Interaction and Energy Level Alignment at Interfaces between Pentacene and Low Work Function Metals

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ABSTRACT

A number of low workfunction metals (samarium, alkali metals) were deposited onto vacuum sublimed thin films of pentacene. The change in the valence electronic structure of the organic material was studied by in situ ultraviolet photoemission spectroscopy (UPS). Alkali metal intercalation leads to the appearance of a new photoemission feature within the pentacene energy gap, due to a charge transfer from the alkali atoms to the lowest unoccupied molecular orbital (LUMO) of the organic material. The energy spacing between this emission feature and the relaxed highest occupied molecular orbital (HOMO) of the pristine molecule is 1 eV. From X-ray photoemission spectroscopy core level analysis, we estimate a concentration ratio of two alkali metal atoms per pentacene molecule at maximum intercalation level, leading to a complete filling of the LUMO. This is consistent with the results from UPS that the new emission is always observed below the Fermi-level. Samarium is found to exhibit a more subtle interaction with pentacene: the molecular orbitals remain almost unperturbed upon Sm deposition. The resulting energy level alignment at this interface seems to be very favorable for the injection of electrons from Sm into pentacene, as the HOMO-onset is found at 1.8 eV below the metal Fermi edge. This value is close to the 2.2 eV HOMO-LUMO gap of pentacene measured by UPS and inverse photoemission spectroscopy, thus corresponding to a small electron injection barrier.

INTRODUCTION

Many conjugated organic materials are considered excellent candidates for the application in novel electronic and opto-electronic applications [1-4]. Pentacene in particular has attracted considerable attention since it was shown to exhibit structural and electronic properties that have been successfully used in high performance devices, i.e., field effect transistor and electrically pumped laser [5,6]. The chemical and electrical properties of interfaces of organic compounds determine to a large extent charge carrier injection and device stability, and are thus extremely important for device performance. Yet little information is presently available in literature on pentacene interfaces [7], in particular with metals that could be used for carrier injection. We begin to address this issue by investigating the interaction between pentacene and

low work function metals, i.e., Sm and alkali metals. Many studies of interfaces between conjugated organic materials and low work function metals have demonstrated that strong chemical interactions can take place between metal atoms and the organic molecules [8-11]. These reactions, which are sometimes accompanied by substantial diffusion [12], are often unwanted, as they change the expected interface properties.

EXPERIMENTAL DETAILS

The photoemission experiments were performed on the FLIPPER II beamline in Hasylab at DESY [13] in an ultra-high vacuum (UHV) system consisting of a preparation-evaporation chamber (base pressure 2×10^{-10} mbar) and an analysis chamber (base pressure: 1×10^{-10} mbar). The evaporations of pentacene, alkali metals and Sm were performed *in situ*, at pressures of ca. 5×10^{-9} mbar for pentacene, 2×10^{-9} mbar for Sm, and lower than 1×10^{-9} mbar for alkali metals. Pentacene (purchased from Aldrich Chem. Co.) was evaporated from a resistively heated pinhole source, Sm was evaporated from a Knudsen-type cell, alkali metals (Li, Rb) from SAES S.p.A. dispensers. *In situ* sputtered gold films on silicon oxide (prepared *ex situ*) are used to determine the position of the Fermi level and the resolution of the electron spectrometer (ca. 0.15 eV width of the intensity drop from 80% to 20 % on the Au Fermi-edge). Au/SiO$_2$ also serves as substrate for the deposition of the Sm films. The rates of deposition of the pentacene (bulk density: 1.33 g/cm^3 [14]) and Sm (bulk density: 7.54 g/cm^3) overlayers are monitored with a quartz microbalance. No correction is made for possible differences in sticking coefficient between the microbalance and the actual sample. The materials are evaporated in a stepwise manner, with very small initial coverages. Following each incremental deposition, the samples are transferred under UHV to the analysis chamber. The secondary electron cutoff is recorded with the sample biased negatively with respect to the electron spectrometer. The energy positions of the cutoff and of the top of the highest occupied molecular orbital (HOMO) are determined by linear extrapolation to the background. The vacuum level of the surface is obtained by adding the photon energy to the cutoff energy. The ionization energy (IE) of the sample (equal to the work function in the case of the metallic surface) is therefore obtained at each stage of the experiment as the difference between the incident photon energy and the total width of the energy distribution curve. We estimate the error in energy determination to be smaller than +/- 0.1 eV. A photon energy of 22.2 eV was used. For the study with alkali metals, an intercalation level of 100 % corresponds to a sample where no change in the photoemission spectra was observed for further exposure to the alkali metal flux.

