Modification of PTCDA/Co Interfacial Electronic Structures Using Alq3 Buffer Layer

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ABSTRACT: The interfacial electronic structures and energy level alignment between 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and Co substrate with a tris-(8-hydroxy-quinoline) aluminum (Alq3) buffer layer have been investigated using synchrotron-based photoelectron spectroscopy (PES). It was found that the electronic structures at the PTCDA/Co interface can be modified by inserting an Alq3 buffer layer. As long as all Fermi levels are established at PTCDA/Alq3/Co interfaces, the electron injection barrier (Δh) at the PTCDA/Co interface decreases by 0.3 eV with an Alq3 buffer layer, which is independent of the thickness of the Alq3 interlayer. This energy level alignment can be satisfactorily explained by substrate to organic overlayer charge transfer through the buffer layer. Our findings have potential applications in spin-valve devices based on n-type organic materials by reducing the interfacial electron injection barrier.

I. INTRODUCTION

Since the discovery of giant magnetoresistance,1,2 researchers have focused on developing faster spintronic devices with lower energy consumption compared to conventional charge based electronic devices.3−5 In recent years, π-conjugated organic semiconductors have been extensively investigated as active components in organic spintronics due to their extremely weak spin−orbit and hyperfine interactions, as well as exceptionally long spin coherent length, which is essential for spin transport in spintronic devices.6−11 Organic spintronic devices, such as the organic spin-valve, consist of two or more ferromagnetic electrodes for spin injection/detection and a sandwiched nonmagnetic organic space layer for spin transport. The transport of spin-polarized charge carriers across ferromagnetic electrode/organic space layer interfaces and the energy level alignment at the interface play critical roles in determining the electrical properties such as charge and spin injection. The electron (hole) injection barrier, which is defined as the energy difference between the Fermi level (Ef) of the ferromagnetic electrode and the lowest unoccupied molecular orbital (LUMO) (highest occupied molecular orbital, HOMO) of the organic transporting layer, is one of the key parameters determining the device performance.12 The enhanced conductance will be achieved by the increase of carrier density due to the reduced electron injection barrier. Therefore, it is of great importance to engineer the organic/ferromagnetic interface and optimize the interfacial carrier injection barriers for enhancing the device efficiency.13,14

Previously we had reported that the hole injection barrier (Δh) between cobalt and p-type organic materials, such as copper(II) phthalocyanine and pentacene, can be tuned by the inorganic metal oxide buffer layer of MoO3.15 The Δh is reduced after inserting the large work function (WF) MoO3,15,16 or an organic electron acceptor buffer layer.17,18 We therefore expect that the insertion of an organic buffer layer that can effectively reduce the substrate WF will also alter the electron injection barrier (Δe) for n-type organic semiconductors.19 A model spininterface, tris(8-hydroxy-quinoline) aluminum (Alq3) with its chemical structure shown in Figure 1a, on cobalt substrate was chosen in this work owing to the significant magnetoresistance observed at numerous Alq3 containing spin-valve structures.7,20−24 Furthermore, it was recently found that the Alq3/Co interface acts as a spin filter whereby electrons are trapped in a spin dependent manner; for minority electrons for 0.45 ps and for majority electrons for 0.80 ps.25 This property may lead to new spintronic devices. Upon the adsorption of Alq3 molecules, the WF of Co decreases remarkably due to the formation of an interfacial dipole and the permanent intrinsic dipoles of Alq3 molecules as evidenced from both experiments24 and theoretical calculations.26 Hence, the energy level alignment between the substrate and subsequently deposited n-type organic semiconductor is dominated by the modified surface potential, and a reduction of Δe is expected.19,27 In this work, 3,4,9,10-perylene-
tetracarboxylic-dianhydride (PTCDA) with chemical structure shown in Figure 1b is selected as the active layer as a PTCDA-based organic spin-valve exhibiting a magnetoresistance up to 12% at room temperature had been recently demonstrated.28

Furthermore, single crystalline PTCDA films have been widely used as the n-type conducting channel material in organic field effect transistors (OFETs) over the last few decades.29,30

In this work, we demonstrate the successful modification of electronic structures, in particular the deduction of interfacial $\Delta_{o}$ between PTCDA and ferromagnetic cobalt substrate by introducing a thin Alq3 interlayer. This had been done by comparing the energy level alignment diagrams for PTCDA on Co film and on Alq3 modified Co substrates obtained from synchrotron-based photoemission spectroscopy (PES).

