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"Band bending" in copper phthalocyanine on hydrogen-passivated Si(111)

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Abstract

Ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) were employed to study the electronic density of states of copper phthalocyanine (CuPc) layers deposited onto hydrogen passivated Si(111) substrates. The highest occupied and lowest unoccupied molecular orbital (HOMO respectively LUMO) features are found to shift gradually in the same direction with increasing film thickness. At approximately 15 nm, the shifts saturate with a total amount of about 0.4 eV.
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1. Introduction

Considerable attention has been given to phthalocyanine materials in the last years because of their increasing importance in organic-based devices. Their attributes such as chemical and thermal stability and the tendency to form highly ordered layers result in an increase of device efficiency [1]. Therefore, metal phthalocyanines are promising candidates for applications, e.g. in organic light emitting diodes, organic field effect transistors, photovoltaic solar cells and gas sensors. While a large number of articles were published regarding the characterization of bulk CuPc, only very few studies describe the interface formation between CuPc and different types of substrates, e.g. metals or semiconductors. Metal–organic interfaces have received considerable attention due to their important role in the injection of carriers into the organic layer [2–5]. Organic–organic heterojunctions were investigated

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regarding carrier transport in multilayer light emitting structures [6]. Organic–inorganic semiconductor heterojunctions did not receive the same attention. They could, however, become relevant for future devices, in particular hybrid solar cells.

With respect to energy level alignment, it was shown for metal–organic interfaces that the vacuum levels in general do not align [4,7,8]. This assertion is also accepted for organic–inorganic semiconductor interfaces [3]. The difference in vacuum levels is attributed to interface dipoles, for which values between 0.2–1 eV were found for several metal–organic interfaces using photoemission spectroscopy. Another important issue is the occurrence of a "band bending"-like electrostatic energy shift for organic layers which was observed in many metal–organic systems [9]. In most cases, this shift is confined to a regime of only a few nanometres, which cannot be accounted for using the conventional band bending theory of inorganic semiconductors. Considering the Schottky model [10], at the CuPc/Au interface which has a built-in potential of 1.2 eV (interface dipole), for a depletion width of 10 nm the calculated density of carriers has a value of 1.2×10^{17} cm^{-3}. This value is 10 orders of magnitude higher than the carrier concentration estimated from electrical measurements for undoped organic semiconductors such as metal phthalocyanines [11].

Energy shifts occurring in small thickness ranges i.e. 15 nm can be due to a change in the intermolecular interaction, for instance, due to a change in the molecular orientation as a function of the film thickness. This observation has been made for CuPc films grown on MoS$_2$ substrates [12]. Angular resolved ultraviolet photoemission spectroscopy using synchrotron radiation was used to determine the energy position of the HOMO and the orientation of the molecules as a function of the film thickness. For a layer thickness of 0.3 nm, the HOMO is found ≈1.05 eV below the Fermi level, while for films of 5 nm thickness, the HOMO shifts by about 0.3 eV to higher binding energies. Following the intensity of the HOMO as a function of emission angle and sample azimuth, the tilt angle of the CuPc molecular plane with respect to the substrate surface is determined to be 0° and 10° for the 0.3 and 5 nm thick films, respectively.

Shimada et al. [13] studied the behaviour of CuPc on three types of layered substrates (no dangling bonds): semiconducting MoTe$_2$, semi-metallic highly oriented pyrolytic graphite (HOPG) and metallic TaSe$_2$. The substrates were chosen due to their different work function. Flat band condition—absence of both energy shifts and interface dipoles—was observed on HOPG and MoTe$_2$. In the case of CuPc on TaSe$_2$, two mechanisms were proposed: an interface dipole and "band bending" by n-type carriers with an overall value of 0.5 eV. Moreover Peisert et al. [14] demonstrated the presence of both mechanisms: interface dipole and "band bending" at the CuPc/Au interface. The value for the interface dipole was estimated to be 1.2 eV. On the other hand, for the CuPc/GeS(110) interface no "band bending" is present and the determined interface dipole has a value of 0.5 eV. All these studies employ a combination of ultraviolet photoemission spectroscopy and X-ray photoemission spectroscopy, which allows the determination of HOMO position of the organic material and the interface chemistry, but not the LUMO position. The LUMO can be determined by employing inverse photoemission (IPES) experiments. Having the energy position for both HOMO and LUMO, the transport gap E_t can be determined.

