The electronic structure of pentacene revisited


Abstract

Recently, there have been reports of the valence band photoemission of pentacene films grown on various substrates with particular emphasis on the highest occupied molecular orbital (HOMO) and its dispersion. In various works, evidence for HOMO band dispersion as high as 0.5 eV, even for polycrystalline films, has been presented. In apparent contradiction to these results, we have previously reported a band dispersion of only 50 meV, measured on a well characterised film with a single polymorph and single crystalline orientation, 5A(0 2 2). Here, we first present the two-dimensional momentum distribution of the HOMO of a 5A(0 2 2) film. Then the development of the valence band spectra for films grown at room temperature and low temperature are compared, and we show that morphological aspects can lead to the apparent observation of high HOMO dispersion. Finally, with the aid of the two-dimensional momentum distribution of the HOMO, we show that a reasonably large dispersion (0.25 eV) does indeed exist in 5A(0 2 2).

Ultraviolet photoemission spectroscopy (UPS) has an important place in the study of organic films and their interfaces, not the least because of the pioneering work of K. Seki and W. Salanek which have emphasized the direct information it yields regarding the valence band all important to the opto-electronic properties of these materials. Here, with the example of pentacene, we illustrate some of the pitfalls in interpreting UPS and then demonstrate the capabilities of modern angle-resolved instrumentation. The electronic structure of pentacene (5A) has recently attracted considerable interest particularly because of the high mobilities reported in 5A thin films. Consequently, there have been reports of the valence band photoemission of films grown on various substrates with particular emphasis on the HOMO and its dispersion [1–6]. In various works, evidence for HOMO band dispersion as high as 0.5 eV, even for polycrystalline films, has been presented. Recently, we have reported the intra- and intermolecular band structure of 5A measured on a well characterised film with a single polymorph (the polymorph determined by Holmes et al. [7,8]) and single crystalline orientation, 5A(0 2 2). In these films, the intermolecular band width of the HOMO, in a direction perpendicular to the molecular axis, was shown to be surprisingly small (50 meV) [6], in apparent contradiction to the previously reported dispersions [1]. Here, we first present the momentum distribution of the HOMO of a 5A(0 2 2) film. Then the development of the valence band spectra for films grown at room temperature and low temperature are compared, and we show that morphological aspects can lead to the apparent observation of high HOMO dispersion. Finally, with the aid of momentum maps of the HOMO, we show that indeed a reasonably large dispersion in agreement with band structure calculations, does exist in 5A(0 2 2).

The pentacene films were grown and measured in situ in ultra high vacuum (UHV). The (2 × 1) oxygen reconstructed Cu(1 1 0) substrate surface was prepared by cleaning the copper crystal by repeated cycles of Ar+ bombardment and annealing at 800 K. The pentacene films were grown and measured in situ in ultra high vacuum (UHV). The (2 × 1) oxygen reconstructed Cu(1 1 0) substrate surface was prepared by cleaning the copper crystal by repeated cycles of Ar+ ion bombardment and annealing at 800 K. The clean crystal was exposed to 40 L (1 L = 1 × 10−6 Torr s) oxygen at 600 K. The pentacene (Fluka) was deposited in situ from a thoroughly degassed evaporator such that the pressure in the system remained in the 10−10 mbar range during film growth. Nominal growth rates of 2–5 Å min−1, as monitored by a quartz microbalance assuming a density of 1.33 g cm−3, were used. The geometric and electronic structure and the morphology of these films has been fully characterised with UV- and X-ray photoemission, X-ray absorption spectroscopy (NEXAFS), X-ray diffraction (XRD, both θ/2θ scans and pole figure analysis), low energy electron diffraction and reflectance difference spectroscopy. Unless otherwise stated, films were grown at 100 K and measured at room temperature (300 K).
The angle-resolved photoemission (ARUPS) experiments were performed both using a VG ADES 400 spectrometer and a toroidal electron analyser (TEA) described elsewhere [9]. Both systems had a base pressure of 10^{-10} mbar and basic sample preparation and characterisation facilities. The ADES system was equipped with a noble gas discharge lamp (unpolarised Helium I radiation, hv = 21.2 eV) and a moveable electron energy analyser, allowing angle-resolved ultraviolet photoelectron spectroscopy in the specular plane with an angular resolution of ±1° and a total energy resolution of 80 meV at room temperature. A photon incidence angle of α = 60° was used. The TEA system was connected to the TGM-4 beamline at the synchrotron radiation facility BESSY II. A photon energy of hν = 35 eV was used. The photon incidence angle was α = 40°, and the polarisation direction was always in the specular plane. For angular emission data converted to momentum k, the formula k = 0.51 (E_{kin})^{1/2} sin θ [Å^{-1}] was used. The experiments are compared with calculations based on first-principle density functional theory performed with the ABINIT package, a plane-wave based implementation of density functional theory for periodic systems [10].