II. EXPERIMENTAL SECTION

The sample preparation and PES measurements were carried out in situ at the Surface, Interface, and Nanostructure Science (SINS) beamline of Singapore Synchrotron Light Source.31 All the measurements were performed at room temperature in an ultrahigh vacuum (UHV) chamber with a base pressure of 1 x 10⁻¹⁰ mbar.

The Si(111) substrates with native silicon oxide were annealed at 500 °C overnight in an UHV chamber. After cooling down to room temperature, smooth uniform Co films of ~50 Å were deposited onto the silicon oxide/Si(111) by an e-beam evaporator,32,33 serving as the substrate for the subsequent depositions of organic molecules. The depositions of vacuum-purified Alq3 and PTCDA molecules were conducted using a standard Knudsen cell. The organic film thickness was calibrated by the attenuation of substrate Co 3p intensities.

The PES measurements were performed immediately after each deposition. The valence band (VB), C 1s, and Al 2p spectra were measured with a photon energy of 60, 350, and 110 eV, respectively. The WF was measured using a 60 eV photon energy with a −10 V applied bias. All PES spectra were collected at normal emission using a VG Scienta R4000 analyzer. The binding energy (BE) is referred to the $E_{p}$ of a sputter-cleaned gold foil in electrical contact with the sample. The sample WF was determined by the secondary electron cutoff (SECO) in the PES spectra.34

III. RESULTS AND DISCUSSION

A. PES Study of PTCDA on Bare Co Substrate. Figure 2a shows the evolution of SECO with increasing PTCDA thickness. The initial WF of the pristine Co thin film is about 5.2 ± 0.1 eV, in accordance with the previous observations.15,19

Upon the deposition of 3.3 Å PTCDA, the WF undergoes a rigid shift toward lower kinetic energy to a value of 4.9 eV. Then, WF remains almost constant within an uncertainty of ±0.1 eV even with further deposition of PTCDA molecules as thick as a nominal PTCDA thickness of 52 Å. This WF decrease, which coincides with vacuum level shift, can be attributed to the push back effect originating from Pauli repulsion.34–36

The VB spectra as a function of PTCDA thickness on Co are displayed in Figure 2b. The spectral features of PTCDA molecules become clearly visible at 3.3 Å. At a higher molecular coverage of 52 Å, the characteristic molecular frontier orbitals which correspond well with the VB profile of PTCDA multilayer on Au(111)37 and TiO2(110)38 become dominant. However, the Co 3d substrate signal remains visible upon the deposition of a 52 Å thick PTCDA overlayer, suggesting a layer plus island growth mode, which is also confirmed by the attenuation of the Co 3p signal as a function of the film thickness (data not shown). At the same time, the entire molecular spectral features including the HOMO states (as guided by the solid bars) shift to higher BE with the deposition of PTCDA and saturate at 52 Å. As seen from the close-up of VB features shown in Figure 2c, no clear signature of gap states is observed, indicating the weak interaction between PTCDA and Co. Considering the weak interaction and the thickness independent WF shift at the PTCDA/Co interface, the observed VB spectra shifts are attributed to the final-state screening of the photohole.39 The band bending effect is not applicable, which otherwise would lead to WF decrease as a function of PTCDA thickness. As shown in Figure 2c, the HOMO onset positions (denoted by dashed lines) shift to higher BE and saturate at 1.7 eV. Given that the transport band gap of PTCDA determined as the HOMO−LUMO edge is 2.5 eV,40 the distance between the LUMO onset and $E_{p}$, from which $\Delta_{o}$ is determined, can be calculated to be about 0.8 eV at the PTCDA/Co interface.

Figure 3 shows the C 1s spectra for PTCDA on Co. The profiles of all the spectra look identical with no new features observed, confirming the rather weak molecule−substrate interactions. The shift of the main peak to higher BE by about 0.5 eV also aligns well with the HOMO onset shift of ~0.4 eV, revealing their common origin of the photohole.
screening effect. In addition, this screening effect causes slight broadening of all C 1s features when PTCDA molecules are close to the substrate surface.\(^{41}\) For example, the full width at half-maximum (fwhm) of the dominant peak increases from \(\sim 1.15\) eV at 104 Å to \(\sim 1.30\) eV at 3.3 Å.

