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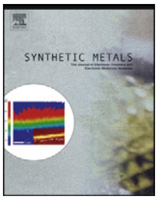

The interfacial electronic structure between pentacene and multilayer graphene

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ABSTRACT

The electronic structure at the interface region between pentacene and multilayer graphene (MLG) was investigated by *in situ* ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy. The secondary electron cutoffs, highest occupied molecular orbital (HOMO), and core-level changes were measured after deposition of pentacene on MLG to investigate the electronic structure at the interface. From the results, it was confirmed that there was neither band bending nor an interface dipole at the pentacene/MLG interface, even though a vacuum level shift was observed due to the three-dimensional growth of pentacene. In addition, there was no chemical reaction observed at the interface. The complete interfacial energy level band diagram of pentacene/MLG was also obtained to confirm the hole and electron injection barriers.

1. Introduction

During the last decade, organic semiconductors have received significant attention in many practical applications including displays [1], transistors [2], lasers [3], and memory [4,5]. Even though organic semiconductors have many practical applications, it is difficult to increase their charge injection properties to achieve high performance organic semiconducting electronics. Therefore, it is necessary to match the work function of the electrode layer to the energy level of the organic semiconducting materials because of the importance of charge injection from the electrode to the organic semiconducting materials. Conventional Al electrodes have very poor electrical contact with pentacene because of the small work function of Al [6]. Some groups have reported device performance enhancement using transition metal oxide electrodes with a high work function [7,8]. However, the conductivity of a transition metal oxide is difficult to control because it varies with thickness, stoichiometry, and surface chemistry [9]. Recently, graphene, a two-dimensional crystalline sheet of carbon atoms, has demonstrated remarkable electronic properties which qualify it for applications in future electronic devices [10]. There have been many previous reports of using graphene as an electrode in organic devices [11,12]. However, surprisingly, little is known about the detailed interfacial electronic structure between the organic semiconductor and graphene. Therefore, in this report, we studied the electronic structure at the interface of pentacene and multilayer graphene (MLG). To study the electronic structures at the interfaces, we utilized *in situ* ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) after step-by-step deposition of pentacene on the surface of MLG. We investigated the vacuum level, highest occupied molecular orbital (HOMO), and core levels to study the interfacial electronic structure.

2. Experimental

To investigate the interfacial electronic structure between pentacene and MLG, triple layers of graphene were prepared on SiO_2/Si substrates. The graphene layer was grown on Cu foil by chemical vapor deposition (CVD). Cu foils were placed inside a quartz tube furnace and heated to 1000 °C. Graphene was synthesized under a

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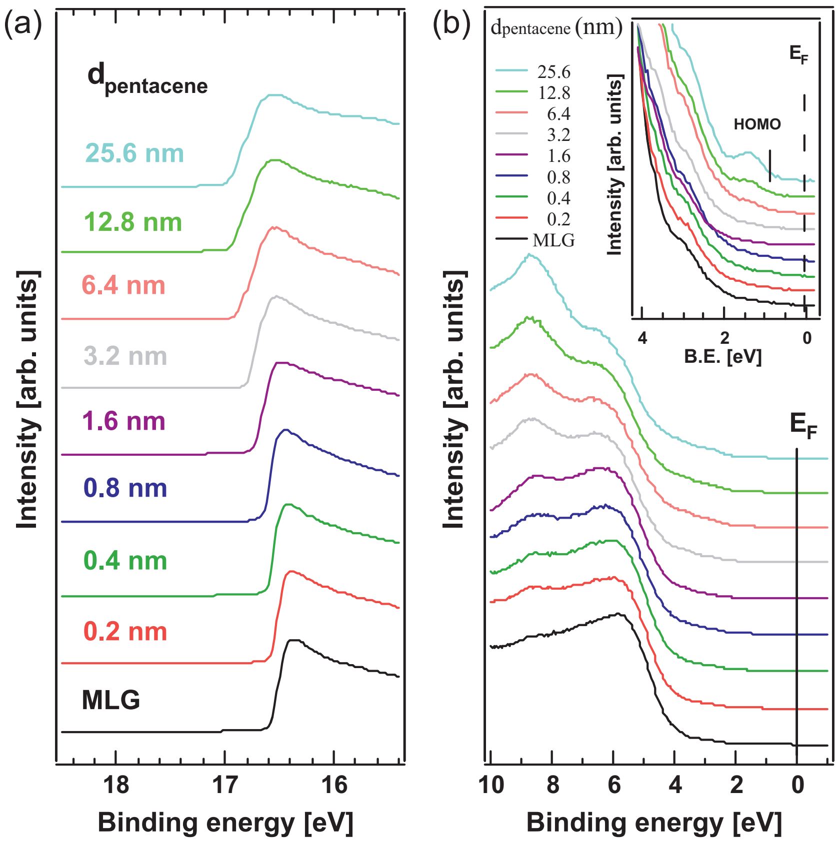