By controlling the film morphology and molecular orientation during growth, a homogeneous thin film of uniaxially aligned molecules, a necessity for band structure determinations, was produced. Fig. 1 shows the 5A valence band (E(kx)) measured along the molecular long axis in the 5A(0 2 2) plane (c.f. Fig. 5, a model of a 5A(0 2 2) oriented crystal can be found in Ref. [6]). By using synchrotron radiation and a toroidal electron spectrometer for ARUPS, the electronic valance band structure could be measured up to a maximum kx value of k_{max} = 2.7 Å^{-1} and a binding energy E_B = -10.5 eV, where the deeper lying sigma orbitals were also included. The band maps obtained here are almost identical to those reported for 5A(0 2 2) films measured with unpolarised He I radiation [6]. It was found that the π band emissions were weakest for normal incidence and strongest for an incidence angle of 60°, indicating that the polarisation of importance is in the z direction, perpendicular to the surface and molecular axis. The π wave functions of 5A have weight either on linking (and end) carbon pairs or on the 10 outer (apex) carbon atoms of the molecule. The two molecular π-bands of pentacene, are referred to as the apex (containing the HOMO) and linking π-band and contain five and six orbitals, respectively. The apex π-band (orbital positions indicated by ×) starts at the Γ-point and runs up to the HOMO, with its orbital positions in energy and momentum being clearly discernible. Of the linking π-band (orbitals indicated by +) only the upper three orbitals can be easily distinguished, while the lower three are superimposed onto emissions from pentacene σ orbitals deeper than -5 eV binding energy.

From Fig. 1 the strength of the angular dependence of the photoemission data for pentacene becomes immediately apparent. For instance, in normal emission the 5A HOMO will be nearly invisible and HOMO-1 to -3 will be weak, whereas these orbitals are very distinct at higher off-normal angles. To illustrate how different the spectra can be at different experimental geometries, line scans at the Γ-point and k_0 = π/a (interring spacing a = 2.35 Å) are shown. Thus, in photoemission of molecular systems, it is important – even for simple valance band orbital “finger prints” – that different experimental geometries are investigated. This becomes particular crucial when mixed morphologies lead to a superposition of spectra offset from each other; e.g. by differences in screening, as we will show later.

In earlier work on single crystalline films of sexithiophene (6P) [11], sexithiophene (6T) [12] and pentacene [6], we have shown that the one-dimensional Fourier transforms (FT) of the π orbitals of an isolated molecule give a good description of their appearance in ARUPS both in terms of k, position, k width and relative intensities. For 6P, 6T and the linking π band of 5A, the FT gives an almost perfect agreement, while the orbitals of the apex band of 5A were found at a higher k value experimentally than in the FT. This is illustrated for the HOMO (top of the intra-molecular apex π band) in Fig. 2, which shows the photoemission intensity of the HOMO as a function of kx compared to a calculation of the intensity from a bulk 5A crystal and the one-dimensional Fourier transform of an isolated 5A molecule. Below, the HOMO orbital calculation is shown with the interring spacing of a = 2.35 Å.

