Cambridge University Press
978-1-107-41197-5 - Materials Research Society Symposium Proceedings: Volume 708: Organic Optoelectronic Materials, Processing and Devices
Editor: Steven C. Moss
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Metal/Organic Interfaces—Electronic Structure and Charge Injection

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978-1-107-41197-5 - Materials Research Society Symposium Proceedings: Volume 708: Organic Optoelectronic Materials, Processing and Devices
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Mat. Res. Soc. Symp. Proc. Vol. 708 © 2002 Materials Research Society **BB2.3**

A photoemission spectroscopic study of the interface formation in organic thin film transistors

Neil J. Watkins, Serkan Zorba, Li Yan and Yongli Gao
Department of Physics and Astronomy,
University of Rochester, Rochester, NY 14627 U.S.A.

ABSTRACT

Pentacene is widely used in organic thin film transistors due to relatively large mobilities. It has been suggested that the functional behavior in these organic thin film transistors occurs within the first few molecular layers of the device at the interfaces between the organic and the metals and dielectrics used in fabrication of the thin film transistors. This makes understanding the electronic behavior of the interfaces involved in these devices critical. In order to better understand these interfaces we investigated the interface formation using photoemission spectroscopy to examine layer by layer growth of pentacene on Au and Ag and vice versa. We observed indications of dipole formation at the interfaces between the metals and organics for organic on metal deposition. On the other hand, more complex material intermixing takes place during metal on organic deposition and as a result, the electronic structure of the interface differs from that of organic on metal deposition.

INTRODUCTION

In the past few years, the performance of organic thin-film transistors has improved considerably due, in part, to use of pentacene as an active material [1-3]. Pentacene is of use in these organic based devices due to its relatively high mobility [3-9]. Pentacene based devices have exhibited, at room temperature, performance comparable to hydrogenated amorphous silicon devices: on/off current ratios at 10 V in the range of 10^6, room temperature mobilities as high as 2.7 cm /Vs, and operating voltages as low as 5 volts [8,9]. At low temperatures, pentacene device mobilities are as high as 10 cm /Vs [9]. Superconducting behavior has been observed in single crystal pentacene field effect transistor devices [10]. Fractional quantum Hall measurements have also been made with these same device structures [11].

It is generally believed that device performance is heavily influenced by the characteristics of the interfaces between the organic and the metals and dielectrics used in fabrication of the thin-film transistors [8,12,13]. For instance, it has been shown that the morphology of pentacene films affects device mobilities. Thin film transistors can be built using device geometries such as staggered and staggered-inverted. These different geometries require that the electrodes and dielectric be deposited or grown in reversed orders. This variety makes understanding any differences in the interface properties that may result from different orders of growth of interest. We have examined the formation of interfaces between pentacene and Au and Ag.

EXPERIMENTAL DETAIL

Photoemission measurements were made using two techniques. X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) studies were performed using a VG ESCA Lab system equipped with an unfiltered He I (21.2 eV) gas discharge lamp and a Mg Kα X-ray source (1251 eV). UPS spectra were recorded with a bias of 5.0 V to enable the observation of the low energy secondary cut-off. The base pressure in the analysis chamber was 8x10^{-11} Torr. The substrates used for the experiments were Au-coated silicon wafers and were cleaned by Ar plasma etching followed by evaluation of surface cleanliness by XPS. This was followed, in situ, by deposition of the substrate material for the interface studies. All steps of the sample preparation were performed at room temperature in an ultra high vacuum (UHV) system.

The experimental approach used was a layer by layer measurement cycle. In this approach a clean substrate is prepared in the vacuum chamber and then characterized using XPS and UPS. The material under investigation is then deposited onto the substrate and the surface is recharacterized. More material is then deposited and the surface is once again recharacterized. This is repeated until the sample is characterized as equivalent to a bulk sample of the deposited material. This procedure attempts to map the electronic and chemical structure in the deposited material as a function of distance from the interface. We separately exposed a 300 Å layer pentacene to several hours of XPS and UPS measurements and saw no evidence of radiation induced damage.

DISCUSSION

XPS: Au/Pentacene

In Figure 1 we show evolution of the carbon peak as Au is deposited onto pentacene. This peak shows a couple of important features. As the Au thickness increases, up to 4 Å, the carbon peak position shifts 0.5 eV to higher binding energy. While the peak does shift there is no change

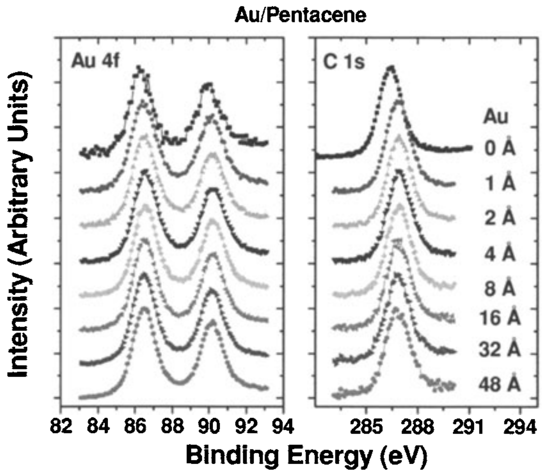

Figure 1. Gold 4f and Carbon 1s XPS peaks as a function of Au thickness. The gold peaks at 0 Å of gold coverage represent the gold substrate that the pentacene is deposited onto.