DISCUSSION

Alkali metal intercalated pentacene films

It is known, that the intercalation of alkali metals into organic films leads to a significant decrease in sample work function [15]. Thus we have chosen Sm as the substrate for the pentacene films for the alkali metal (AM) intercalation study because, as we will show below, samples consisting of pentacene on Sm exhibit an already relatively low work function.

However, the Sm surfaces used here were slightly oxidized, resulting in a somewhat smaller HOMO-E_F (E_F...Fermi-level) spacing than reported for extremely clean Sm surfaces (see also below). For the pristine pentacene films (ca. 100 Å thick) we measure a HOMO-E_F spacing of 1.6 eV (topmost curves in Fig.1 (a) and (b)), and the sample work function is determined to be 3.3 eV. Subsequent deposition of AMs leads to (i) a shift of the pristine pentacene features towards lower kinetic energy, (ii) the appearance of two new photoemission features in the formerly empty energy-gap of the organic material, and (iii) a decrease in sample work function (determined from the secondary electron cut-off; not shown). In Fig. 1 the initial shift of the pentacene HOMO is evident. However, at ca. the fourth curve from the top, this shift seems to be reversed. The reason for this is the fact that not all pentacene molecules within the UPS probing-volume have undergone charge transfer from Li or Rb at intermediate intercalation levels. The AM atoms transfer electrons to the pentacene LUMO, leading to a destabilization of the HOMO-derived molecular orbital [16,17]. At 100 % intercalation level (lowest curves in Fig. 1), this destabilized HOMO is observed at a kinetic energy of 15.3 eV (for Rb; c.f. Fig. 1 (b)). The new photoemission peak at high kinetic energy (16.3 eV in Fig. 1 (b)) is thus derived from the filled LUMO. The above mentioned "reversal" of the shift of the pentacene HOMO is due to a decrease in intensity of the pristine pentacene HOMO and an intensity increase of the destabilized HOMO-derived peak of pentacene reacted with the AM. In a separate study (data not shown) of X-ray photoelectron spectroscopy on pentacene films intercalated with AMs we found that there were 2 AM atoms per pentacene molecule in the sample for 100 % intercalation level. From this observation we can conclude that negative bipolarons (dianions) are formed in AM intercalated pentacene films [16,17]. This is supported by the fact that no photoemission intensity at E_F is observed throughout the entire study [18].
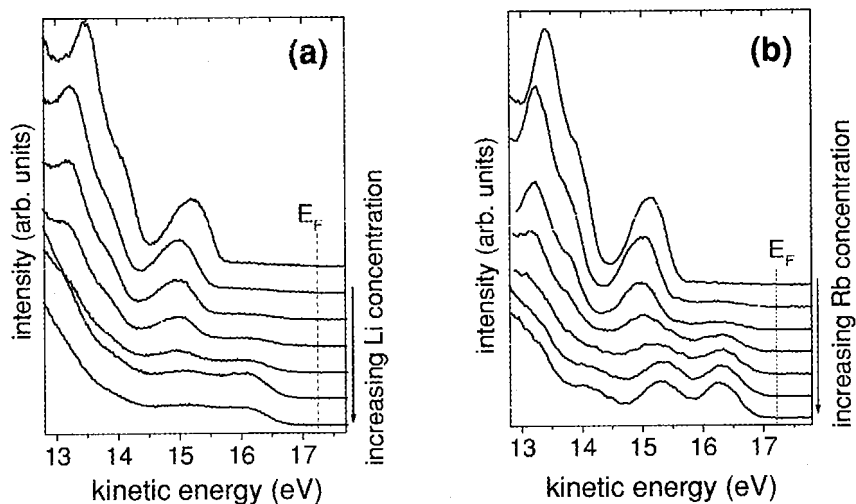
Figure 1. UPS spectra of 100 Å thick pentacene films (substrate: slightly oxidized Sm) for (a) increasing concentrations of Li and (b) Rb.

However, there are differences in the valence electron spectra for Li and Rb intercalation: at 100 % intercalation level, the spacing between the HOMO (of the reacted pentacene) and E_F is 0.3 eV smaller for Rb than for Li, and the resolution of the two new intra-gap states is much worse for Li. Possible reasons for this might be increased disorder for Li intercalation, or different positions of the AM counterions in the two cases. Experiments are currently being performed, which should provide insight into this open question.

