1 **Interfacial chemical and electronic structure ofCobalt**
2 **depositionon2,7-dioctyl[1]benzothieno[3,2-b]benzothiophene**
3 **(C8-BTBT)**

4 Menglong Zhu^{1,2}, Lu Lyu^{1,2}, Dongmei Niu^{1,2,a)}, Hong Zhang^{1,2}

^{a)} E-mail: mayee@csu.edu.cn and ygao@pas.rochester.edu

Yuhe Zhang^{1,2}, Peng Liu^{1,2} and Yongli Gao^{1,2,3,a)}

¹*Institute of Super-microstructure and Ultrafast Process in Advanced Materials, School of Physics and Electronics, Central South University, Changsha, Hunan, 410083, P. R. China*

²*Hunan Key Laboratory for Super-microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha, Hunan, 410083, P. R. China*

³*Department of Physics and Astronomy, University of Rochester, Rochester, NY14627, USA*

ABSTRACT

Interfacial chemical and electronic structure of Co deposition on 2,7-dioctyl[1]benzothieno[3,2-b]benzothiophene(C8-BTBT) was investigated by ultraviolet photoemission spectroscopy (UPS) and X-ray photoemission spectroscopy (XPS). Chemical reaction of cobalt with C8-BTBT at the interface is confirmed by a new component of S 2s peak which is electron-rich compared to the original one of C8-BTBT molecules. Intensity evolution of the core level in XPS indicates that the adsorption of Co atoms is mainly at the surface without deeper diffusion into C8-BTBT layer. Initial deposition of Co atoms downward shifts the core levels of C8-BTBT by electron transfer from isolated Co atoms or clusters to the C8-BTBT. Further deposition of Co upward shifts the core levels of C8-BTBT because of the neutralization of the thicker metal Co film. Our investigation suggests an inert buffer layer inserted to protect organic layer from reaction or decomposition and to lower the carrier barriers for both the electron and hole to improve the performance of Co/C8-BTBT-based OFETs.

Keywords: photoemission spectroscopy(PES), Interface, C8-BTBT, Co.

1. Introduction

Organic semiconductors (OSC) possessing extra merits of mechanical flexibility, light weight and processability have attracted extensive research and experienced rapid development[1,2]. The studies of organic/metal interfaces have played an important role for understanding the performance of organic semiconductor devices[2–4]. In practice, the top electrodes of these devices are mostly constructed by deposition of metal onto the organic layer. In the case of evaporating organic materials on a metal substrate, there is an abrupt interface between the two materials. In contrast, when evaporating metal on organic, the hot metal atoms have larger kinetic energies, which may encourage metal diffusion into and interaction with the soft organic materials[5]. Furthermore, the condensation energy released by the evaporated metal may result in additional damage or reaction of the organic materials[6–8]. Thus the metal/organic interfacial properties and phenomena would be well defined and very different from the interface in which the organic is evaporated on metal system[9].

It is well known that conduction electrons of ferromagnetic metal are significantly spin-polarized owing to the spin-splitting of the density of states near the Fermi level (E_F). Thus, a spin-polarized current can in principle be injected into another material by using ferromagnetic metals as contacts[10–12]. An important requirement is given by the sufficient quality of the interface between semiconductor layer with metal contact to preserve integrity of both materials and allow spin-polarized injection. Moreover, the long spin relaxation time in OSCs has not led to a significantly long spin-diffusion length λ_s as most of the OSCs have very low carrier mobility[13,14]. According to the relationship of

$\lambda_s = \sqrt{(k_B T / e) \mu t_s}$, where k_B is the Boltzmann constant, T the temperature, μ the carrier mobility and t_s the spin relaxation time[15], organic materials of higher carrier mobility is strongly desirable to achieve longer spin diffusion length and improve device performance. Li *et al.* reported exceedingly high magnetoresistance ratio of 90.0% at 4.2K and 6.8% at room temperature using high carrier mobility semiconductor of P(NDI2OD-T2)[16]. Recently, Yuan *et al.* reported record-breaking high field effect transistor mobility up to $43 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ using 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene(C8-BTBT) thin film as the channel semiconductor[17], and the application and synthesis of [1]benzothieno[3,2-b]-[1]benzothiophene derivatives are now arousing much research interests[18,19]. Furthermore, Co has high spin polarization[20,21] and is among the most commonly used ferromagnetic electrode for both injection and detection of spin-polarized current[22–24]. Therefore, C8-BTBT and Co are selected as representative organic semiconductor and ferromagnetic electrode materials, respectively.

