Low-energy electron transmission for the analysis of the interface barrier formation and the density of the unoccupied electronic states in the ultra-thin layers of fluorinated copper-phthalocyanine

Abstract: The interfacial structure made from the thermally deposited 5 – 7 nm thick layers of hexadecafluoro copper phthalocyanine (F_{16}-CuPc) and of the unsubstituted copper phthalocyanine (CuPc) was subjected to the studies. The surface work function and the density of the unoccupied electron states (DOUS) located 5-20 eV above the Fermi level (E_F) were investigated during the CuPc/F_{16}-CuPc interface formation using the very low energy electron diffraction (VLEED) method and the total current spectroscopy (TCS) measurement scheme. The DOUS peak structure of the organic films studied obtained from the TCS results showed a good correspondence to the main \( \pi^* \) and \( \sigma^* \) DOUS bands obtained from the density functional theory (DFT) calculations. The interfacial barrier was characterized by the negative charge transfer from the CuPc overlayer to the F_{16}-CuPc underlayer occurred within the 5 nm thick interfacial region in the CuPc overlayer which was accompanied by the decrease of the surface work function from 4.9±0.1 eV to 4.3±0.1 eV. The stabilization of the \( \pi^* \) DOUS bands, as well as restructuring of the low lying \( \sigma^* \) bands was observed in the in the case of the fluorinated film (F_{16}-CuPc) compared to the case of the unsubstituted CuPc film.

Keywords: Organic semiconducting films; Surface electronic phenomena (work function, surface potential, surface states, etc.); interface charge transfer; DFT calculations; Density of states

1 Introduction

Electronic properties of thin and ultra-thin conjugated organic films and of their hetero-junctions with metals and inorganic semiconductors have attracted scientific interest because of possible applications in chemical sensing, light-emitting and photovoltaic devices [1–5]. The surface science techniques were used successfully to characterize the interfacial band alignment and the density of the electronic states at organic film interfaces with metal and semiconductor surfaces [6, 7]. The electronic structure of the organic layers can be tuned by introducing polar substituents into the molecules [3, 8–10]. The electron withdrawing effect upon the substitution by fluorination would lead to stabilization of the energy positions of the edges of the forbidden energy gap and to narrowing of the bandgap [10, 11]. There has been reported that fluorination of the conjugated rings affects the whole peak structure of the density of the valence and of the unoccupied electronic states (DOS and DOUS, respectively) [12, 13]. For instance,
the fluorination of condensed benzene resulted in that the
\( \pi^* \) and low lying \( \sigma^* \) DOUS maxima were restructured and
shifted 0.5 – 1.5 eV towards lower electron energies [13].
Studies of the unoccupied electronic states can provide in-
formation about the interface formation complementary to
the information on valence electronic states, obtained tra-
ditionally by photoelectron spectroscopy. DOUS in the en-
ergy range 5 – 20 eV above the \( E_F \) can be obtained theore-
tically [10, 11] and experimentally by using the dissociative
electron attachment (DEA) technique [14, 15] or by moni-
toring secondary electrons backscattered from the sample
surface by means of very low-energy electron diffraction
(VLEED) using the total current spectroscopy (TCS) as a
measurement scheme [16, 17].

A number of surface science studies have been de-
voted to the films of copper-phthalocyanine (CuPc) and
fluorinated copper-phthalocyanine (\( \text{F}_{16}\text{-CuPc} \)) [6, 18–20].
The ionization potential of the \( \text{F}_{16}\text{-CuPc} \) films was deter-
mined as about 6 eV, which is approximately 1.1 eV higher
than the ionization potential of the unsubstituted CuPc.
There has been shown that CuPc molecules act as electron
donors relatively to the silicon, titanium and zinc oxide
surfaces [21] while electron acceptor behavior is expected
from \( \text{F}_{16}\text{-CuPc} \) [6, 20]. In this paper the authors present the
TCS results on the band alignment and on DOUS at the in-
terface of the CuPc and \( \text{F}_{16}\text{-CuPc} \) ultra-thin layers. The ex-
perimental DOUS and the DOUS obtained using the den-
sity functional theory calculations are compared.

