Available online at www.sciencedirect.com

SCIENCE DIRECT®

Nuclear Instruments and Methods in Physics Research B 199 (2003) 475–480

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Synchrotron radiation studies of inorganic–organic semiconductor interfaces

D.A. Evans [a,*], H.J. Steiner [a], A.R. Vearey-Roberts [a], A. Bushell [a], G. Cabailh [b], S. O'Brien [b], J.W. Wells [b], I.T. McGovern [b], V.R. Dhanak [c,d], T.U. Kampen [e], D.R.T. Zahn [e], D. Batchelor [f]

[a] *Department of Physics, University of Wales, Aberystwyth SY23 3BZ, UK*
[b] *Physics Department, Trinity College, Dublin 2, Ireland*
[c] *Surface Science Research Centre, University of Liverpool, L693BX, UK*
[d] *CLRC Daresbury Laboratory, Warrington WA4 4AD, UK*
[e] *Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany*
[f] *BESSY GmbH, Albert-Einstein-Straße 15, D-12489 Berlin, Germany*

Abstract

Organic semiconductors (polymers and small molecules) are widely used in electronic and optoelectronic technologies. Many devices are based on multilayer structures where interfaces play a central role in device performance and where inorganic semiconductor models are inadequate. Synchrotron radiation techniques such as photoelectron spectroscopy (PES), near-edge X-ray absorption fine structure (NEXAFS) and X-ray standing wave spectroscopy (XSW) provide a powerful means of probing the structural, electronic and chemical properties of these interfaces. The surface-specificity of these techniques allows key properties to be monitored as the heterostructure is fabricated. This methodology has been directed at the growth of hybrid organic–inorganic semiconductor interfaces involving copper phthalocyanine as the model organic material and InSb and GaAs as the model inorganic semiconductor substrates. Core level PES has revealed that these interfaces are abrupt and chemically inert due to the weak bonding between the molecules and the inorganic semiconductor. NEXAFS studies have shown that there is a preferred orientation of the molecules within the organic semiconductor layers. The valence band offsets for the heterojunctions have been directly measured using valence level PES and were found to be very different for copper phthalocyanine on InSb and GaAs (0.7 and −0.3 eV respectively) although an interface dipole is present in both cases.

1. Introduction

The exploitation of the semiconducting nature of organic molecules in thin film form has been remarkable in recent years. However, the precise relationship between molecular and electronic structure and device performance is still poorly understood and there is a healthy interest in studying model systems based on both polymers and small molecules. It is accepted that no one experimental technique can cover the entire size range from molecule to device while also providing complementary structural, optical and electronic

---

[*] Corresponding author. Tel.: +44-1970-622803; fax: +44-1970-622826.
E-mail address: a.evans@aber.ac.uk (D.A. Evans).

0168-583X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0168-583X(02)01595-1

information. A combination of techniques is thus essential and synchrotron radiation methods are among the most powerful available probes. In the field of small organic molecule structures, many studies of the fundamental properties have adopted an approach using surface science techniques during the in situ growth of the key interfaces [1–9].

In such studies, two main types of molecules have emerged as prototypes – perylene derivatives (in particular perylene tetracarboxylic dianhydride, PTCDA) [1–4] and metal phthalocyanines [5–9]. These molecules can form highly ordered structures even though the chemical bonding between the molecules and the substrate is generally weak. The energy band profiles reveal band offsets and interface dipoles which cannot be predicted using simple models, and the organic film can modify the surface density of states on the substrate. Synchrotron radiation photoelectron spectroscopy (PES) in the VUV-soft X-ray regime has been extensively applied to monitor the interface bonding and band alignment in the growth of all-inorganic heterojunctions, and this approach can be applied with equal success to hybrid organic–inorganic interfaces. It appears that these systems are in many cases more ideal than the corresponding inorganic junctions where there is often an interfacial layer [10].