In this communication, we report our recent investigation on the interface formation of Co/C8-BTBT using ultraviolet photoemission spectroscopy (UPS) and X-ray photoemission spectroscopy (XPS). We **observed** that energy level bending and chemical reaction occurred in C8-BTBT with deposition of Co overlayer. We also **found** that the Co atoms are mostly accumulated within the surface. The energy level alignment of the interface can be clearly determined.

2. Experiment Details

The experimental setup has been described previously[25,26]. Briefly, photoemission

spectroscopy (PES) and vapor deposition of thin film were performed in a multi-chamber ultrahigh vacuum system including a spectrometer chamber, an *in-situ* organic molecular beam evaporation (OMBE) and molecular beam epitaxy (MBE) chamber. The spectrometer chamber is equipped with a SPECS PHOIBOS 150 hemispherical energy analyzer as well as a monochromatic SPECS XR-MF X-ray source($\text{Al K}\alpha = 1486.7 \text{ eV}$) and a SPECS microwave UV light source ($\text{He I} = 21.21 \text{ eV}$). The UV light spot diameter is about 1 mm. A total energy resolution is about 70 meV for the present UPS as determined from the Fermi edge of clean Au (111). The UPS of the secondary cutoff edge were recorded with negative 5V sample bias. The binding energies of all spectra were calibrated to the Fermi level of the energy analyzer. All the PES measurements were performed at room temperature.

A native oxide layer was formed on a boron doped p-type Si(111) wafer by firstly immersing in boiling $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:2:10) solution for 15 min, followed by 3 min dipping in $\text{HF}:\text{H}_2\text{O}$ (1:20) solution, and finally in boiling $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:15) solution for 10 min. After each step the samples were rinsed in deionized water[27].The thickness of the native oxide layer was estimated to be 1.0 nm[28].The deposition of C8-BTBT was performed by evaporating at an average rate of 1-2 Å/min from a resistively heated boat. The amount of the deposition was monitored using a quartz crystal microbalance(QCM).The thickness of C8-BTBT on SiO_2 substrate is 8.0 nm. Co film is deposited layer by layer on the C8-BTBT film in molecule beam epitaxy(MBE) chamber.

3. Results and discussion

3.1 Evolution of the Electronic structure at the Co/C8-BTBT interface

The evolution of the UPS spectra of Co/C8-BTBT as a function of Co coverage is

shown in Fig. 1. The spectra have been normalized to the same height for visual clarity. The secondary electron cutoff and highest occupied molecular orbital (HOMO) onset values are all determined by linear extrapolation of the leading edge of the spectrum as marked by the short bars. Figure 1(a) shows the cutoff region of the UPS data. The work function (WF) of the bare SiO_2 substrate is measured to be 4.41 eV. The subsequent deposition of 8 nm C8-BTBT moves the cutoff toward higher binding energy (BE) by 0.80 eV, indicating the WF to be 3.61 eV and interface dipole to be 0.80 eV at the interface of C8-BTBT/ SiO_2 . The deposition of Co gradually increases the WF from 3.33 to 4.62 eV for Co thickness from 0.3 to 9.6 nm.

The low BE regions of the UPS spectra are shown in Fig. 1(b). With deposition of 8 nm C8-BTBT film, the HOMO onset is at 2.23 eV. At an initial Co thickness of $\Theta = 0.3$ nm, there are dramatic changes in the UPS spectra and HOMO features of C8-BTBT become hard to be distinguished. Furthermore, there is a high density of state that begins to develop just below the E_F , indicating the arising of the Co 3d states [9]. The on-set of Co 3d is measured to be about 0.15 eV below the Fermi level, which suggests that Co has not formed a homogeneous and complete film. As Θ increases, the Co 3d feature becomes stronger around the E_F . At the final step of $\Theta = 9.6$ nm, the Fermi edge of the metal is clearly visible, indicating that cobalt film is in a pure metallic state. Charging effects can be excluded as the Fermi level agrees with that of a single crystal Co substrate in our laboratory. It is important to note that the Fermi edge has become clearly visible at $\Theta = 0.6$ nm, which is a relatively small mass thickness, indicating that the diffusion of the Co atoms into the underlying C8-BTBT layer is not strong, probably due to the high reactivity of Co atoms. At the highest Θ , the work

function is still not saturated and still smaller than that of the single crystal Co, which may be attributed to the higher roughness or surface segregation of C impurities[29].