**B. PES Study of PTCDA on Alq\(_3\) Precovering Co Substrates.** The SECO and VB spectra as a function of PTCDA thickness on 60 Å (multilayer) Alq\(_3\) precovering Co substrate are shown in Figure 4. Upon the deposition of 60 Å Alq\(_3\), the WF decreases sharply to 3.4 eV from 5.2 eV of pristine Co (cf. part a of Figure 4). As reported previously, the WF decrease is attributed to the interface dipole caused by the push back effect, interfacial dipole, and the permanent intrinsic dipoles of Alq\(_3\) molecules.\(^{24,26}\) In the subsequent depositions of PTCDA, the WF increases and finally stabilizes at around 4.6 eV at a nominal thickness of 26 Å PTCDA. Figure 4b displays the evolution of VB spectra with increasing PTCDA thickness. PTCDA features are overlapped with Alq\(_3\) features below 6.6 Å. Both features from PTCDA around 6 eV (denoted by solid bars) and Alq\(_3\) (denoted by dashed bars) shift to lower BE in this region. From a nominal thickness of 13 Å, the signal from the PTCDA overlayer becomes dominant, judging from the fact that the features of those peaks (denoted by solid bars in part b of Figure 4) remain almost unchanged from 13 to 52 Å PTCDA. As seen in Figure 4c, the HOMO of PTCDA overlaps with that of Alq\(_3\) in the interfacial region below 13 Å. Therefore, it is difficult to distinguish the contribution from PTCDA to determine its HOMO onset in this region. At 13–52 Å PTCDA, the HOMO onset is determined to be at 2.0 eV BE. The \(\Delta_\epsilon\) at the interface between PTCDA and 60 Å Alq\(_3\)/Co can be calculated to be 0.5 eV, considering the band gap of 2.5 eV. Note that \(\Delta_\epsilon\) at the PTCDA/Co interface is about 0.8 eV; therefore, the insertion of the Alq\(_3\) buffer layer can effectively reduce \(\Delta_\epsilon\) by 0.3 eV.

The core level spectra will serve as an additional tool to investigate the energy shift induced by the introduction of Alq\(_3\). As seen in Figure 5a, Al 2p peaks shift to lower BE by \(\sim 0.4\) eV upon the deposition of PTCDA molecules, and saturate at 13 Å. On the other hand, the C 1s spectra (cf. part b of Figure 5) at the PTCDA/Alq\(_3\) interface shift to lower BE. Due to the strong spectral overlaps of the PTCDA main peak and Alq\(_3\) signal, the well resolved C 1s component at high BE associated
with C=O groups of PTCDA molecules is used to evaluate the energy shift within PTCDA film.\textsuperscript{38} As indicated by the solid bars, there is a shift of about 0.3 eV toward lower BE. In addition, no new features are observed from Al 2p and C 1s spectra, indicating the relatively weak interactions between PTCDA and Alq\textsubscript{3} molecules. Taking into account the thickness dependent energy shift of both Al 2p and C 1s signals and the weak interactions between PTCDA and Alq\textsubscript{3} demonstrates the formation of an interface dipole upon PTCDA adsorption caused by the electron transfer toward PTCDA.