In order to relate changes in electronic states and bonding to structural and morphological changes, other complementary techniques are required. However, it is possible to apply other synchrotron radiation techniques to obtain this missing information; for example, the technique of X-ray standing wave spectroscopy (XSW) can discriminate between competing structural models, and has been successfully applied to adsorbates on low-index faces of inorganic semiconductors [11]. Since many of the small organic molecules used are planar, a further synchrotron radiation technique is increasingly used to monitor the structure of the organic film. Near-edge X-ray absorption spectroscopy (NEXAFS) uses the polarisation of the synchrotron beam to probe the orientation of the organic molecule relative to the substrate surface [3,7].

The model systems chosen here to illustrate the use of these techniques in the study of inorganic–organic interfaces are copper phthalocyanine (CuPc) films on the (0 0 1) faces of the inorganic semiconductors InSb and GaAs. Phthalocyanines and PTCDA have been shown to form initially ordered layers on GaAs(0 0 1) only if the surface is passivated by chalcogen atoms prior to exposure to the organic molecules [1,2]. However, both molecules have been shown to form ordered layers on the In-terminated (0 0 1) and (1 1 1) surfaces of InSb and InAs [8,9]. The orientation of the molecules is also strongly dependent on the substrate preparation. CuPc appears to lie flat on ordered surfaces but stands on end on disordered surfaces [7]. The organic molecules can also show a coverage-dependent orientation – CuPc which initially adsorbs as an ordered layer on InSb(1 1 1) shows an orientation away from normal in the thicker film [6]. Inorganic–organic interfaces have a well-defined band offset and often a large interface dipole; for example, the dipole at the CuPc–InSb(1 1 1) interface is comparable to the valence band offset (0.5 and 0.7 eV respectively) [6].

Since it appears that the organic molecules require passivated GaAs but unpassivated InSb surfaces for ordered growth, these two substrates provide a useful comparison for organic thin film growth. This study compares the adsorption of CuPc on the narrow gap InSb(0 0 1) surface and the wider gap S-passivated GaAs(0 0 1) surfaces using synchrotron radiation techniques combined with low energy electron diffraction (LEED) to provide a parallel probe of composition, electron density of states, Fermi level position and structure.

2. Experimental

The growth of organic thin films and the preparation of the III–V semiconductor surfaces were performed in situ at the SRS and BESSY storage rings. PES experiments were performed using low energy photons (50–200 eV) at beamline 4.1 at the SRS and photoelectrons were collected at normal emission using a hemispherical electron energy analyser (Scienta). NEXAFS experiments were performed at beamline PM1 at the BESSY II synchrotron radiation facility and photoelectrons were collected in partial yield mode using a range of substrate-beam geometries.

In all experiments, the organic semiconductor thin films were prepared by thermal evaporation from Knudsen cells in ultrahigh vacuum (UHV). Stable evaporation rates of ~0.1 nm min^{-1} were obtained at pressures $<1 \times 10^{-9}$ mbar. The InSb(0 0 1) surfaces were prepared by cycles of Ar ion sputtering and annealing at 400 °C; the structural integrity was monitored using LEED and the chemical composition by XPS. The GaAs(0 0 1) surfaces were prepared by chemical etching of n-type wafers (Freiberger Compound Materials) using dilute S_2Cl_2 and rinsing in tetrachloroethene. The 2 × 1 reconstructed surface was obtained by annealing to 400 °C in UHV.

3. Results and discussion

The In4d and Sb4d core level spectra shown in Fig. 1 illustrate the use of synchrotron radiation PES to monitor interface bonding. These shallow core level electrons were photoexcited from the near-surface region of the clean InSb(0 0 1) surface (Fig. 1(a)) and the CuPc-covered surface (Fig. 1(b)) using soft X-rays of photon energy 65 eV. The Sb 4d and In 4d emission spectra are resolved into spin-orbit split doublets, and a single component for each spectrum yields a satisfactory fit (solid lines) through the data points. The InSb(0 0 1) surface prepared by Ar-ion sputtering and annealing yields a characteristic c(8 × 2) LEED pattern corresponding to the In-terminated surface [8,13]. Although the surface involves In dimerisation, only a single binding energy component is needed to fit both In 4d and Sb 4d spectra [13]. Following the growth of a 1.2 nm CuPc overlayer, both core levels are attenuated to 37% of their original intensity, but there is little change in lineshape apart from a slight increase in the overall broadening (Fig. 1(b)). This remarkable observation reflects the weak bonding at the interface between the inorganic and organic layers, and suggests that this interface is abrupt at the molecular level. Furthermore, there is no shift of either peak following CuPc adsorption, and this suggests that the Fermi level remains near the conduction band minimum for this n-type material.

