

## The effect of surface treatment on interface formation between pentacene and polymer dielectrics

Seung Jin Han<sup>1,2</sup>, Jae Hoon Kim<sup>1</sup>, Yongsup Park<sup>3</sup>, Kyu-Ha Back<sup>4</sup>, Gi-Heon Kim<sup>4</sup>, Lee-mi Do<sup>4</sup>, Sa-Hwan Hong<sup>2</sup>, Dal-Hyun Kim<sup>2</sup>, and Jeong Won Kim<sup>2,\*</sup>

<sup>1</sup>Department of Electronics and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seoul 133-791, Korea

<sup>2</sup>Korea Research Institute of Standards and Science (KRISS), 1 Doryong-dong, Daejeon 305-340, Korea

<sup>3</sup>Department of Physics, Kyung Hee University, 1 Hoegi-dong, Dongdaemun, Seoul 130-701, Korea

<sup>4</sup>Electronics and Telecommunications Research Institute (ETRI), 161 Gajeong-dong, Daejeon 305-700, Korea

TEL:82-42-868-5761, e-mail: jeongwonk@kriss.re.kr.

**Keywords:** pentacene, OTFT, interface, UV/Ozone treatment, polymer dielectrics

### Abstract

*Electronic and structural properties of the interfaces formed by pentacene deposited on a polymer-based dielectrics are investigated by electron spectroscopy, atomic force microscopy, and water contact angle measurement. There is strong influence of surface treatment of the polymer dielectrics on the energy level alignment and the surface topography upon the pentacene deposition.*

### 1. Introduction

In the past few years, the performance of organic thin film transistors has been improved considerably [1-3]. Among the conjugated oligomers used as active materials in the fabrication of organic thin film transistor, pentacene is one of the most promising materials due to its high field-effect mobility. Since the performance of pentacene-based organic thin film transistors (OTFTs) is comparable to that of hydrogenated amorphous silicon thin film transistor, a growing interest has been focused on the process of OTFTs for the applications to low-cost and large-area flexible displays [4-5]. As the characteristics such as mobility and on/off ratio of the OTFTs are greatly influenced by the interfacial structure formed between organic semiconductor and gate dielectrics, the preparation of the underlying dielectrics and

deposition of semiconductor layer are critical steps to improve their performance. Polymethyl methacrylate (PMMA)-derivative polymers are one of the new materials used as dielectric insulators in organic semiconductor transistors. Such layers are used recently as a buffer layer between the pentacene and the dielectric gate layer to enhance electronic properties [6]. We examine the electronic properties of interfaces formed by pentacene deposited on a polymer-based dielectrics (K1) pre-coated on a Si substrate. In particular, to pursue any effect of surface modification of the K1, we treated the K1 surface by UV/Ozone (UVO) irradiation and compared it with not-treated one. The UVO treatment is a well established method for cleaning surfaces and removing organic contaminants. Such treatment has been employed before for the SiO<sub>2</sub> dielectric layer which affects threshold voltage and mobility of an OTFT.

### 2. Experimental

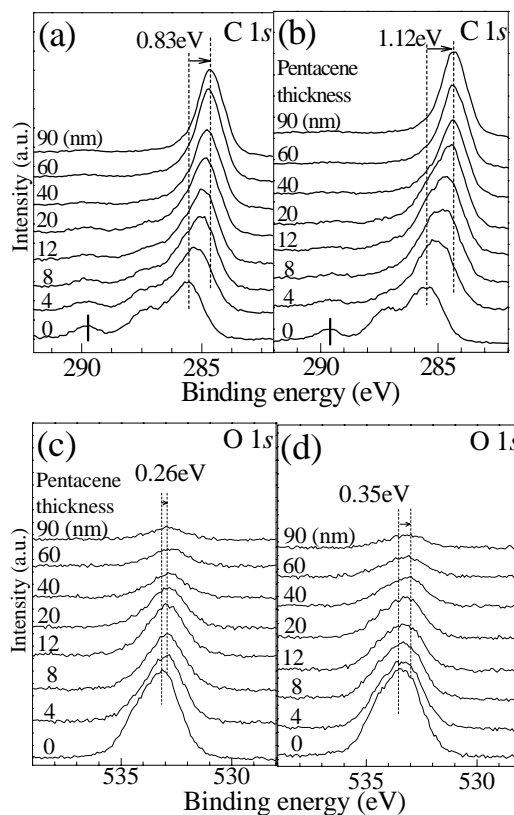
We examined the chemical reaction, energy level alignment, and dipole formation of interfaces formed by pentacene deposited on a PMMA-derivative polymer-based dielectrics (K1) pre-coated on a Si substrate. The K1 is a mixture of PMMA based copolymers and trimellitic anhydride dissolved in