To investigate whether the tuning effect of $\Delta_\varepsilon$ at the PTCDA/Co interface is dependent on the thickness of the Alq\textsubscript{3} buffer layer, the thickness of the Alq\textsubscript{3} interlayer is reduced to 3.3 Å. In Figure 6a, the WF of Co film drops to 4.4 eV after the growth of 3.3 Å Alq\textsubscript{3}. In the subsequent depositions of PTCDA, the WF increases gradually and finally stabilizes at around 4.7 eV with a nominal thickness of 26 Å PTCDA. This vacuum level shift of ~0.3 eV after the growth of PTCDA is attributed to the formation of an interface dipole with its negative terminal at the PTCDA overlayer. However, the magnitude of vacuum level shift is smaller than that of PTCDA on 60 Å Alq\textsubscript{3}/Co (~0.5 eV), implying a weaker metal to PTCDA electron transfer.\textsuperscript{34} Figure 6b shows the evolution of VB during the depositions of PTCDA. Minor modifications and weak Alq\textsubscript{3} contributions of the features of the spectrum are observed due to ultrathin Alq\textsubscript{3} coverage. At lower coverage of PTCDA (e.g., 3.3 and 6.6 Å), the VB features from PTCDA can be distinguished in the presence of strong Co 3d substrate signals. The PTCDA occupied molecular orbitals start to dominate at a nominal thickness of 26 Å. The shifts of the entire spectra with an ultrathin Alq\textsubscript{3} buffer layer at the PTCDA/Alq\textsubscript{3}(3.3 Å)/Co interface are mainly attributed to screening of the photohole. The band bending effect should be ruled out due to opposite VB and vacuum level shifts. As shown in Figure 6c, the positions of the HOMO onset shift to higher BE and remain constant from 26 to 104 Å. The lower BE onset of the HOMO (guided by the dashed lines) is determined to be at around 2.0 eV at 26 Å PTCDA, and therefore, the resulting $\Delta_\varepsilon$ is ~0.5 eV, similar to the observation of PTCDA on the 60 Å Alq\textsubscript{3}/Co substrate. This finding indicates that the tuning effect of $\Delta_\varepsilon$ at the PTCDA/Co interface is independent of the thickness of the Alq\textsubscript{3} buffer layer. The 3.3 Å Alq\textsubscript{3} film can tune the interfacial $\Delta_\varepsilon$ as effectively as the 60 Å one.

C. Energy Level Alignment Diagrams of PTCDA on Bare Co and Alq\textsubscript{3}/Co Substrates. On the basis of the PES results, the energy level alignment diagrams for PTCDA on bare Co film, 60 Å Alq\textsubscript{3}/Co, and 3.3 Å Alq\textsubscript{3}/Co substrates are displayed in Figure 7. As shown in Figure 7a, the ionization potential (IP) and electron affinities (EA) for PTCDA are measured to be 6.6 ± 0.2 and 4.1 ± 0.2 eV, consistent with the values reported in the literature.\textsuperscript{42,43} Due to the large energy offset between the WF of substrate (5.2 eV) and IP or EA, the charge transfer between metal and organic film is not energetically favorable. The vacuum level is aligned at the PTCDA/Co interface with an interface dipole ($\Delta_\varepsilon$) of 0.3 eV due to the push back effect. The situation is dramatically different when Alq\textsubscript{3} is used as the buffer layer (cf. parts b and c of Figure 7). The WF of 60 Å Alq\textsubscript{3} covered Co substrate of 3.4 eV is even smaller than the EA of 4.1 eV for PTCDA. If vacuum level alignment was assumed, the LUMO of PTCDA would be placed directly below the $E_F$ of substrate. Upon the formation of contact, electrons can spontaneously flow from the $E_F$ of Alq\textsubscript{3}/Co to the PTCDA film, which is accompanied by an upward shift of vacuum level. The strong charge transfer between Alq\textsubscript{3} and PTCDA can be
ruled out due to a large energy mismatch between PTCDA EA and Alq3 IP (the Alq3 IP of 5.7 eV is ~1.6 eV higher than the PTCDA EA of 4.1 eV). Consequently, it is proposed that electrons are transferred from Co substrate to PTCDA molecules possibly by hopping through the unoccupied states of the Alq3 buffer layer. A similar observation has been reported for depositing hexaza-trip henylene-hexacarbonitrile (HATCN) on 12 Å Alq3 precovering Ag(111)44 and C60 on 6 Å α-sexithiophene (6T) covered Ag(111).55 The charge transfer can lead to the formation of a built-in dipole with its negative terminal at the top layer side. The Ev is first pinned at ~0.2 eV below the LUMO at 0.7 Å PTCDA thickness with Δf = 0.2 eV. With further deposition of PTCDA, an upward band bending of ~0.3 eV within the PTCDA overlayer occurs due to decreased charge transfer away from the interface. Ef moves away from the LUMO until equilibrium is established at the PTCDA/Alq3/Co interface. On the other hand, the BE shift of both the core level and VB of Alq3 arises from the potential drop across this buffer layer. It is worth noting that there is no significant BE shift of the HOMO of Alq3 at the PTCDA/Alq3 (100–150 Å) interface due to the absence of a potential drop, supporting the proposed scenario. Similar interfacial charge transfer and energy level alignment for organic molecules deposited on organic films or organic molecules precovered metal surfaces had been reported, such as HATCN/Alq3/Ag(111),44 F16CuPc/Alq3,57 F10CuPc/DIP,28,49 CuPc/Alq3/Mg,30 CuPc/C60/Mg,51 and C60/6T/Ag(111).45,52 The interface dipole of Δf = −0.5 eV accompanied with band bending of 0.3 eV within the PTCDA overlayer and a potential drop of 0.4 eV through the Alq3 buffer layer contributes to a total vacuum level shift of 1.2 eV. When PTCDA and 60 Å Alq3/Co substrate equilibrium is realized, Ev is finally pinned at states 0.5 eV below the LUMO of PTCDA with Δf = 0.5 eV and Epin = 4.6 eV, which is in good agreement with reported values.53,54 Such states may originate from gap states of sufficient density generated by the extension of LUMO orbitals into the organic band gap due to static and dynamic defects or structural defects such as grain boundaries, impurities, surface roughness, and deposition conditions.53–59