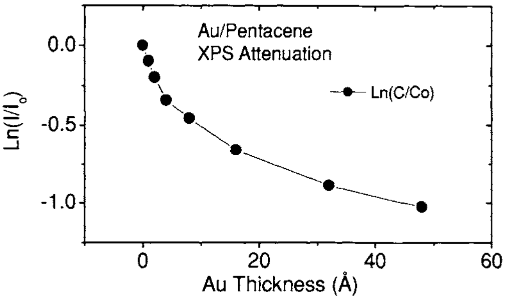

Figure 2. Attenuation of Carbon 1s XPS peak as a function of Au thickness.

in the peak shape that would indicate a chemical reaction at the surface. Looking at the evolution of the gold peak we see only an offset of 0.2 eV compared to the peak position of the Au layer that the pentacene was deposited onto. From the XPS data we can say that there is no chemical reaction at this interface. The changes in the magnitude of the carbon XPS peak, shown in Figure 2, indicate that the growth of gold on the surface is not simple layer by layer growth. The growth may be either clustering or even penetration of the gold into the pentacene substrate.

XPS: Pentacene/Au

In Figure 3 we show the evolution of the XPS spectra as a function of pentacene deposition onto Au. The carbon 1s peak exhibits a gradual shift of 0.25 eV to lower binding energy while the Au 4f peak position remains constant. No evidence of energy level shifting or chemical reaction is seen in this interface.

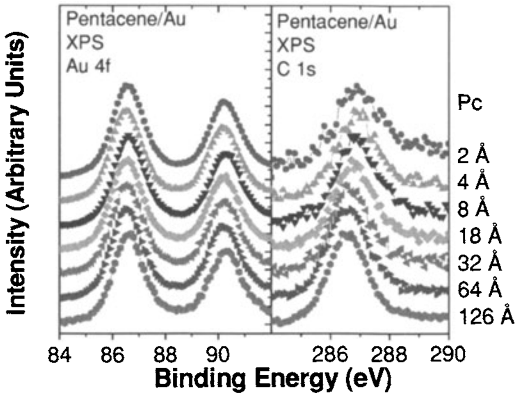

Figure 3. Au 4f and carbon 1s XPS peak as a function of pentacene deposition.

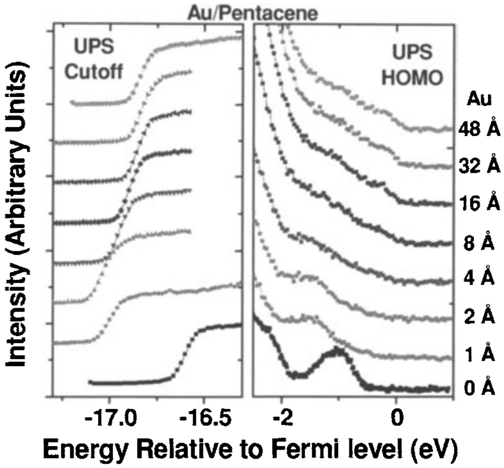

Figure 4. UPS cutoff and HOMO as a function of Au thickness. An initial shift of 0.5 eV away from the Fermi level is seen in both the cutoff and HOMO positions while only the cutoff shows a shift of 0.3 eV back towards the Fermi level as more Au is deposited.

UPS: Au/Pentacene

In Figure 4 we show the evolution of the UPS spectra of the sample as gold is deposited onto the pentacene substrate. A couple of features are evident in these spectra. After 8 Å of gold deposition there is a detectable Fermi level and the pentacene's highest occupied molecular orbital (HOMO) features have been mainly suppressed, indicating the presence of metallic gold on the surface. Yet even after 48 Å of gold the HOMO features that are associated with a metallic gold layer are still not apparent. This is further evidence that the gold has not yet formed a continuous layer, possibly forming clusters on the surface of the pentacene as suggested by the XPS results.

Figure 4 also shows that the vacuum level shifts 0.5 eV closer to the Fermi level upon the deposition of only 1 Å of gold. This is followed by a gradual increase of the vacuum level until it is only 0.2 eV closer to the Fermi level than it originally was for the pentacene surface. This means that the final surface has a work function of 4.2 eV instead of the 5.4 eV that would be expected for a continuous gold surface, suggesting that even though we do have a metallic surface it is not a simple gold surface. The initial shift of the vacuum level of 0.5 eV matches the shift seen in the carbon XPS peak whereas the subsequent shift of 0.3 eV in the vacuum level is not seen in the carbon XPS peak Therefore we attribute the initial shift of 0.5 eV to shifting of the energy levels at the surface while the later 0.3 eV is caused by the formation of an interface dipole.