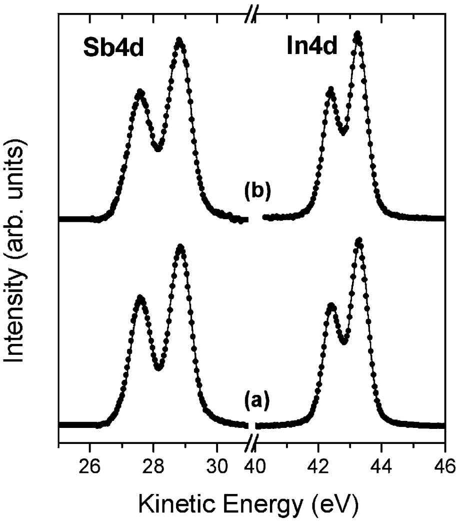

Fig. 1. Photoelectron emission spectra from the Sb4d and In4d core levels of the clean InSb(0 0 1) c(8 × 2) surface (a) and the same surface covered with a 1.2 nm CuPc film (b). The points represent the measured data and the solid lines are a least-squares fit using spin-orbit split doublets generated using Voigt functions. Apart from some broadening, there is little change in either core level spectrum indicating a weak interfacial bonding. Photon energy = 65 eV.

The situation is rather different for the adsorption of CuPc on the S-terminated GaAs(0 0 1) surface (Fig. 2). In this case, the surface, prepared by chemical etching and subsequent heating in UHV, shows a 2 × 1 LEED pattern, and there is less consensus on the precise composition and structure of the surface. Most studies suggest dimerisation as the driving force, but there is less agreement on the composition of the dimers [12,14,15]. Previous synchrotron radiation PES studies suggest that the surface region is largely composed of S and Ga atoms and that there are at least two chemically distinct S sites and at least one non-bulk Ga site [12]. S-incorporation into the GaAs lattice is possible, and other structural techniques are needed to investigate this further. In a study of the S-terminated InP(0 0 1) surface by XSW, it has been shown that a simple S–S dimer model is not consistent with the data, and it appears that, although the S atoms appear to be located at P lattice sites, there is more than one

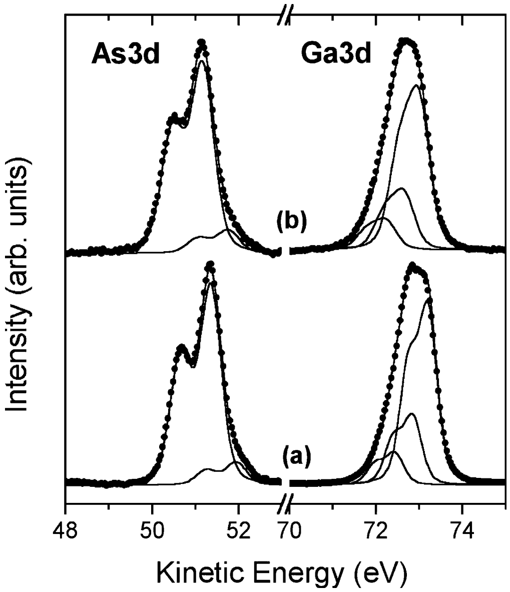

Fig. 2. Photoelectron emission spectra from the As3d and Ga3d core levels of the S:GaAs(0 0 1) (2 × 1) surface (a) and the same surface covered with a 0.5 nm CuPc film (b). The points represent the measured data and the solid lines are a least-squares fit using spin-orbit split doublets generated using Voigt functions. The low kinetic energy components of the Ga3d spectrum correspond to the surface Ga atoms and there is little change on CuPc adsorption. Photon energy = 97 eV.

S site, and again sub-surface S incorporation is suggested [11].

