

Effects of UV/ozone treatment of a polymer dielectric surface on the properties of pentacene thin films for organic transistors

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Ultraviolet photoelectron spectroscopy and atomic force microscopy (AFM) were used to investigate the energy level alignment and growth morphology of pentacene (Pn) films deposited on a PMMA derivative-based dielectric surface with and without ultraviolet/ozone treatment. The treated surface exhibited higher offset values for the highest occupied molecular orbital levels between Pn and the polymer, which would result in higher threshold voltages for the device. However, aligned vacuum levels of the treated surface and the Pn at the interface were observed, suggesting that the dipole field would be reduced in the Pn film on the treated surface. The hydrophilic nature of the treated surface, observed by water contact angle measurement, allowed for a larger grain size of the Pn film, as confirmed by the AFM measurements, which will also favorably contribute to device mobility. © 2008 American Institute of Physics. [DOI: 10.1063/1.2951905]

I. INTRODUCTION

Organic thin film transistors (OTFTs) are drawing considerable interest for the low-cost and large-area flexible electronic device applications. Despite the extensive research efforts to discover better materials for the active layer of OTFTs, pentacene (Pn) remains one of the best molecules for device applications due to its high field-effect mobility and easy film formation properties.¹⁻⁴ It is well known that the OTFT device characteristics, such as mobility, threshold voltage, and on/off ratio, are greatly influenced by the interfacial structures between organic semiconductors and the gate dielectrics. Therefore, the preparation and treatment of the dielectric layer, as well as the formation of the semiconductor layer on the dielectric, are crucially important for improved device performance. Many studies were devoted to the investigation of the interfacial properties between Pn and inorganic gate insulators in trying to find their correlation with device performance.⁵⁻⁷

In addition to the conventional inorganic materials such as SiO₂, Al₂O₃, and HfO₂, various organic materials were also tried for the gate dielectric in OTFTs. The organic gate dielectric is a key ingredient for the realization of all-organic transistors, which is important for flexible display and other low-cost device applications. Insulating polymers including poly-4-vinylphenol, polyimide, parylene, and polyaniline have been successfully employed for the gate dielectric and have shown to enhance device performance.⁸⁻¹¹ In addition, polymethyl methacrylate (PMMA) derivative polymers are

one of the new materials for the gate dielectric or buffer layer, exhibiting high field-effect mobility and low threshold voltages.^{12,13} Additional interface engineering using a self-assembled monolayer under the Pn layer also exhibited excellent subthreshold voltage characteristics.¹⁴⁻¹⁶

In this paper, we examined the interface energy level alignment and the formation morphology of Pn films deposited on a polymer dielectric layer, which is composed of PMMA-derivative (K1). K1 is a mixture of PMMA-based copolymers and trimellitic anhydride dissolved in di(ethylene glycol) methyl ethyl ether. It was previously shown that some of the OTFT devices exhibited enhanced threshold voltage and carrier mobility when the insulator surface was treated with ultraviolet/ozone (UVO),¹⁷ which is a well-established method for removing organic and other contaminants from the surface. We studied the Pn/K1 interface by employing the K1 surface with and without UVO treatment to clarify its effects on the interface electronic structure and film formation properties. The ultraviolet photoemission spectroscopy (UPS) investigation of the interface between the Pn and UVO-treated K1 polymer dielectrics revealed that the highest occupied molecular orbital (HOMO) level offset values are larger than those of the untreated surface, which would result in a higher threshold voltage. However, alignment of vacuum levels of the treated K1 surface and the Pn at the close vicinity of the interface suggests that the dipole field will be reduced in the Pn film on the treated K1 surface, resulting in higher device mobility. It is also shown that the hydrophilic nature of the UVO-treated K1 accommodates a large grain size of the Pn film on its surface as confirmed by the atomic force microscopy (AFM) measurements, which

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will also contribute to the higher mobility. It is due to the fact that the UVO-treated polar surface prefers the vertical alignment for the Pn molecular orientation and, at the same time, gives rise to a smaller interface dipole within the Pn film.

