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In-situ monitoring of the growth of copper phthalocyanine films on InSb by organic molecular beam deposition

D.A. Evans[a,*], H.J. Steiner[a], R. Middleton[b], T.S. Jones[b], C.H. Chen[c], K. Horn[c], S. Park[d], T.U. Kampen[d], D. Tenne[d], D.R.T. Zahn[d], A. Patchett[e], I.T. McGovern[e]

[a]*Department of Physics, University of Wales, Aberystwyth SY23 3BZ, UK*
[b]*Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College, London SW7 2AY, UK*
[c]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany*
[d]*Technische Universität Chemnitz, D-09107 Chemnitz, Germany*
[e]*Physics Department, Trinity College, Dublin-2, Ireland*

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Abstract

Thin films of the organic semiconductor copper phthalocyanine (CuPc) have been grown on the InSb(1 1 1)A 2 × 2 surface by organic molecular beam deposition (OMBD). Soft X-ray photoelectron spectroscopy (SXPS) using synchrotron radiation, low energy electron diffraction (LEED) and Raman spectroscopy have been applied to monitor the bonding and energy band line-up at the CuPc–InSb interface. LEED shows that the first layer of CuPc is ordered. SXPS data reveal that the chemical interaction between the overlayer and the substrate is limited. The lineshapes of the shallow In and Sb core levels change very little during the growth of the CuPc film. Emission from the valence states of both InSb and CuPc was also monitored and the valence band offset for this hybrid system was determined to be (0.75 ± 0.14) eV. Raman spectroscopy confirms the limited interaction at the junction and further reveals that the structure of the CuPc film changes with increasing thickness.

Keywords: Phthalocyanine; Spectroscopy; Interface

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1. Introduction

Organic semiconductor thin films can be grown with single layer precision using organic molecular beam deposition (OMBD) in ultrahigh vacuum (UHV) and these structures have been used to fabricate a wide range of electronic and opto-electronic devices [1,2]. One important class of materials is the metal phthalocyanines (MPc's) which have been shown to form ordered ultrathin films on a range of substrates [3–6]. MPc's find application in organic LED's, solar cells and thin film transistors. This study concentrates on the growth of copper phthalocyanine (CuPc) films on InSb, a narrow-gap inorganic semiconductor. InSb is widely used in infra-red devices and quantum well structures where the InSb forms heterojunctions with wider gap materials such as CdTe [7,8]. Key questions in the use of such structures are the abruptness of the interface, the crystalline quality of the layers and the magnitude of the interface potential barrier. To address these issues, a range of complementary techniques are required and the surface science approach

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

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involves the monitoring of the growing heterojunction from the clean substrate surface to the thick film.

The (1 1 1)A surface of InSb has been shown to reconstruct by a rehybridisation of the surface bonds, and results in a structure with In-vacancies and a 2 × 2 periodicity [9]. In this study, low energy electron diffraction (LEED), soft-X-ray photoelectron spectroscopy (SXPS) and Raman spectroscopy are used to monitor the changes occurring during CuPc thin film growth on the InSb(1 1 1) surface. This combination allows the atomic and electronic structure to be probed in situ during the junction growth. In a previous LEED study of this system, it has been shown that the initial adsorption of CuPc results in an ordered layer and a $(\sqrt{12} \times \sqrt{12})R30^\circ$ structure [6]. A model for this ordered structure was proposed although it was not possible to identify precisely the specific adsorption site of the CuPc molecules. More detailed spectroscopic studies are required to understand the nature of the interaction between CuPc and InSb(1 1 1)A and to understand the development of thicker films. Recent studies have shown that other organic semiconductors adopt well-ordered structures on III–V semiconductor surfaces, although a passivating layer is usually required to eliminate dangling bonds and ensure ordered growth. Photoelectron spectroscopy studies have revealed that the weak van der Waals bonding between the organic molecules and the substrate leads to quasi-epitaxial growth [10,11]. Furthermore, when combined with valence band spectroscopy, such studies can also determine the energy band profile of the evolving heterojunction [12]. Using this combination of techniques, the junction formation can be monitored up to several layers of deposited material. For thicker films, however, other methods are needed, and the chosen technique in this study is Raman spectroscopy. This technique has been successfully applied to monitor the growth of a range of materials including organic semiconductors [3,7,13].