The As 3d component shown in Fig. 1(a) is dominated by the bulk GaAs component, although a low-intensity component at higher kinetic energy is also present. The intensity of this peak depends on the precise processing steps, and is often absent for S:GaAs 2 × 1 surfaces. These surface As atoms are not believed to play a role in the surface reconstruction [12]. The Ga 3d emission peak is very different to the clean GaAs(0 0 1) surface in that there is a significant low kinetic energy contribution from surface and near-surface Ga atoms. These lower kinetic energy components are related to S–Ga bonds [12] and any changes in the surface bonding during the adsorption of the organic material might be expected to affect these Ga components most strongly. However, as can be seen in Fig. 2(b), there is little change in the relative intensities and positions of the various components although there is an increase in the overall broadening and a large decrease in the absolute intensities as the GaAs substrate is covered by a uniform layer of CuPc. It therefore appears that the bonding between the organic layer and the GaAs(0 0 1) substrate is again weak as observed for the CuPc–InSb(0 0 1) interface. However there is, in this case, a shift of both As and Ga core levels to lower kinetic energy as the surface is covered with CuPc. This movement is due to a shift of the GaAs band edges with respect to the Fermi level. Even though the interfacial bonding is weak, the CuPc adsorption modifies the surface state distribution and with that the charge in the surface states. Since the surface charge in the surface states implies a compensating space charge, changes in the surface state distribution result in changes of the relative Fermi level position.

Although the PES technique yields chemical and electronic information, it is less sensitive to the structural changes occurring as the organic overlayer is grown. The molecular orientation within the CuPc layer is revealed using NEXAFS spectroscopy to probe the C 1s absorption edge as shown in Fig. 3. The orientation dependence of the CuPc molecule in a thick film on S-GaAs(0 0 1) is reflected in the different relative intensity of the near-edge features at different collection angles. The peaks closest to the absorption edge correspond to π–π^* resonances in the CuPc molecules and these have a maximum intensity when the polarisation vector is parallel to the pi-orbitals, which are perpendicular to the molecular plane in CuPc. The strong variation with angle in the intensity of these peaks is evidence for a preferred orientation of the molecules away from the surface plane. This is in contrast to the adsorption of PTCDA on the S:GaAs(0 0 1) surface, where the molecules prefer to lie parallel to the surface [2]. CuPc molecules have been reported to adopt a flat-lying structure on ordered substrates, and a more upright structure on disordered substrates [7], so the upright CuPc molecules on the ordered S:GaAs(2 × 1) surface appear not to follow this general trend.

Having established that the atomic integrity of the substrate inorganic surface remains intact on CuPc adsorption and that the organic material

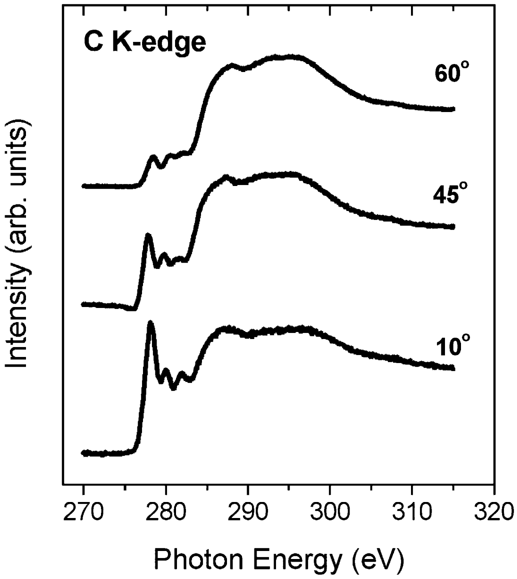

Fig. 3. C K-edge NEXAFS spectra corresponding to a thick CuPc film grown on the S:GaAs(0 0 1) (2 × 1) surface. The strong angle-dependence of the near-edge π–π^* resonances indicate a preferred orientation of the CuPc molecules away from the surface plane.