It is known that wet chemical etching of silicon produces ideally H-terminated Si(111) surfaces [15]. This type of non-reactive surface is preferred for organic molecular beam deposition (OMBD) since it favours ordered arrangement of the organic molecules. The present paper focuses on characterizing the interface formation between CuPc and H–Si(111) using UPS and IPES measurements as a function of film thickness. The results of this work complement the picture of thickness dependent energy level shifts in organic materials, particularly in the class of phthalocyanine materials.

2. Experimental

Hydrogen-passivated p-type, (111) oriented silicon with a doping concentration of approximately

1.5×10^{15} cm^{-3} was used as the substrate. The passivation process consists of a wet chemical etching in a solution containing HF 40%. After the passivation process, the samples were transferred into UHV. All measurements were performed on freshly evaporated organic layers. Sublimed CuPc provided by Sensient Imaging Technologies GmbH (former SynTec) was employed with no further purification. The organic material was evaporated from Knudsen cells kept in a temperature range of 340–370 °C. During OMBD, the pressure was better than 2×10^{-8} mbar. The evaporation rates were in the range of 0.1–2 nm/min and the substrate was kept at room temperature. The film thickness and the evaporation rate were determined by means of a quartz crystal microbalance and confirmed by post-growth ellipsometry measurements. The UPS and IPES measurements were performed on two UHV systems (base pressures 3×10^{-10} and 8.5×10^{-10} mbar, respectively), each comprising an analysis and a preparation chamber. UPS spectra were recorded in normal emission with a hemispherical analyser and using He I radiation (21.22 eV), providing an overall resolution of 0.1 eV. The IPES experimental set-up working in the isochromat mode is a ''home'' built system. The fixed-energy photon detector [16] consists of a Geiger–Müller tube with a magnesium fluoride (MgF$_2$) window filled with a gas mixture containing ethanol and argon. The ionisation energy of ethanol and the transmission function of the MgF$_2$ provide a value of 10.9 eV as the nominal detection energy of the detector. A low energy electron gun [17] was used to produce a monoenergetic electron beam. The overall IPES instrumental resolution, estimated from the width of the Fermi edge measured on an Ar sputtered nickel sample, is 0.4 eV. Spectra were recorded at normal incidence with a current density in the range of 10^{-6} A/cm^2. This value is low enough in order not to damage the organic film [3].

3. Results and discussion

Fig. 1 depicts the thickness-dependent ultraviolet photoemission and inverse photoemission spectra of CuPc deposited on H–Si(1 1 1). The spectra were normalized with respect to the highest peak and shifted vertically for clarity. The HOMO and LUMO peak and onset positions are marked by vertical bars. The three UPS characteristic peaks for CuPc[3] already appear at very low coverage (0.5 nm). Zooming into the HOMO region as shown on the right hand side of Fig. 1(a), a strong shift of the HOMO peak and onset positions towards higher binding energies is observed with increasing thickness. The shift shows a saturation tendency above 10 nm. The overall value of the shift is approximately 0.4 ± 0.07 eV. The same amount of shift is found in the LUMO position as a function of thickness as shown in Fig. 1(b). Similar to the UPS case, the CuPc features appear for 0.5 nm and become better resolved for higher thicknesses. The LUMO shifts towards the Fermi level with increasing film coverage. To determine the LUMO peak positions, a polynomial background was subtracted and the remaining peaks were fitted with Gaussian functions. In addition, the LUMO onsets were determined with respect to the Fermi level by a linear extrapolation of the low energy edge of the LUMO feature after background removal. The determination of the LUMO onsets in IPES presents an experimental difficulty due to the broadening effects as a consequence of the resolution (0.4 eV) which leads to a smearing out of the features. However, the onset positions are determined after deconvoluting the spectra with a Gaussian function that has a FWHM of 0.4 eV. In this manner, the effect of the IPES resolution is more or less eliminated.

Fig. 2 summarizes the resulting HOMO–LUMO peak and onset positions as a function of film thickness and with respect to the Fermi level. The HOMO–LUMO peak-to-peak difference calculated for all coverages is approximately 2.9 ± 0.2 eV. The transport gap determined as the difference between the onset positions of LUMO and HOMO is found to be 2.2 ± 0.2 eV. This value is in rather good agreement with the one determined by Hill et al. using UPS-IPES [3] $(2.3 \pm 0.4$ eV), but somewhat larger than the one determined by cyclic voltammetry [18] (1.71–1.84 eV).

