and holes on the InSb side of the heterojunction.

4. Conclusions

When the organic semiconductor CuPc is grown on the InSb(111)A surface at 300 K with a growth rate of 1 nm/min, a uniform film is obtained as inferred from the attenuation of the substrate photoelectron emission peaks. Lineshape analysis of surface sensitive core level emission data reveals that the interface is abrupt with very weak bonding between the InSb surface atoms and the adsorbed molecules. The first molecular layer is ordered, but the surface of the growing CuPc film beyond this coverage is not ordered, although the molecules within the film have a preferred orientation with respect to the surface. From a physical and

chemical viewpoint therefore, the CuPc/InSb(111)A interface is a simple, model organic-inorganic interface. C1s and N1s photoelectron emission data confirm that the CuPc molecules are intact within the layer, and the shake-up satellites associated with benzene and pyrrole C and N peaks provide an insight into the energy and spatial distribution of the highest occupied and lowest unoccupied molecular orbitals. The deeper-lying occupied levels of the CuPc are co-incident in energy with the valence band states of InSb and the evolution of these states provides the band offset for the filled states and the overall energy band profile for this organic-inorganic heterojunction. The presence of an interface dipole at the interface disproves a simple band alignment based on the vacuum level, and the energy bands have a nested arrangement where both band edges in the InSb lie within the HOMO-LUMO gap of the CuPc.

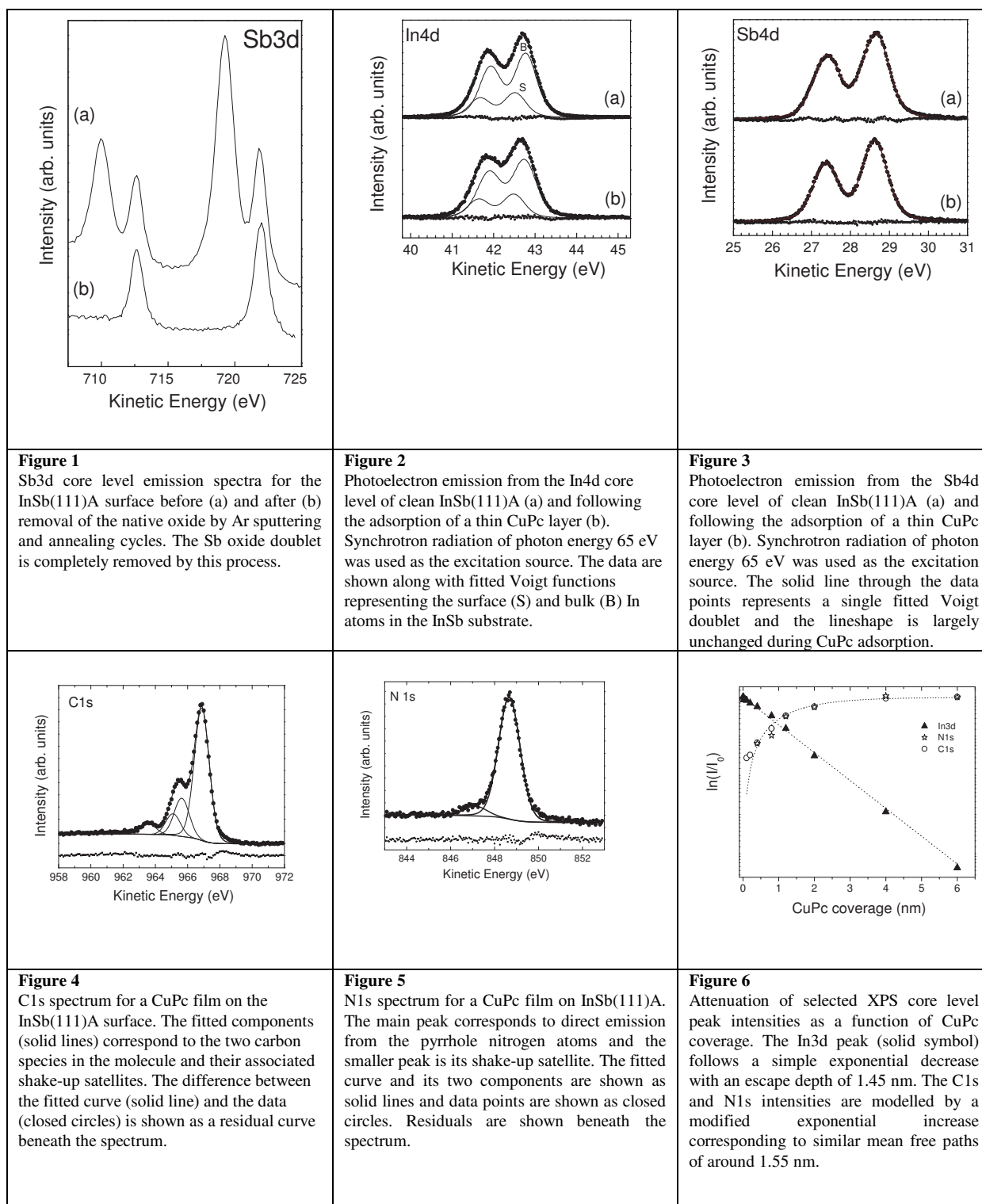
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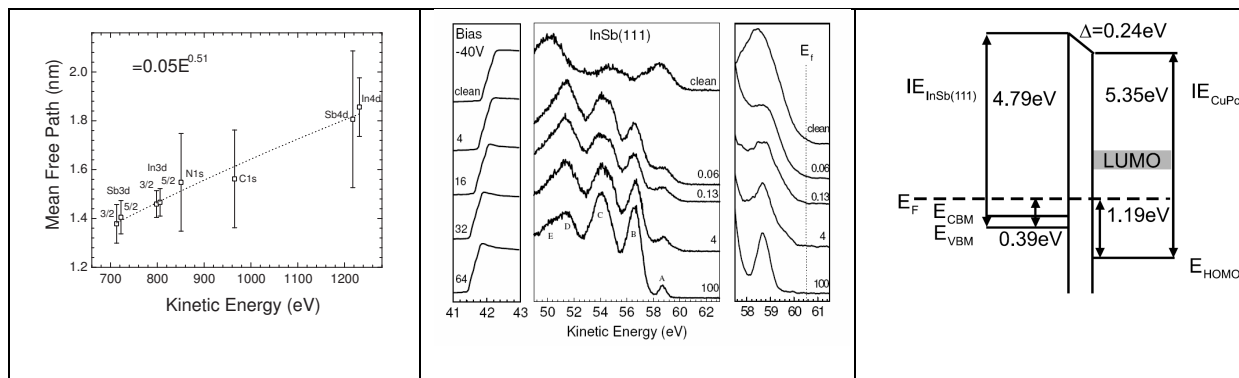


Figure 7 Energy-dependence of electron mean free path in a CuPc film on the InSb(111)A surface. The dashed line represents a least squares fit to the data points, and the fit parameters shown are in agreement with predicted values for these XPS energies.

Figure 8 Photoelectron emission spectra for the valence band region of the InSb(111)A surface and following the growth of a CuPc film. The film thickness is shown in nm for each spectrum. In the main panel, the CuPc molecular states (A-E) are evident even at the lowest coverages. The interface energetics are determined from the band edges shown in the right hand panel and the secondary electron onsets shown in the left hand panel.

Figure 9 Energy band profile for the CuPc/InSb(111)A interface. The heterojunction has a nested configuration and a small dipole is present at the interface.