di(ethylene glycol) methyl ethyl ether. For the chemical and electronic analysis of the interfaces, x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), atomic force microscopy (AFM), and contact angle measurements were performed. The XPS and UPS studies were performed using a VG ESCA Lab 220i system equipped with He I (21.2 eV) gas discharge lamp and a Mg  $K_{\alpha}$  x-ray source (1253.6 eV). The UPS spectra were recorded with a -10 V bias to the sample to enable the observation of the low kinetic energy secondary cutoff. A few-nm-thick layer of the K1 on a pre-cleaned Si wafer was spun at 8000 rpm for 30 s to form a film thin enough to avoid surface charging during the photoemission experiments. Thereafter, it was baked at 150°C for 1 hour on a hot plate. The UVO treatment of the K1 on Si wafer was accomplished using low pressure mercury vapor grid lamp (Jelight Company Inc.) under ambient condition. The samples were introduced into the ultra high vacuum system typically in 20 min. after the UVO treatment. The deposition of pentacene on top of the K1 film was carried out by thermal evaporation and monitored with a quartz crystal microbalance. The deposition rate was kept about 2 nm per min. with the substrate at room temperature. The pentacene films were analyzed by XPS and UPS without exposing to air. A DI Nanoscope 3 AFM was used to measure the topography of the final film surfaces.

### 3. Results and discussion

C 1s and O 1s XPS spectra taken for different pentacene thickness are displayed in Fig. 1. Figs. 1(a) and (b) show C 1s XPS spectra under the deposition of pentacene on the K1 polymer with and without UVO treatment, respectively. The C 1s peaks for K1 surfaces with UVO treatment and without UVO treatment reside at the binding energies of 285.52 and 285.44 eV, respectively and are shifted by 0.83 and 1.12 eV toward lower binding energy upon increasing pentacene thickness. We observe similar spectral behavior for O 1s spectra for the samples with and without UVO treatment respectively through the binding energy shifts of 0.26 and 0.35 eV lower than before pentacene deposition [Figs. 1(c) and (d)]. These shifts of C 1s and O 1s core levels toward lower binding energies indicate that pentacene deposition leads to a new surface dipole formation either by a chemical reaction between the pentacene

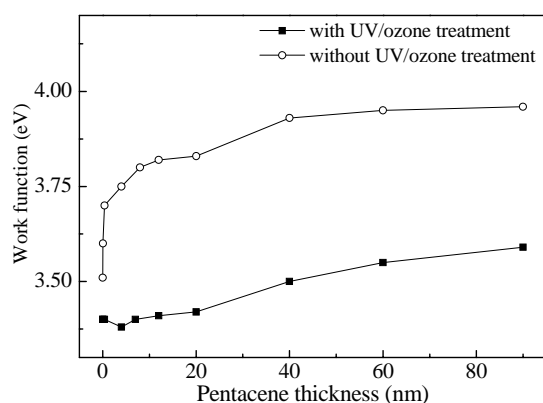
and polymer dielectrics or by a specific molecular stacking. However, the core level binding energy shift is smaller in case of UVO-treated K1 surface compared with that without the UVO treatment.



**Fig. 1. Evolution of C 1s peaks as a function of pentacene thickness deposited on a K1 pre-coated Si substrate: (a) with and (b) without UV/ozone treatment. Evolution of O 1s peaks with the same sequence above: (c) with and (d) without UV/ozone treatment.**

Fig. 2 shows the work function changes measured by UPS for different pentacene thickness (4 – 90 nm) on the K1 surfaces. The work functions of the films in the Fig. 2 are obtained by extrapolating linearly the high binding energy cutoff region and taking both the analyzer function and thermal broadening into account. As pentacene is deposited onto the K1, the high binding energy cutoff positions are shifted toward lower binding energy side (i.e. lowering the work function). At a maximum pentacene coverage,

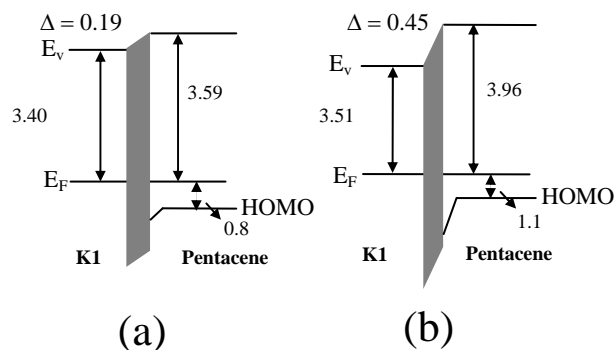
the high binding energy cutoff positions for the UVO-treated and not-treated K1 respectively are shifted by 0.19 and 0.45 eV. The shifts of the high binding energy cutoff also suggest that there occurs a new interface dipole formation between pentacene and K1, but the magnitudes of the interface dipole changes are different on the two different K1 surfaces. In addition, the highest occupied molecular orbital (HOMO) level of pentacene appears upon 4 nm of deposition, and the final positions for the 90 nm of pentacene on the UVO treated and untreated K1 surfaces are respectively determined to be 0.8 and 1.1 eV below  $E_F$  (not show here).



