Electronic Properties of Highly Ordered CuPc Thin Films

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Highly ordered organic crystals or thin films usually show to improved transport properties and that the orientation of organic molecules is crucial for device efficiency. One intriguing way to control the ordering and the molecular orientation of organic molecules on inorganic substrates is by designing the geometric structure of the substrate surface, *e.g.* by the steps and terraces of vicinal surfaces.

Consequently the present work was directed towards a comprehensive study of the electronic properties and of the molecular orientation of highly ordered organic thin films, *i.e.* copper phthalocyanine (CuPc) on antimony (Sb) passivated vicinal silicon surfaces. We therefore performed a series of photon energy dependent photoemission measurements and a systematic Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy study of thin CuPc layers grown on Sb passivated Si(111)-1x1. The measurements were performed at the Multi-User-Multi-Purpose-STage for Angular Resolved Photoemission (MUSTANG) at the Russian German beam line at BESSY. The substrates were passivated *in situ* by antimony. The resulting antimony passivated Si(111) surfaces, from now on being denoted as Sb-Si(111)-1x1, exhibit a 1×1 surface reconstructions as judged by low energy electron diffraction. Additional details about the passivation process and surface reconstruction are given elsewhere [1]. The CuPc layers were deposited by organic molecular beam deposition (OMBD) onto substrates kept at room temperature. The nominal layer thickness was monitored by a quartz micro balance. The C-K edge NEXAFS measurements were performed by sweeping the excitation energy between 280 eV and 320 eV and recording electrons having a selected kinetic energy of 50 eV. The measured data were corrected for the photon flux by division of the spectra by the electron yield of the clean Sb-Si(111)-1x1 sample and normalized to the absorption step edge at 320eV. Valence band photoemission spectra (VB-PES) were measured at normal emission with an incident angle of light of 45°. The total resolution of the VB-PES spectra over the whole energy range used in the present measurements was better than 0.08 eV as estimated from the Fermi edge spectra of gold.

Figure 1 shows the photon energy dependence of normal emission VB-PES spectra in the HOMO and HOMO-1 region of 10 nm CuPc film deposited onto Sb-Si(111)-1x1. The HOMO feature near 1.5 eV hardly shows any shift in its position, while a more pronounced shift of about 0.25 eV is observed for the HOMO-1 feature above 3 eV. An indication for the origin of this shift as a function of the excitation energy is given in figure 1(b) which shows a comparison between the experimental data and the calculated DOS using Gaussian '03 [2]. It can be seen that the molecular orbitals (MOs) below 4 eV predominantly have π character. While a dispersion of the HOMO feature, which has a single π-character is hardly noticeable, the richness of HOMO-1 feature in π- molecular orbitals (between 3.2 eV and 3.6 eV there are six MOs with π-character) most probably explains the relatively strong peak shift as a function of excitation energy. It is worth noticing that there is almost no change in the shape of HOMO-1 as a function of the excitation energy. This finding indicates that the photoionization cross