## 2 Experimental

The films studied were formed from the hexadecafluoro
copper phthalocyanine (\( \text{F}_{16}\text{-CuPc} \)) and from the unsubsti-
tuted copper phthalocyanine (CuPc) available from Sigma-
Aldrich (Fig. 1). These molecular materials were thermally
deposited \textit{in situ} from a Knudsen cell on the surfaces of
the substrates kept at room temperature. A few hours of
baking out at 100 °C in UHV were applied to the molecular
powder prior to the film deposition. The \( \text{(SiO}_2\text{)}_n\text{-Si} \) surface
was used as a substrate in the film structures studied.
The silicon wafers were pre-treated in HF and in \( \text{H}_2\text{O}_2/\text{H}_2\text{SO}_4 \)
solutions and then were placed into the experiment cham-
ber. After such short exposure to air one should expect that
a 3 – 4 nm thick silicon oxide is present on the surface.
The atomic composition of the \( \text{(SiO}_2\text{)}_n\text{-Si} \) surface was tested by
Auger electron spectroscopy, the ratio between the silicon and
oxygen atoms was determined as 1:1.8, which is close to
the atomic composition in a stoichiometric \( \text{SiO}_2 \). In or-
order to form the film structure CuPc/\( \text{F}_{16}\text{-CuPc} \) studied the
layer of \( \text{F}_{16}\text{-CuPc} \) was deposited onto the \( \text{(SiO}_2\text{)}_n\text{-Si} \) sub-
strate, then the layer of the CuPc material was deposited
on top.

![Figure 1: Chemical structure of the hexadecafluoro copper phthalocy-
nine (\( \text{F}_{16}\text{-CuPc} \)) molecule used in the study.](image)

The TCS measurements [16, 21, 22] were made during
the organic film deposition. The UHV system base pressure
was \( 10^{-7} \) Pa. The deposition rate was kept 0.1 nm/min and
the thickness of each organic layer reached up to 8 nm.
The thickness of the overlayer deposited was controlled
using a quartz microbalance as well as using the analy-
ysis of the attenuation of the TCS signal from the under-
layer [16, 21–23]. The LEED unit installed was used as a
main instrumentation for the measurements according to
the TCS method described in detail in [17–19]. The low-
energy electron beam with the energies varied from 0 eV
to 25 eV is used for testing the surface under study. The
electrical current \( J(E) \) of the electrons transmitted through
the sample as a function of the electron beam energy is
registered during the experiment. Typically the derivative
\( S(E) \) of the electric current is registered using the phase-
detection preamplifier [16, 21]. The TCS spectrum consists
of the primary TCS peak and the TCS fine structure. The
energy position of the primary TCS peak is determined by
the surface potential of the surface under study. The Fermi
energy (\( E_F \)) in a semiconducting organic layer and in the
silicon oxide layer is assumed to be a continuation of \( E_F \)
in the conducting substrate. The TCS fine structure \( S(E) \) is
determined by the energy dependence of the elastic scat-
tering of the incident electrons from the sample surface.

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There has been shown that the TCS fine structure is closely related to the density of the unoccupied electron states (DOUS) of the sample surface as if the peaks of the negative second derivative of the transmitted current \( -d^2\langle J(E) \rangle /dE^2 = -dS(E)/dE \) represent the DOUS peaks [21, 24, 25].

The quantum-chemical calculations were performed using the density functional theory (DFT) with the Gaussian software [26]. The virtual orbital energies (VOEs) were calculated using the B3LYP [27] hybrid functional with the standard 6-31G(d) basis set. There has been shown that the as calculated VOEs provide underestimate values of the molecular orbital energies compared to the experimental values [28–31]. In order to correct the calculation results the following scaling procedure has been used successfully in a number of cases for the DOUS peak assignment in the films of small conjugated molecules [15, 25, 29, 31, 32]. For the \( \pi^* \) molecular orbitals the scaled virtual orbital energies (SVOE) are given by the expression \( \text{SVOE} = (\text{VOE} + 1.14)/1.24 \), and for the \( \sigma^* \) molecular orbitals SVOE are given by the expression \( \text{SVOE} = (\text{VOE} + 0.97)/0.79 \) [15, 31]. One should keep in mind that the scaling formulas above have been suggested for the B3LYP/6-31G(d) computational level and may rather not be applied in an accord with another computational approach.