2. Experimental

In all experiments, the CuPc film was grown by OMBD using a well-outgassed, cooled Knudsen cell and the evaporation rate of the cell was calibrated by measuring the film thickness using a quartz microbalance over a range of cell temperatures. The semiconductor substrate (n-type, Te doped InSb, MCP Ltd.) was oriented to give an InSb (1 1 1)A surface, which was cleaned by a repeated sequence of Ar^+ sputtering and annealing. The clean surface yielded a clear 2 × 2 LEED pattern, and the surface was held at room temperature during growth and characterisation. The photoelectron spectroscopy experiments were performed at the TGM3 beamline of the BESSY storage ring using an incident photon energy of 65 eV. Photoelectrons were collected and energy analysed using a hemispherical analyser (VSW Ltd.) for both core and valence level emission. The Raman spectroscopy experiments were performed in a backscattering geometry using an Ar ion laser operating at a wavelength of 514.5 nm and the scattered light was detected using a multi-channel detector. Data were collected with the polarisation of the scattered light parallel (*xx*) and perpendicular (*xy*) to the polarisation of the incident light.

3. Results and discussion

An insight into the bonding between the deposited CuPc and the InSb substrate can be obtained by measuring the binding energy changes in the In 4d and Sb 4d core level emission spectra during thin film growth. Selected spectra are presented in Fig. 1.

The clean surface spectra are typical for the 2 × 2 reconstructed surface of InSb(1 1 1)A [10,14] in that at least two components are required to fit the In 4d data, while only one component is required for the Sb 4d data [9,14]. Due to the low value of the core level shift compared to the spin-orbit splitting, a curve-fitting procedure is needed to extract the two components in the In 4d spectra and details of the fitting procedure are described elsewhere [15,16]. The lower binding energy component is associated with In atoms in the surface bilayer, while the higher binding energy peak is derived from photoelectrons emitted from the In atoms in the bulk InSb. The striking observation here is that no further components are necessary for the spectra measured for InSb surfaces covered with CuPc. The overall intensity is reduced as the coverage increases but the relative intensity of the two In 4d core level components remains constant throughout. This intensity change along with evaporation cell calibration have been used to define monolayer

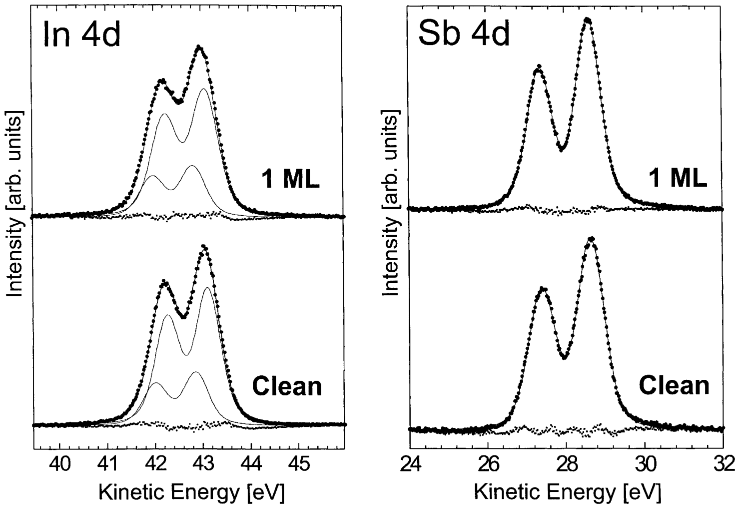

Fig. 1. In 4d and Sb 4d core level emission spectra for the clean InSb(1 1 1) surface and a surface covered by a nominal CuPc layer of 1 ML. Points represent data and solid lines represent fitted curves and fit components. Residuals are shown beneath each spectrum, and the spectra have been normalised to equal height for clarity.