II. EXPERIMENTS

For the analysis of the chemical and electronic properties of the interfaces, we performed UPS, AFM, and water contact angle measurements. UPS experiments were carried out using a modified VG ESCA Laboratory 220i system equipped with a He I (21.2 eV) gas discharge lamp. 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-nanometer-thick layer of the K1 was spin coated at 8000 rpm for 30 s on a precleaned Si wafer to form a film thin enough to avoid surface charging during the photoemission experiments. Thereafter, it was baked at 150 °C for 1 h on a hot plate. The UVO treatment of the K1 film was performed using a low pressure mercury vapor grid lamp (Jelight Co. Inc.) under ambient condition. Thermal evaporation of the purified Pn molecules was carried out on the K1 films at room temperature and the thickness was monitored with a quartz crystal microbalance. The deposition rate was kept at about 2 nm/min. The base pressure of the deposition chamber was 5×10^{-9} Torr. Then, the sample was transferred to an analysis chamber without breaking the vacuum and the UPS spectra were recorded. A Digital Instrument Nanoscope 3 AFM was used to measure the morphology of the films in the ambient conditions.

III. RESULTS AND DISCUSSION

Figure 1 shows Pn thickness dependent work function changes and valence band spectra near the Fermi level for the Pn/K1 interfaces measured by the UPS for the Pn thickness range of 4–90 nm. It is clear that the deposition of the Pn increased the work function for both the UVO-treated and untreated surfaces as evidenced by the shifts in low kinetic energy cutoff. However, for the untreated K1 surfaces, the rate and the amount of work function change as a function of Pn thickness were much greater than those for the treated K1. As seen in Fig. 1(a), for the untreated sample, the changes in work function were mostly completed at about 30 nm of Pn, while the change continues up to 90 nm for the treated sample. The total work function changes of the untreated and treated K1 polymer surfaces at the Pn coverage of 90 nm were 0.45 and 0.19 eV, respectively.

It is the energy level alignment very close to the Pn/dielectric interface that greatly influences the device performance because only a few of the molecular layers at the interface determine the charger carrier transport in the field-effect transistors. Therefore, we focus on the changes at the early stages of the Pn deposition on K1. The work function shifts due to the Pn deposition on the untreated surface are 0.1 eV (4 nm), 0.2 eV (8 nm), and 0.26 eV (12 nm), indicating about 0.26 eV of vacuum level offset at the interface. The UVO-treated surface, on the other hand, exhibited virtually no work function shift up to 12 nm of Pn thickness. This suggests that for the UVO-treated K1 surface, the vacuum

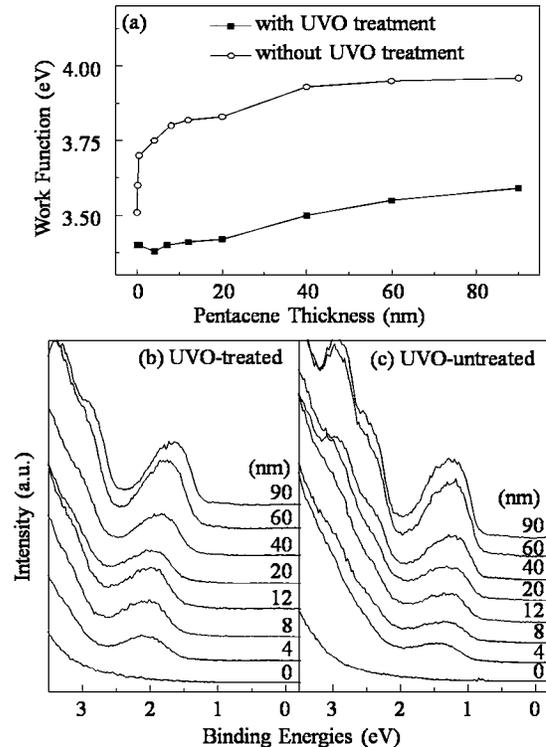


FIG. 1. (a) Work function changes of Pn/K1 interfaces obtained from the low kinetic energy cutoff of the UPS spectra. UPS spectra of HOMO regions for the Pn/K1 interfaces (b) with and (c) without UVO treatment.