Samarium and pentacene

A 90 Å thick film of samarium was deposited onto the Au/silicon oxide substrate. The photoemission spectrum of this film (topmost curve in Fig. 2) resembles that of metallic Sm [19]. The work function of the metallic surface was 2.7 eV. Increasing amounts of pentacene are subsequently deposited onto the Sm. The nominal thickness of the pentacene layer is given on the right side of the figure. The spectra show that small amounts of pentacene effectively attenuate the Sm emission and that distinct emission features of the organic material become evident even for very low coverages. Fig. 2 shows that the first evaporation step (0.3 Å) already produces a new photoemission feature at a kinetic energy of ~ 14.9 eV. As more pentacene is deposited, this feature grows in intensity at constant kinetic energy, and finally is identified as the emission from the pentacene HOMO [20]. Conversely, the photoemission features from the metallic Sm substrate are eliminated for coverages of 30 Å and above, leaving the energy-gap region of pentacene (above the HOMO) free of valence features. The onset of the HOMO is found at 1.85 eV below E_F. For increasing pentacene coverage, the secondary electron cutoff moves abruptly towards higher kinetic energy, and stabilizes (within experimental error) ca. 0.35 eV above the initial value for a pentacene thickness of 5Å. The final sample work function is 3.05 eV, and the ionization potential of pentacene is 4.9 eV. The photoemission feature that appears to be the HOMO of pentacene in Fig. 2 (at 14.9 eV kinetic energy) has a constant kinetic energy throughout the deposition sequence. Close inspection of deeper lying molecular orbitals shows that these levels do not shift either. The absence of bonding-related shifts is a strong indication of a weak interaction between metal substrate and organic overlayer. A strong chemical interaction at the interface would result in substantial changes in the kinetic energy and line-shape of molecular orbitals (MOs) [11,21,22], especially those of purely π-derived MOs like the HOMO. Such a strong interaction can therefore be ruled out here. The absence of any changes in the pentacene derived emission in the present experiment leads us to the conclusion that the interaction of pentacene with the Sm is mainly physisorptive. Analogous observations were made for *p*-sexiphenyl on Sm surfaces [19], for which the attenuation and lineshape change of the metal substrate valence emission close to E_F progress in a similar manner.

The UPS data show the Fermi level of the metal 1.85 eV above the HOMO-onset of pentacene. This value is very close to the charge-transport gap of pentacene of 2.2 eV [14]. We use this value to estimate the charge-transport gap, which results in an injection barrier for electrons from Sm into pentacene of 0.35 eV, an appreciably small value.

From the evolution of the intensity of the pentacene-derived photoemission features, some conclusions on the growth mode of the organic molecules on Sm can be drawn. An almost complete attenuation of the substrate emission above the HOMO occurs between 5 Å and 10 Å of pentacene. For pentacene molecules standing with their long molecular axis perpendicular to
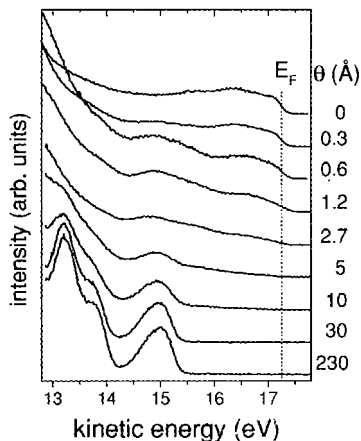
Figure 2. UPS spectra of a Sm metal film for increasing coverage (θ) with pentacene.

the substrate surface, this range of coverage corresponds to 1/3 to 2/3 of one monolayer (the length of one pentacene molecule is ca. 16 Å [23]). Since such a low coverage is incompatible with the strong attenuation of the substrate signal, we suggest that the molecules are oriented with their long molecular axis parallel to the metal surface. The assumption that a complete monolayer is formed around a nominal coverage of 5 Å is supported by the fact that the increase in sample work function also saturates near this film thickness. This finding is similar to reports on the orientation of pentacene and related conjugated molecules on other clean metal surfaces [24-26].

CONCLUSIONS

With ultraviolet and X-ray photoemission spectroscopy we have shown that Li and Rb form negative bipolarons (dianions) in pentacene thin films. However, differences in the lineshape and energy position of the valance electron spectra between the two alkali metals are observed, and (speculatively) attributed to increased disorder in the Li-intercalated film, or a difference in the position of the counterions relative to the pentacene molecules.
Although Sm has a rather low work function (2.7 eV), our UPS data indicate that the interaction at the Sm/pentacene interface is of physisorptive character. The electron injection barrier at this interface is estimated to be 0.35 eV.

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