**Fig. 2. Work function changes determined by high binding energy cutoff positions in UPS spectra for pentacene/K1 with and without UV/ozone treatment.**

Based on the analysis of UPS spectra, the interfacial energy diagrams for the pentacene on the two different initial K1 surfaces are summarized for comparison in Figs. 3(a) and (b). For the UVO-treated polymer surface, relatively small change of electric dipole is induced, which is consistent with the above XPS results where the peak shifts are smaller, as discussed in the following. Since the XPS peak shift can generally be explained by charge transfer, chemical reaction, or polarization screening by the deposited organic semiconductor. The magnitude of the changes in the binding energies of all the elements, along with the appearance of the pentacene HOMO in the UPS spectra after as little as 4 nm of pentacene deposition, suggests there is chemical reaction

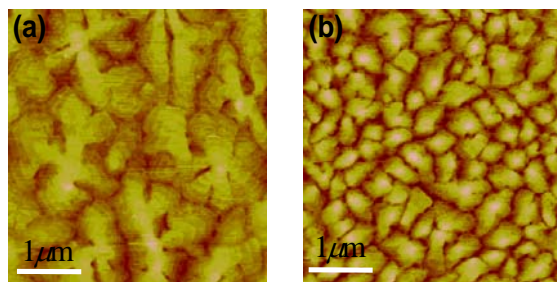
between the K1 and pentacene. Any significant change in the vacuum level also suggests that there is the charge transfer of interface between pentacene and K1. This is similar to the core level shift of pentacene with metal, where linear behavior of the interface dipole with respect to the metal work function was observed that could be an indication of interface charge transfer [7].



**Fig. 3. Energy level diagrams of pentacene/K1 interfaces (a) with and (b) without UV/ozone treatment. The energy scales are eV's.**

In Figure 4, AFM topographs for 60 nm pentacene films deposited on the two different K1 polymer surfaces are displayed. For the UVO treated K1 surface, the grain size of the pentacene film (around  $2.13 \mu\text{m}^2$ ) is much larger than the not-treated case (about  $0.43 \mu\text{m}^2$ ). The root-mean-square (RMS) roughness of the UVO treated K1 initial surface (around 0.48 nm) is slightly larger than the not-treated case (about 0.34 nm). Also, after depositing a pentacene (60 nm) on the K1/SiO<sub>2</sub>, the RMS roughness of the UVO treated K1 surface (around 3.41 nm) is larger than the not-treated case (about 3.06 nm). The difference of the initial roughness may be on reason for generating the differences in the XPS core level shifts in Fig. 1 and work function changes in Fig. 2, in that the changes are gentle in case of UVO treated surface. Moreover, the UVO treatment of the underlying K1 polymer dielectric surface significantly influences the interface dipole formation and pentacene growth, so that the pentacene film has smaller dipole change and larger grain size. The water contact angles of the K1 polymer surfaces before and after the UVO treatment are 60° and 20° respectively. The UVO treatment dramatically decreases the water

contact angle of K1 surface. This is consistent with a previous result that the high surface energy of a polymer film induces a large grain size of pentacene film deposited on it [8].



**Fig. 4.** AFM images for 60 nm of pentacene films deposited on the K1 surfaces (a) with and (b) without UV/ozone treatment.

#### 4. Summary

We have measured energy level alignment by UPS and film morphologies by AFM for pentacene films deposited on polymer dielectrics. The intrinsic behavior of the surface upon the pentacene deposition involves chemical interaction, charge transfer, and interface dipole formation. When the pentacene is deposited on the K1 after the UVO treatment, the interface dipole change is marginal and the grain size

is larger compared to those for pentacene film deposited on untreated K1 surfaces. Such differences seem to be related to difference chemical reactions occurring on the two different interfaces. The strong influence of the UVO treatment of an initial polymer dielectric surface on the interface properties is also expected to cause different OTFT performance for pentacene-based organic semiconductors.

#### 5. References

1. A. Tsumura, H. Koezuka, and T. Ando, *Appl. Phys. Lett.* **49**, 1210 (1986).
2. G. Horowitz, *Adv. Mater.* **10**, 365 (1998).
3. H. E. Katz and Z. Bao, *J. Phys. Chem. B* **104**, 671 (2000).
4. C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, *Science* **283**, 822 (1999).
5. N. Benson, M. Schidleja, C. Melzer, R. Schmechel, and H. von Seggern, *Appl. Phys. Lett.* **89**, 182105 (2006).
6. S. Y. Yang, K. Shin, and C. E. Park, *Adv. Funct. Mater.* **15**, 1806 (2005)
7. N. J. Watkins, Li Yan, and Y. Gao, *Appl. Phys. Lett.* **80**, 4384 (2002).
8. D. Guo, S. Entani, S. Ikeda, and K. Saiki, *Chem. Phys. Lett.* **429**, 124 (2006).