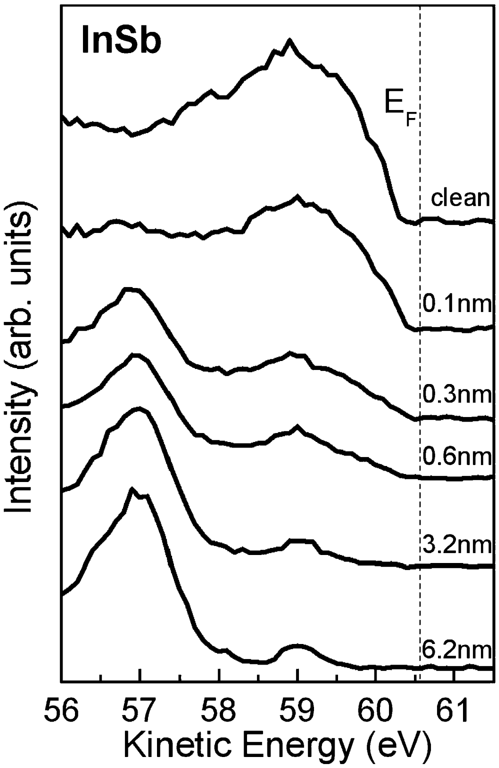

Fig. 4. Valence band photoemission spectra for the clean InSb(0 0 1) c(8 × 2)surface and following selected CuPc coverages. The valence band edge of the clean InSb is clearly defined and the CuPc band edge is defined by the HOMO peak that is apparent above 0.6 nm. Photon energy = 65 eV.

forms a uniform film on these surfaces, it is then possible to probe the nature of the bonding states and the energy band line-up by direct measurement of the valence band photoelectron spectra. For InSb, the valence band maximum is observed at 0.2 eV below the Fermi level as shown in the upper spectrum in Fig. 4. As the CuPc overlayer is grown, the spectrum becomes dominated by the organic molecular levels and the highest occupied molecular orbitals (HOMO) that define the valence band maximum for the organic semiconductor films become established above 0.6 nm. There are no shifts in any of the CuPc levels as the film grows and this confirms that there is no charging or band-bending in the organic layer. From the measurement of the InSb and CuPc valence band maxima, the valence band offset for this hybrid heterojunction is found to be 0.7 eV. This value corresponds to straddled interface (type I heterojunction) with almost equal offset in the valence and conduction band of CuPc. It is also possible using PES to obtain a further parameter for these interfaces – the interface dipole. It has become apparent in recent years that large energy differences can be present at organic heterojunctions, and by measuring the work function changes (via the secondary electron onset for a biased sample) these values can also be obtained. For the InSb(0 0 1)–CuPc system, an interface dipole is indeed suggested and the value is comparable to the valence band offset.

The corresponding development of the valence band emission spectra for the S:GaAs(0 0 1)–CuPc interface, is shown in Fig. 5 and shows many similarities. The clean surface valence band maximum is well-defined and the CuPc HOMO becomes clear at coverages above 0.8 nm allowing the valence band maximum for the organic semiconductor to be measured. However, in this case, there is a significant band bending shift in the substrate levels and a shift in the CuPc levels.

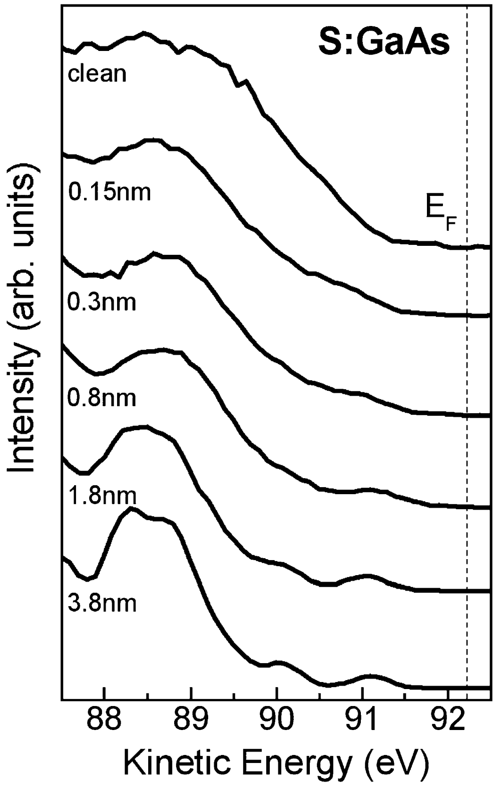

Fig. 5. Valence band photoemission spectra for the S:GaAs(0 0 1) (2 × 1) surface and following selected CuPc coverages. Spectra have been corrected for band-bending shifts. Photon energy = 97 eV.