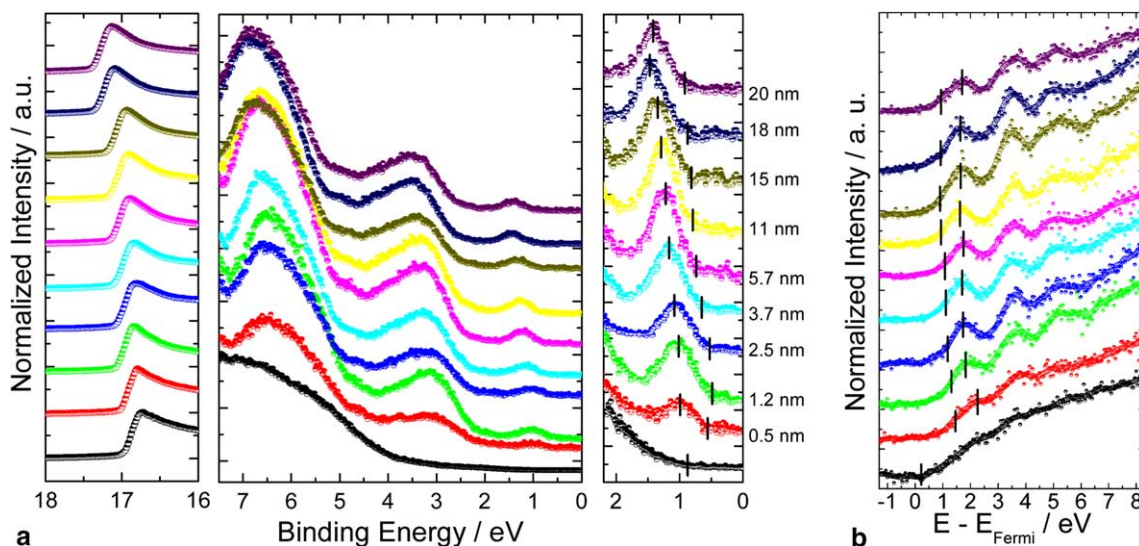The evolution of the electron affinity (EA) determined using the LUMO onset energy

Fig. 1. (a) UPS thickness dependent measurements on CuPc/H–Si(111); (b) IPES thickness dependent measurements on CuPc/H–Si(111).
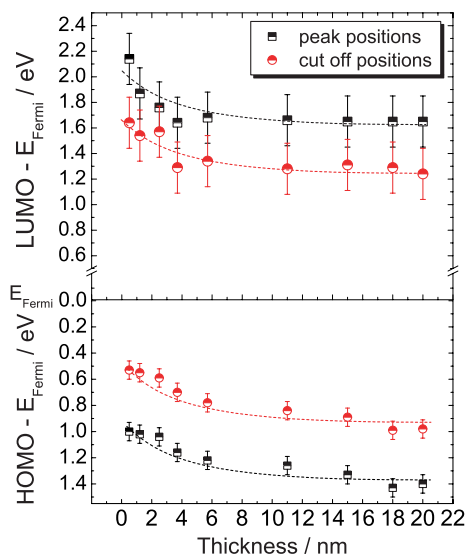

Fig. 2. The HOMO–LUMO peak and onset positions. The dotted curves are plotted as a guide for the eye.

Fig. 3. EA, ϕ and IE of the CuPc film as a function of its thickness. The 0 point thickness represents the values for the H–Si surface.