Fig. 1. UPS spectra in the secondary electron cutoff region collected during the step-by-step layer deposition of pentacene onto the MLG layer.

flowing gas mixture of 20 sccm of CH_4 and 4 sccm of H_2 at a pressure of 900 mTorr for 30 min. To transfer a thin layer of graphene from the Cu foils to the SiO_2/Si substrate, polymethylmethacrylate (PMMA) was spin-coated at 1000 rpm onto the graphene/Cu, and the underlying Cu foil was etched using a Cu etchant. The PMMA/graphene layer was thoroughly rinsed with deionized (DI) water to remove the residual etchant and gently placed on a SiO_2/Si substrate. The PMMA/graphene/SiO_2/Si substrate was dipped into acetone to remove the PMMA layer followed by rinsing with isopropyl alcohol (IPA) and DI water. The transfer process was repeated three times on the same substrate to obtain the MLG film.

To investigate the interface formation and the resulting interfacial electronic structures, pentacene was evaporated in a stepwise manner on the prepared MLG/SiO_2/Si substrate without breaking vacuum at room temperature. The spectra were measured with a SCIENTA (SES-100) analyzer system using X-ray (Mg Kα) and UV (He I) discharged sources with a base pressure of the analysis chamber of 2×10^{-10} Torr. To evaporate thin pentacene layers, a Knudsen-type effusion cell was used at a typical 0.1 nm/s deposition rate of pentacene, which was carefully monitored using a calibrated quartz crystal microbalance.

3. Results and discussion

Fig. 1 shows the UPS spectra obtained during the deposition of pentacene on the surface of the MLG. The spectra shown in Fig. 1(a) were collected in the secondary electron cutoff region. The secondary cutoff position moved noticeably toward a higher binding energy with the deposition of pentacene on the surface of MLG, with shift saturation occurring after deposition of 12.8 nm of pentacene. The total shift was 0.4 eV, which corresponds to the vacuum level shift. The shift in the secondary cutoff position is attributed to the formation of an interface dipole and/or band bending [13]. Fig. 1(b) presents the UPS spectra collected within 10 eV of the Fermi level during the step-by-step deposition of pentacene on MLG. The figure demonstrates the changes in the valence band from MLG to a 25.6-nm-thick pentacene layer. The spectra in the inset reveal an emission feature at about 3 eV below the Fermi level, which is the π band state of graphene [14]. As the pentacene layer thickens, the pentacene HOMO state appears, eventually resulting in a final pentacene HOMO onset on the 25.6-nm-thick layer that is 0.8 eV below the Fermi level.

In Fig. 2(a), the changes in the work function of the MLG surface with the deposition of a pentacene layer are shown. The work function was evaluated from the UPS spectra by subtracting the secondary cutoff position from the photon energy (21.22 eV) of the UV source and by considering the total broadening (0.1 eV) of the spectrometer. It shows that the initial work function of MLG is 4.62 eV, which well agrees with earlier reported studies [15,16]. Hibino et al. reported the work function of graphene as function of the number of layers [15]. They found that the work function gradually increases by about 0.3 eV from monolayer graphene to thick graphene layer. Fig. 2(a) demonstrates that the work function gradually decreases during the deposition of pentacene onto MLG and is saturated when the thickness of the pentacene layer reaches 12.8 nm, resulting in a final work function of 4.22 eV. Generally, the work function change is due to the formation of an interface dipole [13] and/or band bending at the interface. The work function should noticeably change as soon as deposition occurs on the surface due to the formation of an interface dipole. However, in this case, the work function gradually decreases as the pentacene thickness increases. Many research groups already found a very small (negligible) interface dipole in organic/organic interfaces [17]. This means that the work function change in this system is due to band bending or the