Fig. 2. The experimental photoemission intensity behavior at E_F = -1.3 eV (center of HOMO emissions) as a function of momentum parallel to the molecular axis is compared to a calculation of the intensity from a bulk 5A crystal and the one-dimensional Fourier transform of an isolated 5A molecule. Below, the HOMO orbital calculation is shown with the interring spacing of a = 2.35 Å.

![Fig. 1. Photoemission energy versus momentum map obtained at 300 K from angular emission data of a 5A(0 2 2) oriented thin 5A film with angular emission in a plane with the molecular axis (see top schematic of Fig. 5). Dark areas represent high emission intensity. The two π bands are marked with × (apex band) and + (linking band). The Γ-point and k_0 = π/a (where a = 2.35 Å) are marked, and linescans at these k_0 values are shown on the right as spectra in full and dotted lines, respectively. The photon incidence angle was α = 40°.](image-url)
scans at constant energy were performed. In Fig. 3a, the two-dimensional \( k_x, k_y \)-plot of the 5A HOMO measured at a binding energy \( E_F = -1.3 \, \text{eV} \) (averaged over \( \pm 0.3 \, \text{eV} \)) is shown. The dominant features are two distinct maxima at \( k_y = \pm 1.2 \, \text{Å}^{-1} \) which extend in \( k_x \) to \( \pm 1 \, \text{Å}^{-1} \). In addition, four lesser maxima at \( k_x = \pm 1.2 \, \text{Å}^{-1} \) and \( k_y = \pm 2 \, \text{Å}^{-1} \) can be found. The measured HOMO distribution has been compared with the Fourier transforms of the HOMO calculated for two isolated molecules at the proper aromatic plane tilt angles (\( \pm 26^\circ \) with respect to the surface plane) expected for the 5A(022) oriented crystallites in Fig. 3b. The calculation in Fig. 3b assumes that the angular-dependent photocurrent is proportional to the Fourier transform of the initial state wave function which we take from a density functional calculation of an isolated pentacene molecule. The conservation of energy and parallel momentum components then implies that the photocurrent at constant kinetic energy is given by a hemispherical cut through this three-dimensional Fourier transform. Details of the calculation will be presented in a future publication [13]. The agreement with the experiment is very good with all features reproduced.

Our general experience is that films grown below room temperature yield better films than those grown at room temperature. Although at first thought this seems counterintuitive, we have seen in various experiments that lower substrate temperature lowers the molecular mobility without disturbing the ability of the substrate to dictate the molecular orientation and diffusion direction. Important for area averaging surface science techniques is that lower growth temperatures can lead to a higher nucleation density and, thus, minimization of the detrimental photoemission effects associated with severe islanding on the surface. Pentacene films grown on Cu(110)–(2 × 1)O held at low temperature (100 K) and room temperature (300 K) both result in uniaxially oriented pentacene 5A(022) for techniques such as reflectance difference spectroscopy [14], NEXAFS [15] and XRD [8]. In the following we consider the growth at 100 K and room temperature from the point of view of ARUPS and illustrate the problematic effects of different growth morphologies on the measurement of electronic structure.