section of the contributing MOs at different photon energies varies at the same rate. Therefore changes in the position of the HOMO-1 feature due to the photon energy dependent cross section of the contributing MOs can be excluded.
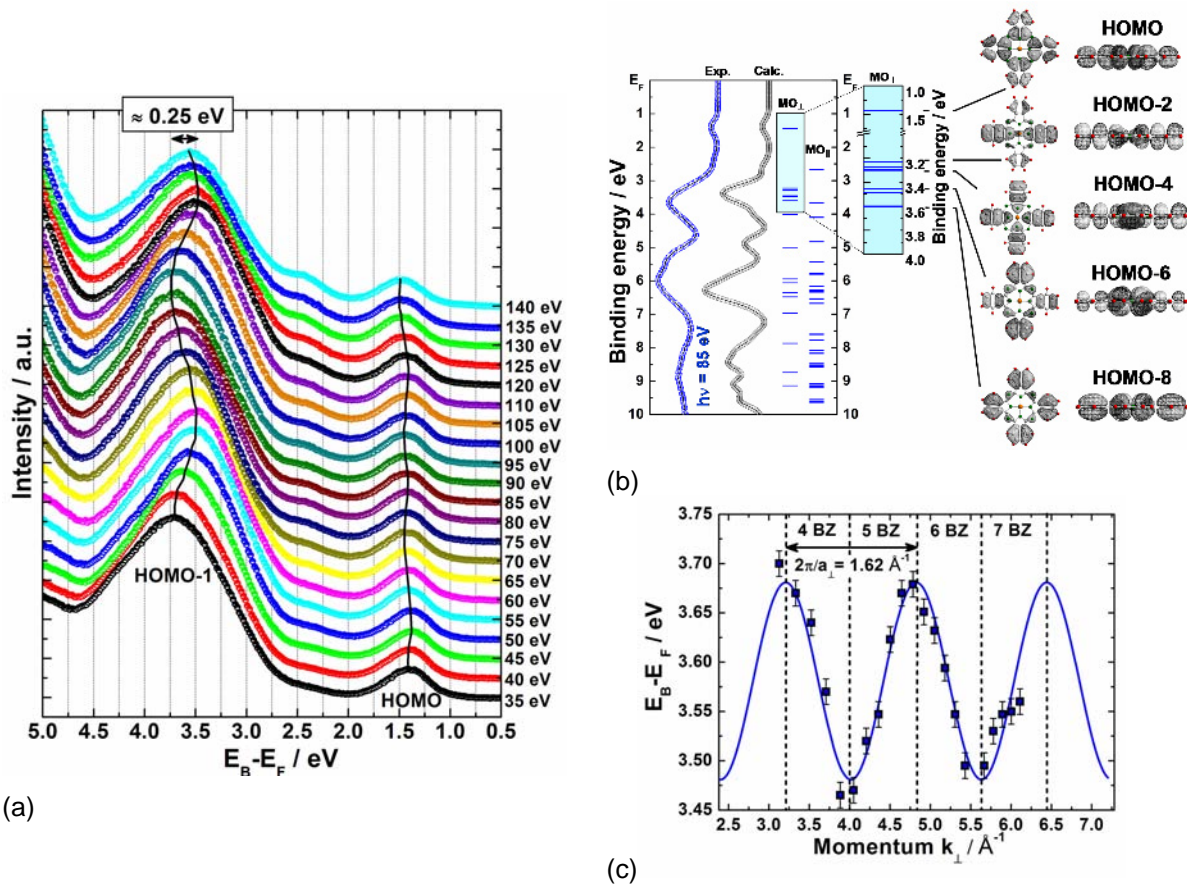

(a)

(b)

(c)

Figure 1. (a) Measured valence band spectra of 10 nm CuPc film deposited onto Sb passivated Si(111)-1x1 surfaces in the photon energy range of $35 \leq h\nu \leq 140$ eV. (b) Valence band spectra measured at 85 eV and the calculated DOS of CuPc using a Gaussian broadening of the energy levels with a FWHM of 0.4 eV. Right side- the MO energies shown by horizontal bars and selected by their character (π - perpendicular to the molecular plane ($MO_\perp$) or σ - parallel to the molecular plane (MO_{II})). In order to picture the π symmetry of the MOs the charge contour of some selected MOs with side and top view are presented as well. (c) Experimental dispersion for the HOMO-1 band (filled squares) and the best fit curve (line) in the tight-binding model.

The energy band dispersion relation for CuPc is obtained by applying a one-dimensional tight-binding theory to the HOMO-1. For the formation of a 1D energy band it is assumed that a unit, *i.e.* a molecule, is repeating along an axis x with a period $a_\perp$. The interaction only takes place with the nearest neighbours its strength being defined by the value t, the transfer integral. By analogy to the Hückel theory, the energy E_B for the HOMO-1 is expressed in terms of wave vector $k_\perp$ as:

$k_\perp = [2m^* \times (h\nu - E_B - V_0]$ and $E_B(k_\perp) = E_B^0 + 2t\cos(a_\perp \times k_\perp)$, where m^* is the effective mass of the electron and V_0 the inner potential which is treated as a fit parameter. Using the normal emission spectra and these two equations the energy of HOMO-1 band and its momentum can be calculated. The results of the best fit for the dispersion along with the experimental data are shown in figure 1(c). A cosine fit of the experimental data was performed where the inner potential V_0 and the transfer

integral t are the two parameters. The best fit between calculated and experimental data is provided by the following set of parameters – inner potential V_0=-5.9 eV and transfer integral t = 0.045 eV. However, information on the intermolecular spacing of the present system, $a_\perp$, is necessary and this can be provided by the NEXAFS results.