3 Results and discussion

The structure of the unoccupied electronic states and the surface potential were monitored by means of the measurement of the series of the TCS spectra during the CuPc overlayer deposition process onto the F\(_{16}\)-CuPc underlayer. The CuPc overlayer thickness changed from 0 to 7 nm. The TCS fine structure obtained from the F\(_{16}\)-CuPc film shows the main peaks F\(_1\)-F\(_6\) at 7.0 eV, 8.5 eV, 10.5 eV, 12.5 eV, 15.5 eV and 19.5 eV, respectively (Fig. 2). During the unsubstituted CuPc film deposition the F\(_1\)-F\(_6\) peak structure from the underlayer was attenuated and the new TCS fine structure appeared. The TCS fine structure obtained from the CuPc film at 7 nm coverage has main peaks T\(_1\)-T\(_7\) at 5.5 eV, 7.5 eV, 9.0 eV, 10.0 eV, 12.0 eV, 15.0 eV and 19.5 eV, respectively (Fig. 2) and they are almost identical to the peaks of the TCS fine structure we obtained earlier for the CuPc films on a number of other substrates [21, 33]. The TCS fine structure obtained at 7 nm coverage remained with a further increase of the deposit thickness up to 10-12 nm until the charging of CuPc/F\(_{16}\)-CuPc film by the incident electrons started to affect the measurement.

The formation of the interface barrier at the CuPc/F\(_{16}\)-CuPc boarder was monitored by means of registering the changes of the energy positions of the primary TCS peak (Fig. 3). The series of the primary TCS peaks measured during the CuPc overlayer deposition is shown in Fig. 3a and the peak position measured as the values \( E_{\text{vac}} - E_F \) is shown in Fig. 3b. Along with the deposition of the CuPc overlayer up to 7 nm, the \( E_{\text{vac}} - E_F \) values changed monotonically from 4.9±0.1 eV to 4.1±0.1 eV and then the saturation occurred (Fig. 3b). The decrease of the \( E_{\text{vac}} \) level corresponds to the negative charge (electron) transfer from the CuPc overlayer to the F\(_{16}\)-CuPc underlayer, which corresponds well to the results of the photoemission studies of these films [6, 18, 20] as well as to the studies of the work function changes upon the introduction of polar substituents into the small organic molecules [12]. The mostly rapid changes of the \( E_{\text{vac}} - E_F \) values occur within the 2 nm of the CuPc deposit while the smaller changes are still observed upon the deposit thickness increase even above 5 nm corresponding to the (Fig. 3b). According to the discussion in [16, 23], it is convenient to choose 5 nm film thickness to distinguish between an abrupt and a relatively extended character of an interface dipole. The changes of the surface potential observed for the CuPc/F\(_{16}\)-CuPc interface are determined by the changes of the surface work function due to the change of the contents of the surface layer along with the overlayer deposition as well as forma-
tion of a relatively broad polarization layer in the organic film [16, 23].

Figure 3: Analysis of the CuPc/F$_{16}$-CuPc interface formation; a) the series of the primary TCS peaks measured during the CuPc overlayer deposition. For numbers at the curves see the caption for Fig. 2; b) the changes of the surface work function measured as the values $\Delta E_{\text{vac}}$ during the CuPc overlayer deposition onto the F$_{16}$-CuPc underlayer.