The molecules were deposited step-wise while monitoring the workfunction via the secondary electron cut-off and the angle-resolved UPS along the Cu[001] azimuthal direction, i.e. in the direction of the long molecular axis, at both normal emission (\( \theta = 0^\circ \)) and at \( \theta = 50^\circ \). Fig. 4a and b summarise the growth of 5A films grown on Cu[110]–(2 × 1)O at 100 K and 300 K, respectively. The behaviour of the workfunction at both substrate temperatures was identical, with a sharp decrease from 4.8 eV to 4.4 eV completed by an exposure of 3.6 Å, beyond which no further changes were observed. The workfunction drop is due to the formation of an interface dipole, and its saturation point is indicative of the completion of the first monolayer. For both temperatures the ARUPS of the monolayers were identical. The HOMO emission of both monolayers has nearly no intensity at normal emission being only visible at high take-off angles in [001] as a peak at 1.1 eV below \( E_F \). Beyond the monolayer the different growth temperatures lead to very different spectral behaviours. The growth at 100 K is almost layer by layer with the strong substrate d-band features totally absent by 14 Å exposure. A rigid shift in the emission features by 0.3 eV to higher binding energy is seen in going from the monolayer to the thin multilayer. As there is no workfunction change, this shift is attributed to the differences in photohole screening between the monolayer and thin multilayer. Going to thick multilayers (330 Å) a further shift of 0.4 eV to high binding energy is observed. Associated with this shift is an energy broadening of all the emission features. Interestingly this shift and broadening is removed by annealing at room temperature (300 K), and the ARUPS becomes identical to that of the thin multilayer in all respects. This annealing effect was irreversible, and thus the 0.4 eV shift cannot be attributed to lower charge carrier mobility at 100 K. We thus suggest that this shift is a charging effect associated with crystalline defects in the thick films grown at 100 K, which are healed out on annealing at room temperature. For the growth at room temperature, little change from the monolayer spectra is evident even by a coverage of 55 Å; by \( \sim 100 \, \text{Å} \) of material, an apparent splitting of the HOMO is observed, and \( \sim 300 \, \text{Å} \) of material is required to obscure the substrate d-band emissions. The HOMO now appears as a broad feature that consists of two emissions separated by \( \sim 0.3 \, \text{eV} \). Such a broad squared off HOMO emission has often been reported in the literature and attributed to band dispersion of the HOMO. In this case, however, we argue that it is the result of severe islanding leading to the superposition of monolayer and multilayer HOMO emission.

In Fig. 5, the HOMO emission from the 330 Å film grown at room temperature for various experimental geometries is shown in detail. Measured in the [1–10] azimuthal direction, perpendicular to the molecules, the HOMO is weak at all take off angles, and a very small dispersion of \( \pm 50 \, \text{meV} \) is observed on close inspection. This behaviour is in agreement with the intermolecular dispersion reported for the low temperature grown 5A(022) [6]. In the [001] direction, parallel to the molecules the HOMO emission goes through a maxima at \( \theta \approx 35^\circ \), reflecting the effects of intramolecular dispersion [6] and confirming the orientation of the
Fig. 4. UPS spectra for subsequent coverages of 5Å on Cu(1 1 0)–(2 × 1)O held at (a) 100 K and (b) room temperature (300 K) for various electron emission angles $\theta$ and specular plane azimuthal orientations. The incident angle of the unpolarised He I radiation was $\alpha = 60^\circ$. The specular plane contained the [0 0 1] substrate azimuth.

molecular axis along this direction. Close inspection reveals that the HOMO emission is seen to consist of three peaks at 0.8, 1.1 and 1.4 eV below $E_F$ whose relative intensities vary with take-off angle. These peaks are very well expressed in the spectra recorded at $30^\circ$ from the [0 0 1] azimuth. The highest binding energy peak (at $E_B = -1.4$ eV) has the energy of the multilayer HOMO grown at low temperature and is attributed to emissions from three dimensional islands. The middle peak has an energy corresponding to the monolayer HOMO seen in Fig. 4a and b and is attributed to the monolayer. At most emission angles the low binding energy feature (at $E_B = -0.8$ eV) is a barely discernable shoulder, but at $35^\circ$ emission and $30^\circ$ off azimuth (and molecular axis) it is a prominent peak. It is also attributed to the monolayer HOMO and will be argued to arise from dispersion effects.

In Fig. 6 the behaviour in the energy region of the HOMO as a function of the azimuthal angle are shown for the pentacene monolayer, the multilayer grown at 100 K and the multilayer grown at room temperature. The results are presented for an electron take-off angle of $27^\circ$ and the $k$-space region thus investigated is indicated by the dashed curve in Fig. 3a. The only significant features in this region from the substrate are the O2p anti-bonding band, which lies at the top of the Cu d-band at binding energies beyond $\sim 1.4$ eV below the Fermi level and is visible only as a weak background. On the formation of the monolayer the HOMO appears as electron emissions oscillating in the region between 0.8 and 1.3 eV below $E_F$. This can be seen as a single peak with FWHM $\sim 0.2$ eV dispersing over 0.35 eV, at most. For the multilayer grown at 100 K and measured at room temperature, there is no evidence of the monolayer emission and the HOMO appears as a similarly oscillating feature at higher binding energy. The extent of the dispersion is significantly less than the monolayer at around 0.25 eV. For the multilayer grown
at room temperature, again, the HOMO is seen dispersing up from $\phi = 0\,^\circ$, however, the emissions are much more diffuse and spread over a range of 0.7 eV. The result clearly suggests that the appearance of the HOMO of the room temperature grown multilayer is the result of the superposition of monolayer and multilayer features.