$$I(\theta) \propto \left[P\left(\cos^2\theta \cos^2\alpha + \frac{1}{2}\sin^2\theta\sin^2\alpha \right) + \frac{(1-P)}{2}\sin^2\alpha \right]$$

(a)   (b)
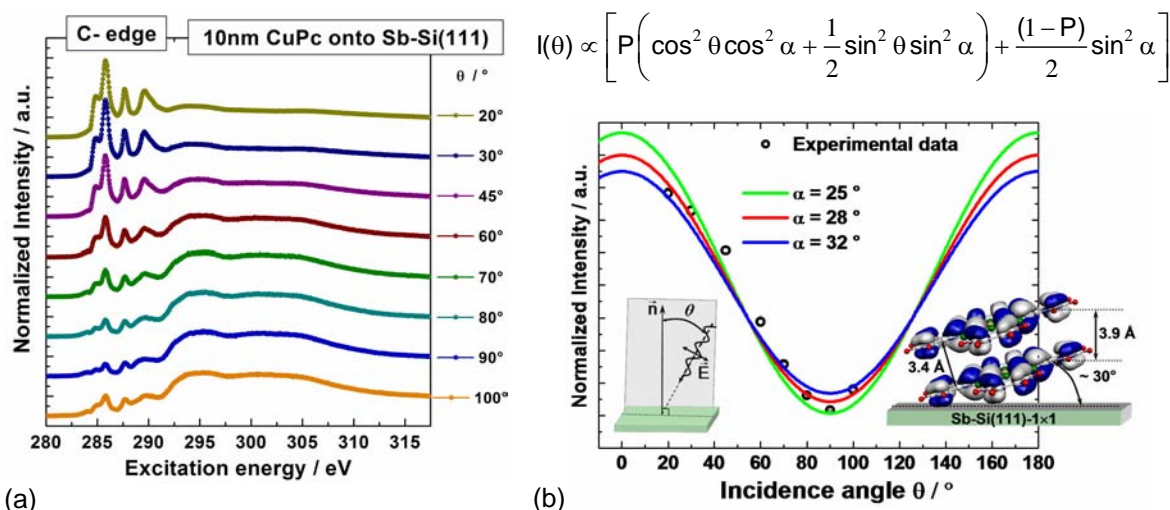
Figure 2 (a) The Carbon K-edge NEXAFS spectra of a 10nm CuPc film on Sb-Si(111)-1x1 as a function of the angle of incidence. (b) Normalized resonance intensity of the π* orbitals as a function of the incidence angle θ – experimental data and fit. The sketches illustrate the experimental geometry for the polarized light (left) and the orientation of the molecules on the substrates together with the calculated intermolecular spacing $a_\perp$ = 3.9 Å.

The angular dependent carbon K-edge NEXAFS spectra of a 10nm thick layer of CuPc onto Sb-Si(111)-1x1 are shown in figure 2 (a). Their quantitative analysis is provided in figure 2 (b). The normalized resonance intensity of the π^* orbitals is fitted using the formula given above figure 2(b), where P is the degree of polarization, θ is the angle of incidence and α the molecular tilt angle. The fitted curve is presented in figure 2(b). The average molecular tilt angles of the CuPc molecules with respect to the substrate surface is determined to be (30°± 3°).

With the distance between the intermolecular planes of 3.4 Å, as experimentally determined [3], we can calculate the length of repeating units (lattice spacing normal to the surface) as $a_\perp$ =3.9 Å as depicted in the figure 2 (b). The calculated $a_\perp$ gives rise to the best fit of the energy dispersion to the experimental data using an inner potential V_0 of -5.9 eV and the transfer integral of 0.045 eV. As shown in this work, we succeeded to observe the HOMO-1 band dispersion for CuPc along the surface normal. The energy-band dispersion is extended over more than three Brillouin zones (4th, 5th, 6th and 7th zone) with a bandwidth of about 0.25 eV.

[1] S. Seifert, G.N. Gavrila, D.R.T. Zahn, W. Braun, BESSY Jahresbericht, 221, 2005.
[2] Gaussian 03 (Revision A.1), Gaussian Inc., Pittsburgh PA, 2003.
[3] R. Hiesgen, M. Räbisch, H. Böttcher, and D. Meissner, Sol. Energ. Mat. Sol. C. 61, 73, 2000.