(ML) coverage as the layer thickness corresponding to the intermolecular spacing in the bulk CuPc crystal (0.35 nm). The absence of large changes in the binding energy and relative intensity of the In 4d components suggests a weakly bound organic film which does not form strong chemical bonds with the surface. The Sb 4d emission spectra are also unperturbed, showing only an overall decrease in intensity as the film grows. There is however a small increase in the broadening of the In 4d components and a small decrease in the broadening of the Sb 4d component. LEED results show that the substrate lattice does influence the overlayer structure and this suggests that there must therefore be some degree of interaction between the substrate and CuPc molecules. At low coverage, the CuPc film forms an ordered layer to yield a commensurate ($\sqrt{12} \times \sqrt{12}$)R30° structure, but the diffraction pattern becomes diffuse at higher coverages, and is not present above 2 ML [6]. The difference in broadening of the core levels may indicate that the CuPc molecules have a preferred adsorption site on the surface.

The valence band emission spectra shown in Fig. 2 broadly support these conclusions, in that the low coverage spectra show features corresponding to both substrate and overlayer states. The clean surface is characteristic of the InSb valence density of states with a well-defined valence band maximum (VBM) near the Fermi-level, while the spectrum corresponding to a thick CuPc layer is dominated by the molecular π-orbitals [4,5]. Both InSb and CuPc features are apparent in intermediate spectra, and the absence of new features indicates a low level of intermixing of the valence states. There is however some overlap in the

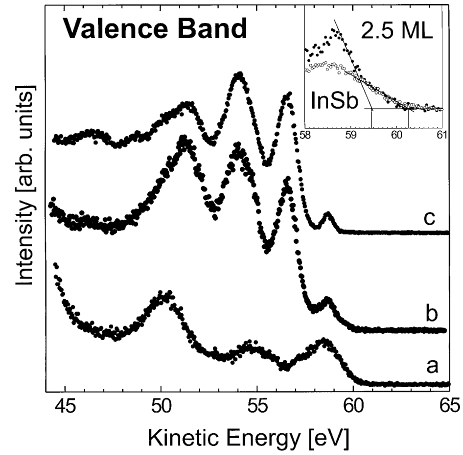

Fig. 2. Photoelectron emission spectra for the valence band of InSb (a); for 1 ML CuPc (b); and a thick CuPc film (c). The inset shows a close-up of the valence band maxima for the clean and CuPc covered surfaces.

states near the VBM and it is possible to identify both InSb and CuPc edges only at some intermediate coverages (inset of Fig. 2). The band offset is determined from the clean InSb VBM and the thick CuPc film, allowing for any spectral shifts due to, for example, band-bending and charging. Although, there is some fluctuation in the In 4d and Sb 4d peak positions during CuPc growth, both are consistently within 0.1 eV of the clean surface positions and this suggests that there is no significant band-bending on the InSb side of the junction. Small shifts of <0.1 eV in the CuPc valence features are also observed, but these are again within the accuracy of the measurements. It therefore appears that the bands are flat in both semiconductors near the heterojunction. The valence band offset is then given directly by the valence band maxima, and a value of (0.75 ± 0.14 eV) is obtained. Since the ionisation energies of CuPc and InSb are similar [15,16], the valence band offset might be supposed to be small. The relatively large value measured suggests that there must be an interface dipole at this junction to balance this offset. (The presence of a large interface dipole is not uncommon for such interfaces [15,16]). This results in a change in the surface workfunction which can be measured from the width of the electron distribution curve (EDC) as the overlayer is grown. For the growth of CuPc on InSb(1 1 1)A, a shift in the low energy onset of the EDC indicates that there is indeed a significant decrease in the workfunction as this hybrid heterojunction is grown [17].