XPS is used to further analyze the detail evolution of the C $1s$, Co $2p_{3/2}$ and S $2s$ core levels during various stages of the Co/C8-BTBT interface formation, as shown in Fig. 2. The spectra have been normalized to the same height for visual clarity and the centroids of the peaks are marked with short bars. With the Co overlayer thickness increasing, the intensity of C $1s$ and S $2s$ peaks from the underneath layer of C8-BTBT decrease gradually because of the limited electron mean free path. Thus the highest thickness spectrum displayed in Fig. 2(a) and (c) are 4.8 and 2.4 nm, respectively. It is clear that the shapes of the C $1s$ and Co $2p_{3/2}$ spectra remain essentially unaltered during the deposition of Co. In Fig. 2(a), the initial BE of C $1s$ core level is at 284.79 eV. A dramatic shift is observed at 0.3 nm Co coverage, which means a big change of environment occurs at the C8-BTBT surface, and then C $1s$ peak shifts gradually to lower BE positions with further deposition of Co. The corresponding BE decreases by 0.44 eV from 285.23 eV at 0.3 nm to 284.79 eV at 4.8 nm. In addition, no new component can be resolved in the C $1s$ XPS spectra. Meanwhile, the broadening of the core level is observed to be very limited. Therefore, the abrupt and continual peak shift of C $1s$ core level indicates that the interaction between C8-BTBT and Co is very strong and results in energy level bending in the C8-BTBT substrate.

Shown in Fig. 2(b) is the XPS spectra of Co $2p_{3/2}$ core level. It also has the same tendency toward lower BE as that of the C $1s$ core level. The corresponding BE decreases by 0.43 eV from 778.84 eV at $\Theta=0.3$ nm to 778.41 eV at $\Theta=4.8$ nm, which results from the improved core-hole screening for thicker Co evaporation[30]. However, no further energy

shift is observed for Θ from 4.8 to 9.6 nm, which suggests pure Co film has probably formed at this range of thickness. The value of the BE is also very closed to that of metallic Co single crystal[31,32].

The evolution of the S 2s core level spectra provide further information about the Co/C8-BTBT interface formation. As illustrated in Fig. 2(c), the S 2s core level spectra have been de-convoluted into two separated peaks by fitting with Gaussian/Lorentzian mixing function. The positions of the two peaks split by ~ 2 eV[33,34]. It can be seen that a new component appears at lower BE and becomes clearly resolved at $\Theta = 0.3$ nm. For a better comparison of the spectral features, this new component is named S 2s(n) to separate it from S 2s(m). The S 2s(m) should be related to the uncoated C8-BTBT surface since its shift with Co deposition is similar to that of C 1s peak. The initial position of S 2s(m) is at about 228.3 eV and with deposition of Co, the S 2s(m) peak shift downward by 0.45 eV, which is quite close to the downward shift of 0.44 eV of C 1s peak. Although the peak intensity of both S 2s(n) and (m) component attenuate gradually, the relative intensity of the S 2s(n) component grows with the increase of the Co coverage compared with that of S 2s(m), indicating that S 2s(n) may arise from interfacial compound or some reaction products of the C8-BTBT with cobalt atoms. In the present spectra, the appearance of the new component and the sudden shift of C 1s and Co 2p_{3/2} core levels occurs simultaneously. In other words, the Co deposition actually produces some new sulfocomponent which causes some electron density redistribution around S, Co and C atoms and the element chemical environment change accordingly. The redistribution makes the S 2s(n) electron-rich and the BE shift upward, opposite to the downward BE shift of Co 2p_{3/2} and C 1s core levels. The

BE of S 2s(n) is closed to the previous reported BE of S 2s in cobalt sulfide[35]. So it is very probably that the ring of benzothiophene in C8-BTBT reacts directly with the Co causing broken down of C-S bond and producing a series of hydrocarbons and chemically adsorbed sulphides. From the prospective of device application, this effect will vary the contact properties, even form interfacial dipole barriers and defect state, which will be detrimental to the performance of C8-BTBT/Co-based device. Therefore, an inert buffer layer, such as MoO₃[36,37] and Al₂O₃[38], may be needed between the Co electrode and the C8-BTBT layer not only to eliminate or prevent desulfurization effect, but also to achieve the favorable energy level alignment in order to improve the device performance.

Detailed analyze of the typical peak intensity change provide information of film growth mode. Presented in Fig. 3(a) are the intensity evolution of C 1s, S 2s and Co 2p core level peaks. It is apparent that the intensity of C 1s and S 2s peaks decrease significantly at the initial stage, and simultaneously the intensity of the Co 2p peak increases considerably, again affirming that most of the deposited Co are accumulated at or near the C8-BTBT surface region and does not penetrating deep into the organic layer. It is of note that the intensity of S 2s(n) at $\Theta = 1.2$ nm achieves the maximum, which means the chemical reaction saturated at this thickness. As shown in Fig. 3(b), the normalized intensity evolution of the C 1s, S 2s and Co 2p peaks are plotted as a function of Co thickness, respectively. The dash slope curves are derived from linearly fitting of the experiment data. It is apparent that the C 1s, S 2s(m) and Co 2p signals change along similar slope. Thus the observed linear variation of the signal intensity implies that the growth of Co on C8-BTBT follows the layer by layer growth mode at $\Theta < 4.8$ nm[39,40], which is consistent

with above mentioned accumulation of Co at C8-BTBT surface without diffusion into C8-BTBT layer.