The $k$-space region displayed in Fig. 6 shows the largest dispersion found for the HOMO in the investigations of the 5A(0 2 2) oriented crystallites. The monolayer has the largest dispersion of 0.35 eV, while the pure multilayer has a dispersion of $\sim 0.25$ eV. The monolayer plane is essentially the same as 5A(0 2 2) bulk planes however, the constraints of commensurability lead to a significant compression, in a manner similar to that observed for 6P and 6T on Cu–({2 × 1})O [16,17], which, in turn, results in the higher dispersion observed [18]. The multilayer dispersion is in good agreement with calculations for the lower of the two HOMO bands of the bulk pentacene structure (Holmes structure [7]) that grows on Cu(1 1 0)–(2 × 1)O. As there are two molecules per unit cell, two HOMO bands are expected. The lower binding energy band is calculated to have a lower dispersion and, in the $k$-space directions where the 2nd band has high dispersion, it should appear as a flat band at less than 0.1 eV above the 2nd band [19]. As can be seen in Fig. 6 there is no evidence of this band in the data suggesting that selection rules may be causing it to be forbidden. In spectra of various films of ‘upright’ pentacene the HOMO appears as two unresolved peaks with very weak ARUPS effects [1]. We have also observed such features for thick films on Cu(1 1 0) and on disordered Cu substrates with a FWHM of the HOMO emission of $\sim 0.7$ eV, in good agreement with the literature. As upright pentacene (5A(0 0 1)) has, in fact, its molecular axis 24$^\circ$ from the surface normal, the domains on an ordered substrate, or the multiplicity of domains of the rotationally disordered polycrystalline films on disordered substrates will yield angle integrated spectra which will approximate the density of states. Angle integration of the pure multilayer spectra of Fig. 6 yields a HOMO density of states with a FWHM of 0.4–0.5 eV, at most, lending support to the notion that the 0.7 eV broad HOMO feature observed from films of ‘upright’ pentacene is the result of the summation of the two HOMO bands, as suggested by Ueno and Kera [1].

In conclusion, we have presented ARUPS results from pentacene films (5A(0 2 2) oriented) grown at 100 K and room temperature on the Cu(1 1 0)–(2 × 1) oxygen passivated surface. Although both films have the same 5A(0 2 2) orientation and very similar UPS spectral fingerprints, the HOMO emission of the room temperature grown film has a higher energy width that could be mistaken for high dispersion of the HOMO band. Growth series at different substrate temperatures illustrate the pitfalls, resulting from final state effects and mixed morphologies, in interpreting valence band photoemission. By combining the results from the growth series at different temperatures and the azimuthally resolved ARUPS of both mono- and multilayers, we demonstrate that the appearance of the HOMO of the room temperature grown film is due to the superposition of monolayer and multilayer emissions arising from severe islanding of films grown at room temperature.

With the aid of the toroidal analyser, we investigated the two-dimensional momentum distribution of the HOMO. This photoemission distribution could be understood in terms of the FT of the orbital of isolated molecules with the orientations found in the (0 2 2) plane. This allowed us to investigate the HOMO dispersion in a region of high photoemission intensity, and a single HOMO band dispersing over 250 meV was found.

Acknowledgements

We wish to thank Roland Resel and co-workers for XRD characterisation. This work was supported by the European Community - Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative” Integrating Activity on Synchrotron and Free Electron Laser Science - Contract R II 3-CT-2004-506008) and by the Austrian Science Foundation (FWF) within the National Research Network “Interface Controlled and Functionalized Organic Films”.

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