position, work function (ϕ) and ionisation energy (IE) as a function of the CuPc thickness is presented in Fig. 3. For simplicity, the band bending of the substrate is omitted so that the energy levels corr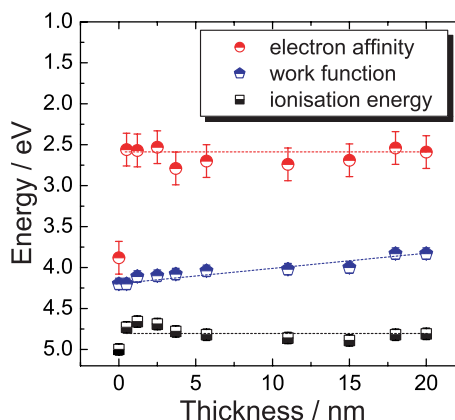esponding to the substrate represent those of the substrate surface. At zero coverage, the values of EA, ϕ and IE of the hydrogen-passivated silicon were included. The EA of H–Si was estimated using the known transport gap of silicon 1.12 eV and the onset position of the valence band maximum (VBM) from the UPS measurement. The dashed lines are plotted as a guide to the eye. When 0.5 nm of CuPc is deposited, a sudden
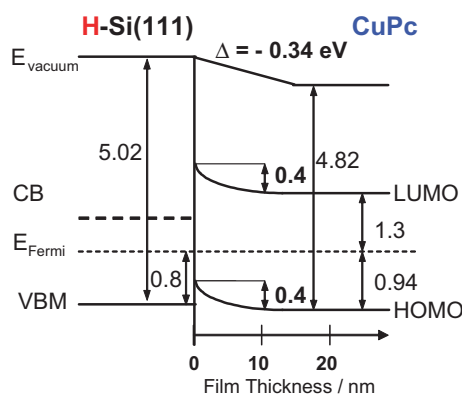
Fig. 4. Schematic energy level diagram of the CuPc/H–Si(111) interface.

change of EA and IE occurs. Proceeding to larger CuPc thicknesses, EA and the IE remain constant. On the other hand, the work function linearly increases as a function of thickness.

Fig. 4 summarizes the measurements by showing the energy band diagram of CuPc/H–Si(111) interface. The determined values for thick CuPc layer (20 nm) are IE $= 4.82 \pm 0.07$ eV, $\phi = 3.88 \pm 0.07$ eV and EA $= 2.5 \pm 0.2$ eV. An interface dipole of 0.34 ± 0.07 eV is measured as well. The onset positions of the HOMO and LUMO were employed in order to sketch the energy band diagram and to calculate these values. In the case of H–Si(111), the onset position of the VBM was taken into consideration for determining the IE $= 5.02 \pm 0.07$ eV and $\phi = 4.22 \pm 0.07$ of the surface. The VBM is obtained in the direction perpendicular to the (111) plane of silicon. However, the conduction band minimum is not situated in the same direction [10]. The conduction band (CB) position of H–Si(111) was determined by IPES and it represents a local minima in the energy scale of the unoccupied states of the hydrogen-passivated silicon surface.

Considering again the spectra in Fig. 1(a) and (b), it should be noted that all the peaks shown are gradually shifting with increasing CuPc thickness while the relative distance between the peaks remains unchanged. This indicates that no chemical interaction occurs during the interface formation process. Furthermore, no marked changes in

the peak shape of the HOMO as well as LUMO features are observed. The values of the full width half maximum (FWHM) for the HOMO and the LUMO are almost constant as a function of film thickness and have values of 0.50 and 1.1 eV without deconvoluting with the instrumental resolution, respectively. Calculations of the band structure for the β-metal free phthalocyanine suggest that the FWHM of the HOMO and LUMO are in the range of 0.1–0.4 eV along the molecular stacks where the molecules have the greatest π–π overlap [19]. The FWHM of the HOMO observed for individual phthalocyanine molecules in the gas phase has a value of 200 meV [20]. In the gas phase, molecule–molecule interaction is negligible and as a consequence, the observed HOMO does not have a contribution from the vibrational coupling of adjacent molecules. Consequently, the broadening of the HOMO even at a low CuPc coverage suggests the development of a band structure, i.e. molecule–molecule interaction.

Above 15 nm CuPc coverage, the energy shift saturates. At this point, the CuPc layer has reached the characteristics of the bulk-like organic material. The CuPc molecular bulk configuration presents the HOMO state at ∼1.6 eV binding energy (BE) and two other molecular levels at higher BE [3,21] with respect to the Fermi level.

The energy shift that appears at the H–Si(111)/CuPc interface might have several explanations. As already discussed for metal–organic interfaces [3,14], the formalism of electrostatic band bending model can hardly explain the formation of these interfaces. Applying Poisson's equation as for inorganic semiconductors, using a depletion width of 15 nm, the built-in potential calculated from the difference of ϕ of H–Si and CuPc, and the reported relative dielectric constant of CuPc (about 5) [22], the charge carrier density is found to be very high, i.e. 2.3×10^{16} cm^{-3}. Consequently, the results of such an interpretation would be unreasonable since the intrinsic carrier concentration of CuPc[11] was previously estimated to be ∼10^7 cm^{-3}.