These shifts have been subtracted from the data of Fig. 5 to reveal a valence band offset of −0.3 eV which corresponds to a staggered heterojunction (type II heterojunction).

4. Conclusions

Synchrotron techniques applied in parallel provide a powerful probe of the key features of inorganic–organic semiconductor heterojunctions. Molecular-scale information regarding the structure, electronic structure and chemical bonding can be obtained along with parameters such as the heterojunction band offset, band bending and interface dipole. Such studies on the InSb–CuPc interface in particular have shown this interface to be a model system with weak interfacial bonding, an abrupt interface, no band-bending and a well-defined valence band offset and interface dipole. CuPc adsorbs as a uniform layer on the S:GaAs surface with a negative valence band offset.

Acknowledgements

The authors would like to thank the staff of the SRS and BESSY facilities for their ready assistance and A.A. Cafolla for the core level data analysis software. This work was supported by the EU-LSI programme and the EPSRC (GR/M67414), and was performed within the EU DIODE network (HPRN-CT-1999-00164).

References

[1] Y. Hirose, S.R. Forrest, A. Kahn, Appl. Phys. Lett. 66 (8) (1995) 944.
[2] S. Park, T.U. Kampen, D.R.T. Zahn, W. Braun, Appl. Phys. Lett. 76 (22) (2000) 3200.
[3] S. Park, T.U. Kampen, T. Kachel, P. Bressler, W. Braun, D.R.T. Zahn, Appl. Surf. Sci. 90 (2002) 376.
[4] I.G. Hill, A. Kahn, J. Appl. Phys. 85 (1999) 2116.
[5] T. Chasse, C.-I. Wu, I.G. Hill, A. Kahn, J. Appl. Phys. 85 (1999) 6589.
[6] D.A. Evans, H.J. Steiner, R. Middleton, T.S. Jones, H. Chen, K. Horn, S. Park, T.H. Kampen, D. Tenne, D.R.T. Zahn, A. Patchett, I.T. McGovern, Appl. Surf. Sci. 175–176 (2001) 374.
[7] H. Peisert, T. Schweiger, J.M. Auerhammer, M. Knupfer, M.S. Golden, J. Fink, P.R. Bressler, M. Mast, J. Appl. Phys. 90 (2001) 466.
[8] J.J. Cox, S.M. Bayliss, T.S. Jones, Surf. Sci. 425 (1999) 326.
[9] J.J. Cox, T.S. Jones, Surf. Sci. 457 (2000) 311.
[10] G. Neuhold, K. Horn, K.O. Magnusson, D.A. Evans, J. Vac. Sci. Technol. A 13 (1995) 666.
[11] I.T. McGovern, A. Koebbel, A. Leslie, E. Dudzik, C.E.J. Mitchell, A.B. McLean, A. Patchett, D.R.T. Zahn, D.A. Evans, D.P. Woodruff, B.C.C. Cowie, Appl. Surf. Sci. 166 (2000) 196.
[12] D.N. Gnoth, D. Wolfframm, A. Patchett, S. Hohenecker, D.R.T. Zahn, A. Leslie, I.T. McGovern, D.A. Evans, Appl. Surf. Sci. 123–124 (1998) 120.
[13] P. John, T. Miller, T.-C. Chiang, Phys. Rev. B 39 (1989) 1730.
[14] C.J. Sandroff, M.S. Hedge, L.A. Farrow, C.C. Chang, J.P. Harbison, Appl. Phys. Lett. 54 (1989) 362.
[15] X. Wang, X. Hou, Inst. Phys. Conf. Ser. 1245 (1996) 267.