level alignment is valid at the interface. The differences in vacuum level offset imply different magnitudes of interface dipole formation for the two interfaces. The magnitude of the vacuum level offset of the untreated K1 interface is comparable to that of Pn/ Al_2O_3 (0.25 eV change).⁵ For the UVO-treated surface, it is similar to Pn/ SiO_2 with vacuum level alignment.⁶ The presence of an interface dipole might have originated from a strong interaction between molecular orbitals of Pn and the untreated K1 polymer surface. In fact, C 1s and O 1s x-ray photoelectron spectroscopy (XPS) core level spectra (not shown) revealed more pronounced changes in the chemical states of carbon and oxygen for the untreated surface upon Pn deposition, which implies that the origin of the interface dipole is probably due to chemical reactions. Since the chemical change and resultant interface dipole formation for the untreated samples occur within the thickness range most relevant to the charge carrier conduction, which is about two layers of Pn, this difference in interface dipole can have a significant impact on the conduction of mobile charge carriers in real devices.

The valence band region for each surface upon Pn deposition is displayed in Figs. 1(b) and 1(c). For bare K1 surfaces, the onsets of valence band peaks relative to the Fermi level E_F (band offset) were at 4.0 and 4.2 eV for the untreated and treated ones, respectively (not shown). The difference in surface energy is also manifested in water contact angle measurements. The K1 polymer surface without the UVO treatment exhibited a contact angle of 60° , while that of the treated surface was 20° . The UVO treatment rendered the surface highly hydrophilic, which we believe is due to

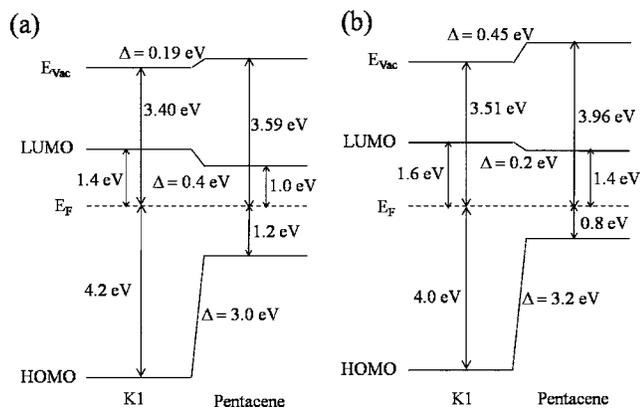


FIG. 2. Energy level diagrams of Pn/K1 interfaces (a) with and (b) without UVO treatment, derived from the results in Fig. 1. In (a), the vacuum level offset is nearly zero up to 12 nm of Pn but eventually becomes 0.19 eV at 90 nm. In (b), the offset is 0.26 eV near the interface and increases to 0.45 eV at 90 nm.

the changes in the chemistry, although a possibility for the surface roughness change cannot entirely be ruled out.

The HOMO level of Pn is clearly present at the Pn thickness above 4 nm, and the onset positions of the HOMO were 0.9 (untreated) and 1.6 eV (treated). The HOMO onsets gradually shifted to the lower binding energy side with increasing Pn thickness. At the Pn thickness of 90 nm, the onsets of the HOMO levels on the untreated and UVO-treated K1 surfaces are 0.8 and 1.2 eV, respectively. We believe that there is no possibility for the kind of wave function overlap described in Ref. 18 between the substrate and the Pn layer and concomitant Fermi level pinning. It was recently reported that the HOMO peak of the Pn crystalline film is actually composed of more than one peak, and an angle-resolved UPS showed that each peak has different dispersion characteristics, suggesting a strong intermolecular interaction between stacked Pn molecules.^{19,20} One of the consequences of such dispersions is the broadened HOMO peaks evident in our angle-integrated UPS measurements of multi-grain Pn films.