Raman spectroscopy allows thicker overlayer films to be probed, although the technique is also sensitive to changes at the monolayer level. A typical spectrum for a thick (400 ML) CuPc film on InSb(1 1 1)A is shown in Fig. 3. A detailed discussion of all the spectral features is given elsewhere [18]. In this paper, however, only those features relevant to the structure of the CuPc film beyond monolayer coverage are discussed. The substrate LO and TO phonon modes (at 178 cm^{-1} and 188 cm^{-1} in Fig. 3) are not changed significantly during CuPc growth, in agreement with the SXPS results, which suggest that the interface is abrupt with the CuPc molecules weakly bonded to the substrate surface. The higher wave number peaks are associated with the vibrational modes of the CuPc molecules, and are consistent with studies of CuPc films on other substrates [3,13].

During the growth of the CuPc film, differences in the spectra recorded for low and high coverages suggest that there is a change in the overlayer structure during growth [18]. In a Raman study of CuPc on gold substrates Basova and Kolesov have proposed a method to distinguish between the α and β phases of CuPc using two polarisation arrangements [3]. Their data were collected with parallel and crossed polarisation as for the data in Fig. 3. The absence of the B_{2g} peak (at 1483 cm^{-1}) in their spectra was taken

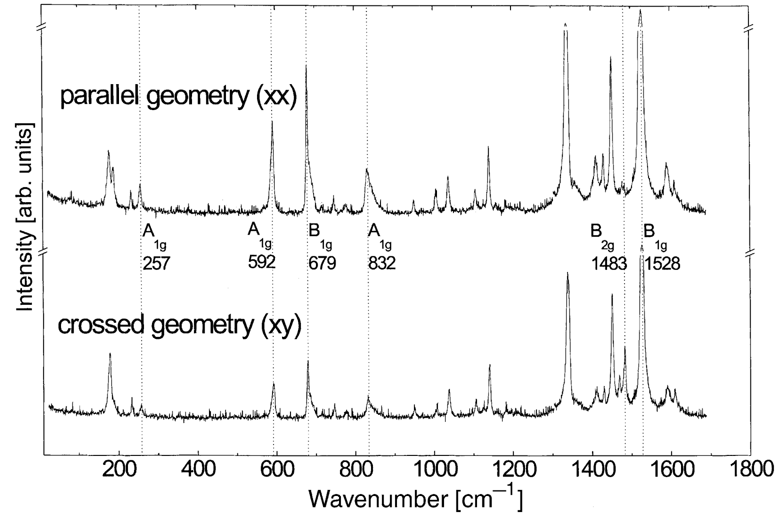

Fig. 3. Raman spectra for a 400 ML CuPc film recorded in parallel (*xx*) and perpendicular (*xy*) polarisation geometries.

as an indication of a distinct orientation of the CuPc molecules with respect to the substrate normal (*z*-axis). This peak is also absent in the data shown in the upper spectrum of Fig. 3 for the CuPc film grown on InSb(1 1 1)A. The identification of the two phases of CuPc is based mainly on the intensity ratios of spectral features under parallel polarisation (*xx*) and cross polarisation (*xy*) and the data of Fig. 3 reflect this difference in intensity. These data agree more closely with the presence of the β phase, although on other substrates this phase is generally formed only upon annealing [3]. The reasons for the observation of this phase at room temperature are not yet understood and additional studies are in progress to address the structural evolution of CuPc thin films on the InSb(1 1 1)A surface.

4. Conclusions

The formation of an ordered organic–inorganic interface has been demonstrated, in which the III–V semiconductor template does not require surface passivation before CuPc growth. The organic molecules initially form an ordered layer commensurate with the substrate surface mesh, although thicker films show features characteristic of the β phase where the molecules are oriented at around 45° to the substrate normal. Although, the chemical bonding at the interface is weak, there is evidence of mixing of the valence states. A valence band offset of $(0.75 \pm 0.14\,\text{eV})$ is measured for this hybrid heterojunction.

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