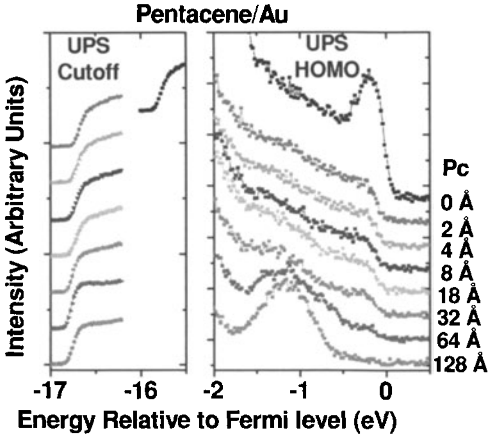

Figure 5. UPS cutoff and UPS HOMO evolution as a function of pentacene deposition onto gold. A total shift of 1 eV away from the Fermi level was seen in the UPS cutoff after the deposition of 18 Å of pentacene. Only gradual changes in intensity of features were seen in the UPS HOMO.

UPS: Pentacene/Au

In Figure 5 we see the changes caused by deposition of pentacene onto Au. There is an initial shift of the vacuum level 0.8 eV closer to the Fermi level after the deposition of 2 Å of pentacene. This shift increases to a total of 1 eV after the deposition of 18 Å of pentacene. While these changes are observed in the cutoff position we see no apparent change in any feature position within the UPS spectra. A decrease in Au UPS features and a gradual increase in the pentacene UPS spectral features is observed. When combined with the lack of indications of energy level shifts in the XPS spectra the shifts in the vacuum level indicate a interface dipole when pentacene is deposited onto Au.

Summary

In Figure 6 we show the energy diagrams for the pentacene interfaces with Au and Ag determined using this type of analysis, the Ag data having been discussed more in depth in a previous paper [14]. It can be seen that neither Au nor Ag formed a pure metal surface when deposited onto pentacene, as indicated by the Au* and Ag* symbols. As seen in Figure 6, when metal was deposited onto pentacene energy level shifting was observed. The doping region width in these cases, w > 50 Å, was estimated from XPS core level analysis [15].

CONCLUSION

We have examined interfaces formed between pentacene and Au and Ag. For the pentacene on Au and Ag interfaces we observed immediate formation of a surface dipole. For the metal on pentacene interfaces we saw both Au and Ag exhibiting signs of metal penetration of the

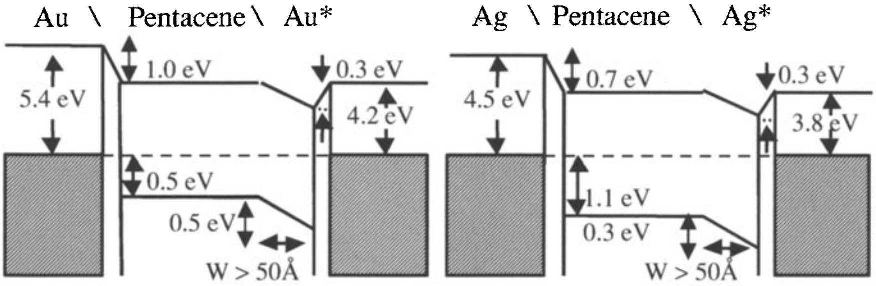

Figure 6. Energy Diagrams of the interfaces between pentacene and Au and Ag. The Au* and Ag* indicate the creation of a metallic surface that does not exhibit the properties of a clean metal surface of the Au or the Ag. Deposition is from left to right.

pentacene film coupled with formation of metal clusters. Both Au and Ag formed asymmetric interfaces with pentacene.

ACKNOWLEDGMENTS

This work was supported in part by NSF DMR-9982988.

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Mat. Res. Soc. Symp. Proc. Vol. 708 © 2002 Materials Research Society **BB2.4**

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

N. Koch[1], J. Ghijsen[2], R. Ruiz[3], J. Pflaum[4], R. L. Johnson[5], J.-J. Pireaux[2], J. Schwartz[6], and A. Kahn[1]
[1] Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, U.S.A.
[2] Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, B-5000 Namur, Belgium
[3] Vanderbilt University, Department of Physics and Astronomy
Nashville, TN 37235, U.S.A.
[4] 3. Physikalisches Institut, Universitaet Stuttgart, D-70569 Stuttgart, Germany
[5] II. Institut für Experimentalphysik, Universität Hamburg, D-22761 Hamburg, Germany
[6] Department of Chemistry, Princeton University, Princeton, NJ 08544, U.S.A.

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

Cambridge University Press
978-1-107-41197-5 - Materials Research Society Symposium Proceedings: Volume 708: Organic Optoelectronic Materials, Processing and Devices
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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.