Based on the analysis of the UPS spectra above, the energy level alignment diagrams for the interfaces between Pn and the two different K1 surfaces are summarized in Fig. 2. The lowest unoccupied molecular orbitals (LUMO) for the PMMA and Pn were deduced from the previous band gap measurements (5.6 and 2.2 eV, respectively).^{21,22} The ionization energies of the Pn films on both cases are identically 4.8 eV. The measured HOMO energy level offsets between Pn and K1 are 3.0 and 3.2 eV for the treated and untreated K1 surfaces, respectively. The corresponding values for the LUMO energy levels are 0.4 and 0.2 eV, respectively. These values were measured at a Pn thickness of 90 nm. The more relevant values for the device performance would be the ones measured at 4 nm, where the HOMO energy level offsets are 2.6 and 3.1 eV for the treated and untreated K1 surfaces, respectively, and the LUMO level offsets are 0.8 and 0.3 eV. The larger HOMO level offset for the UVO-treated surface can lead to a higher threshold voltage for a *p*-type field-effect device.²³ However, we believe that a more significant difference affecting the measured device mobility is that the

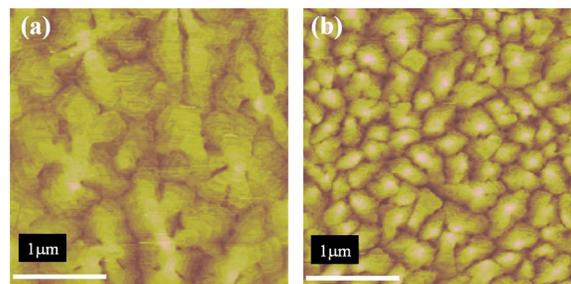


FIG. 3. (Color online) AFM images of 60 nm thick Pn films deposited on K1 polymer dielectrics (a) with and (b) without UVO treatment.

vacuum levels are aligned for the UVO-treated K1 surface with no energy level offset, while it is 0.26 eV for the untreated K1 surface. For the UVO-treated interface, the energy level offset eventually becomes 0.19 eV but is spread out through the thickness range of 90 nm. Therefore, the resultant dipole field will be minimal and will virtually have no influence on the holes flowing within the few Pn layers close to the Pn/K1 interface. For the untreated K1 surface, an almost 0.26 eV change occurs within the range of 12 nm in the Pn layer. This will, in turn, give much stronger dipole field. One can imagine that the holes flowing in the channel layer would be greatly influenced by this electric field, resulting in a worse measured mobility in these devices.²⁴

One of the most important factors contributing to the device mobility is undoubtedly the grain size of the multi-grain Pn films. If the grains are larger, so is the mobility, until the adverse effect of intergrain hopping starts to appear. To investigate the effect of UVO treatment of the K1 surface on the Pn grain size, AFM images were taken for 60 nm Pn films deposited on treated and untreated K1 polymer surfaces as shown in Fig. 3. The average grain size of the Pn film on the treated K1 is about 1.5 μm , while that on the untreated surface is about 0.65 μm . The UVO treatment of the K1 surface significantly increased the grain size of the Pn film, which would result in higher device mobility. The hydrophilic (polar) nature of the treated surface would prefer a vertical arrangement of the Pn molecules because it is easier for the polar surface to induce polarization along the longitudinal direction of the molecule. It is known that the vertical geometry and better lateral stacking exhibit larger grains and higher carrier mobility for Pn-based semiconductors.¹³ As mentioned previously, the channel resistance is dominated by the grain boundaries for small grains, whereas for large grain sizes, it is dominated by the intragrain mobility,²⁵ which is indeed the case for our UVO-treated K1 surface.

In summary, UPS investigation of the interface between Pn and UVO-treated K1 polymer dielectrics revealed that the HOMO level offset values are larger than those of the untreated surface, which would result in a higher threshold voltage. However, the alignment of vacuum levels of the treated K1 surface and the Pn at the close vicinity of the interface suggests that the dipole field would be reduced in the Pn film on the treated K1 surface, resulting in the higher device mobility. It is also shown that the hydrophilic nature of the UVO-treated K1 accommodates a large grain size of Pn film on its surface, as confirmed by the AFM measure-

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