Even though the conventional band bending model is quite unlikely to explain the energy shifts at the CuPc/H–Si interface, this model was not completely ruled out in previous publications

[13,23]. The formation of inorganic–organic semiconductor interfaces is still under discussion. Possible factors which can affect the interfacial layer are chemical interaction, polarization in the molecular layer and a surface rearrangement. The appearance of the energy shift due to charge transfer occurring as a result of chemical interaction may be excluded since the distance between the gradually shifting peaks as well as their line shape remains unchanged. In the case of chemical interaction, the appearance or disappearance or at least changes in the line shape of features in the valence band is expected. Polarization in the molecular layer is consistent with such energy shifts in the HOMO position as found by Peisert et al. [14] and initially considered for other organic molecules as well, i.e. perylene derivatives [3]. The distribution of charge on the molecules changes with the changing of environment from the hydrogen-passivated silicon substrate to the thick CuPc film. Moreover, this is also influenced by the slightly different arrangement of the molecules in the vicinity of the substrate compared with the ones in the thick film. Furthermore, the surface roughness of the substrate may also play a role in the overall molecular arrangement. Nakamura et al. [24] determined the growth mode of CuPc on a NH_4F passivated Si(111) substrate. The molecular column of CuPc was found to be parallel to the surface on a relatively rough substrate, while the column was found perpendicular to the Si(111) plane on an atomically flat substrate. The hydrogen passivation involving HF immersion was already proven to produce a relatively rough substrate surface [25,26]. Considering that the FWHM values of the HOMOs are not changing, the adsorption geometry of CuPc molecules may be estimated. The molecules seem to form clusters even at a monolayer coverage, which would grant them already bulk like properties and result in band formation. Peisert et al. [14] determined that CuPc on polycrystalline gold behaves in a similar way. Comparing the polycrystalline gold surface and the H–Si(111) surface, a common characteristic is found: namely the relative large roughness of both substrates. Although the wet chemical treatment based on HF dip gives

an ideally hydrogen terminated surface, this surface is non-uniform [27]. By means of STM, the estimated value of the roughness is about 3–4 Å. This may favour the clustering of the molecules in the first monolayers. Furthermore, in order to determine the influence of the surface roughness on the energy shifts, we performed another set of UPS-IPES experiments on CuPc/H–Si(111) systems with a slightly different hydrogen-passivation treatment (spectra are not shown here). The details of the passivation procedure are given elsewhere [28]. The roughness of H–Si(111) is then in the range of 2–3 Å as judged from STM images. The ionisation energy and the work function of the H–Si(111) are in excellent agreement with the ones determined above. The values are 4.94 ± 0.07 and 4.24 ± 0.07 eV, respectively. Moreover, the same value of 0.4 ± 0.07 eV is found to represent the energy shift of HOMO and LUMO as a function of CuPc film thickness. The shift saturates in the same manner above 15 nm. These results indicate that the surface roughness of the substrate does not play a major role for the energy shifts at the interface.

Several other studies have shown that the molecules change their orientation as a function of layer thickness [29–31]. An incomplete overlapping of the CuPc molecules results in a partial superposition of the π-orbitals. As a consequence, when a change in molecular orientation occurs, it will result in a change of the intermolecular interaction and will affect of the π-electron system. The HOMO and LUMO features correspond to π-character molecular orbitals [21,32]. Consequently, any change of molecular orientation will influence the recorded UPS and IPES spectra and the HOMO and LUMO features, respectively. Following this hypothesis, angular dependent NEXAFS was performed on the CuPc/H–Si(111) system. These NEXAFS spectra reveal a change in the molecular orientation of CuPc from monolayer range to thick films. At 0.5 nm CuPc, the orientation of molecular plane with respect to the substrate was found to be $70° \pm 2°$ while for 20 nm the angle is $90° \pm 1°$ [33]. Thus, the rearrangement of the CuPc molecules is most likely the reason for the observed energy shifts at the

CuPc/H–Si(1 1 1) interface, since the energy shifts are independent of surface treatment and surface roughness.

4. Summary

The interface between CuPc and hydrogen-passivated silicon was investigated using UPS and IPES and their electronic properties were determined. The measurements as a function of film thickness show a energy shift of 0.4 eV of the HOMO and LUMO bands at the CuPc/H–Si(1 1 1) interface. The transport band gap, however, remains constant at 2.2 ± 0.25 eV. The rearrangement of the CuPc molecules is attributed as being the cause of such type of energy shifts. The energy level alignment was determined for the CuPc/H–Si(1 1 1) system.

Acknowledgement

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