The energy level alignment diagram for Co/C8-BTBT interface is summarized in Fig. 4. Because the HOMO features of C8-BTBT in the UPS become increasingly undistinguishable after deposition of thicker Co overlayer, here we use the C *1s* level in XPS to determine the energy level alignment. As discussed above, band bending occurs indeed at this interface, thus the shift trend of the HOMO level should be consistent with that of C *1s* level. Therefore, the position of C *1s* level is used to track HOMO for thicker Co coverage. The HOMO position of bare C8-BTBT film lies at 2.23 eV below the E_F . Taking into account that C8-BTBT possesses a wide band gap of 3.84 eV obtained from literature[41], the position of the LUMO in C8-BTBT is located at 1.61 eV above the E_F , indicating that the C8-BTBT film used here is an n-type semiconductor material.

As described in XPS in Fig. 2, the dramatic BE shift of 0.44 eV for C *1s* and S *2s* core levels occurred at Co thickness of $\Theta = 0.3$ nm. The shift can be attributed to the initial interface reaction between isolated Co atoms and/or clusters and C8-BTBT, which effectively doped the organic materials n-type by 0.44 eV through electron transfer from Co atoms to C8-BTBT layer[42,43]. The UPS cutoff spectrum shown in Fig. 1 also has a similar shift at this 0.3 nm thickness, supporting the notion of initial n-doping of C8-BTBT. In fact, the spectrum has two edges: the smaller one to the left from the still exposed C8-BTBT, and the stronger one to the right from Co that covers parts of the surface. With further deposition of Co atoms, Co overlayer becomes more metallic, which then neutralizes the doping of C8-BTBT[44], i.e., the excessive electrons in C8-BTBT flow back to the

Fermi level of metallic Co. This brings upward energy level shift of C8-BTBT in the interface region, gradually restoring the HOMO and LUMO of C8-BTBT back to -2.23 and 1.61 eV as reference to Fermi level, respectively. Thus the overall energy level alignment is a flat band in C8-BTBT, and flat in Co. The interface dipole is $4.62 - 3.61 = 1.01$ eV. The interface barrier height for the hole injection is 2.23 eV. Electron barrier from Co to C8-BTBT is as high as 1.61 eV. Both the electron barrier and the hole barrier are too high for efficient carrier injection, suggesting some interfacial modification such as a buffer layer may be needed[45].

4. Conclusion

In conclusion, the interfacial chemical and electronic structure of Co/C8-BTBT system have been investigated with increasing Co overlayer thickness using XPS and UPS. At deposition of Co overlayer, the diffusion of Co atoms into C8-BTBT film is not dominate and Co atoms are mostly adsorbed at or accumulated near the surface. Chemical reaction of Co and C8-BTBT at the interface can be confirmed by the appearance of a new component of S 2s(n), which is relatively electron-rich compared to the corresponding S 2s(m) of the original C8-BTBT molecules. Our investigation suggests an inert buffer layer needed between the two materials to protect organic layer from reaction or decomposition. The energy level alignment shows that both the electron and hole barrier across the interface are too high and some interfacial modification methods should be developed to improve the performance of Co/C8-BTBT-based OFETs.

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Fig. 1. UPS spectra of Co/C8-BTBT as a function of incremental Co deposition.(a) cutoff region, (b) valence band region. The work function and Fermi level are also labeled.

Fig. 2. XPS spectra: (a) C 1s, (b) Co 2p_{3/2} and (c) S 2s core levels at different Co thickness.

Fig. 3. (a) The intensity evolution of the C 1s, S 2s and Co 2p peaks. (b) Intensity of C 1s, S 2s and Co 2p during the formation of Co/C8-BTBT. The data for each core level are plotted as $\ln(I_s/I_{s0})$ and $\ln(1-I_s/I_{s0})$, respectively, which would have a straight line if the Co overlayer growth was in layer by layer mode. The dash lines are linearly fitting of the experiment data.

Fig. 4. The energy level alignment diagram at the Co/C8-BTBT interface. The chemical reaction zone is also marked.