Figure 7c shows the energy level diagram with a 3.3 Å Alq3 buffer layer. For Alq3 covered Co, WF of 4.4 eV is well below Epin of PTCDA which is obtained at the PTCDA/Alq3 (60 Å)/Co interface. Electrons can transfer from the Ef of Co substrate to the LUMO of PTCDA molecules through the Alq3 buffer layer when PTCDA is brought into contact with the Alq3/Co substrate. An interface dipole of Δf = −0.3 eV arises after equilibrium, which leads to the increase of the WF. The Ef is finally pinned at the gap states which are ~0.5 eV below the LUMO of PTCDA.

As clearly shown, the insertion of an Alq3 buffer layer at PTCDA/Co interfaces reduces Δf by 0.3 eV when equilibrium is realized at PTCDA/Alq3/Co interfaces, which is independent of the thickness of the Alq3 interlayer. The tuning effect of Δf is independent of the thickness of the Alq3 buffer layer because Ef is finally aligned with the gap states as long as the Ef of the Alq3/Co substrate is not larger than the gap states of the top layer. The validity of the tuning effect on Δf due to Ef pinning could be extended to the C60/Co system with the Alq3 buffer layer, which was reported previously.59 In that case of C60 grown on Alq3/Co substrates, Ef is pinned at gap states ~0.3 eV below the LUMO. In addition, it is worth noting that, for the C60/Co system with a 3 Å Alq3 buffer layer, WF is the same as Epin of C60 molecules, i.e., ~4.3 eV. The charge transfer between C60 and 3 Å Alq3/Co substrate is not energetically favorable. Therefore, the vacuum level is aligned without formation of an interfacial dipole.

IV. CONCLUSIONS

The interfacial electronic structures and energy level alignment at the interfaces between n-type organic material PTCDA and Alq3/Co substrates are studied using synchrotron-based PES. It is found that the insertion of the Alq3 interlayer at the PTCDA/Co interface can reduce Δf by 0.3 eV, when equilibrium is established at the interfaces. Therefore, Alq3 is shown to be an effective buffer layer for reducing Δf between ferromagnetic metals and n-type organic molecules. The successful demonstration of reduction of Δf between n-type organic semiconductor and magnetic electrode Co by introducing an Alq3 buffer layer at the interface may pave the way for improving the interfacial electron injection efficiency and the overall performance of the organic spintronic devices employing n-type organic semiconductors. Moreover, when equilibrium is established at PTCDA/Alq3/Co interfaces, the tuning effect of Δf is found to be independent of the Alq3 buffer layer thickness. Ef after the growth of organic molecules is finally pinned to the molecular gap states. This energy level alignment can be satisfactorily explained by substrate to organic overlayer charge transfer and the resulting interface dipole. Our results will add to the understanding of energy level alignment at organic–organic heterojunctions in contact with metal electrodes.

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Notes
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REFERENCES