In order to perform the DOUS analysis of the films studied, a negative derivative of the experimental TCS fine structure of the F$_{16}$-CuPc underlayer and of the 7 nm thick CuPc overlayer (Fig. 2) were analyzed. The DOUS curves can be presented in the form of $-dS(E)/dE$, according to the relevant part of the discussion presented in Section 2 (Fig. 4, curves 1 and 2). The curve 3 in Fig. 4 shows the DOUS of a CuPc film we plotted according to the literature data, based on the studies by means of X-ray absorption spectroscopy, inverse photoemission spectroscopy and theoretical calculations [34, 36]. The peak assignment of the DOUS of the CuPc film (Fig. 4, curve 2) can be made using the suggestions from the [34–36] as follows. The double peak in the energy range 5.5 – 6.0 eV and the peak at 7.5 eV (Fig. 4, curve 2) correspond to the $\pi^*$ DOUS bands, the fine structure in the energy range 8-13 eV corresponds to the $\sigma^*_1$ (C-C, C-N) DOUS band, the broader peaks at the energies 14-17 eV and 18-22 eV correspond to the higher lying $\sigma^*$ bands related to the double bonds C=C, C=N in the CuPc molecules. One can observe a good correspondence between the DOUS peak structure of the CuPc films obtained by TCS (Fig. 4, curve 2) and the DOUS according to the literature data (Fig. 4, curve 3). The major deviation between these two DOUS curves is seen in the energy range 8-13 eV where the TCS results show a more pronounced fine structure with three maxima. Let us compare the DOUS of the fluorinated film F$_{16}$-CuPc and the DOUS of the unsubstituted CuPc film (Fig. 4, curves 1 and 2, respectively). The higher lying DOUS peaks at the energies 14 – 17 eV and 18 – 22 eV have the analogous positions in the cases of the F$_{16}$-CuPc and CuPc film. The DOUS bands $\sigma^*_1$ energy region have a slightly different peak structure (Fig. 4, curves 1 and 2), particularly a contribution from the C-F bonds in F$_{16}$-CuPc can be the reason for the broadening of the DOUS peak at 13 eV upon the fluorination (Fig. 4, curve 1). The $\pi^*$ DOUS bands in the case of the F$_{16}$-CuPc film are shifted 1 – 2 eV towards lower electron energies relatively to the case of the CuPc film. These differences between the curves 1 and 2 in Fig. 4 correspond well to the effect of fluorination on DOUS of CuPc films reported in literature [10–13, 18]. Particularly, there has been reported that the fluorination had a major influence on the stabilization of the $\pi^*$ bands and on the restructuring of the $\sigma^*_1$ bands while the higher lying $\pi^*$ bands were less affected [12, 13].

In order to obtain a more detailed DOUS peak assignment of the phthalocyanine films studied the DFT calculations were applied. The quantum-chemical calculations of the energy positions of the unoccupied molecular orbitals have been made for the F$_{16}$-CuPc and CuPc films studied at B3LYP/6-31G(d) level as we reported in our earlier paper [23]. After applying the scaling procedure described in the Section 2 the values of the scaled virtual orbital energies (SVOE) were obtained. The highest occupied molecular orbital (HOMO) energy and SVOE for case of the F$_{16}$-CuPc film are schematically presented in Fig. 5a. Each of the orbitals calculated was visualized within the Gaussian software package and this way there was possible to assign the $\pi$ (in the case of HOMO), $\pi^*$ or $\sigma^*$ character to the orbital under consideration. The filled circles show the grouping of the $\pi^*$ or $\sigma^*$ orbitals in the case of the F$_{16}$-CuPc film (Fig. 5a). Let us mention that in the energy range 8-13 eV one observes both $\pi^*$ or $\sigma^*$ orbitals according to the present calculation results (Fig. 5a) while the assignment we made according to the literature data (Fig. 4, curve 3) corresponded to the $\sigma^*$ orbitals in this energy range. The
4 Conclusions

The modification of the structure of the unoccupied electronic states upon deposition of the ultrathin CuPc layer onto the fluorinated F$_{16}$-CuPc underlayer was determined using the incident beam of low-energy electrons according to the TCS method. The surface work function decreased from 4.9±0.1 eV to 4.3±0.1 eV during the formation of the CuPc/F$_{16}$-CuPc interface while the overlayer thickness increased up to 5 nm, which corresponds to the negative charge transfer from the CuPc overlayer to the F$_{16}$-CuPc underlayer. The comparison of the DOUS spectra of the unsubstituted film (CuPc) and of the fluorinated film (F$_{16}$-CuPc) showed that the fluorination was accompanied by the stabilization of the HOMO band, LUMO and the $\pi^*$ bands in the energy range from 8 eV to 13 eV above $E_F$.

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References


