

Dependence of Substrate Work Function on the Energy-Level Alignment at Organic-Organic Heterojunction Interface

Alexandre Lira Foggiatto^{1*}, Hiroki Suga², Yasuo Takeichi³, Kanta Ono³, Yoshio Takahashi⁴, Takahiro Ueba⁵, Satoshi Kera⁵ and Takeaki Sakurai¹

¹ University of Tsukuba

1-1-1, Tennoudai, Tsukuba, Ibaraki 305-8573, Japan. Phone: +81-2-9853-6177 *E-mail: alexandrelfgt@hotmail.com

² Hiroshima University

1-3-2, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan

³ High Energy Accelerator Research Organization (KEK)

1-1 Oho, Tsukuba 305-0801, Japan

⁴ The University of Tokyo

7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

⁵ Institute for Molecular Science

38, Nishigonaka, Myodaijichi, Okazaki, Aichi, 444-8585, Japan

Abstract

We investigated the interface of boron subphthalocyanine chloride (SubPc)/*α*-sexithiophene (6T) grown on MoO₃, Cs₂CO₃ and SiO₂ using ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS). We demonstrated that a p-doping and n-doping of induced by MoO₃ and Cs₂CO₃ work function, respectively, on the ambipolar-type material, 6T, can induce charge transfer at the organic-organic heterojunction (OOH) interface, and this effect can be controlled by annealing the film. We suggested that the reduction of the molecular disorder induces a reduction in the density of gap states, which controls the charge transfer and charge accumulation.

1. Introduction

It was reported that an organic solar cell achieved a power conversion efficiency of 8.4%, using as acceptor SubPc and boron subnaphthalocyanine chloride (SubNc), and with 6T as donor. [1] Regardless of such fascinating efficiency, one could improve the performance more by tuning the density of gap states (DOGS) at the interface after adjusting the molecular arrangement. The origin of gap states in organic semiconductor has been extensively studied using ultraviolet photoelectron spectroscopy (UPS). [2] The DOGS is appeared as the HOMO/LUMO-tail states into the band gap region which is originated by defects and influenced especially in high polar molecules because the misalignment of permanent electric dipole induces a local electric field which induces tailing of the density of states.

In this work, we investigate the influence of the substrate work function (WF) and the role of the tail states in the energy-level alignment (ELA) at the OOH interface. We used UPS and XPS to study the ELA of SubPc/ 6T deposited on the substrates of MoO₃, [3] Si/SiO₂, and Cs₂CO₃.

2. Experimental

The UPS/XPS measurements were performed at Photon Factory (PF), High Accelerator Research Organization (KEK), Japan. Si (100) wafers, cleaned ex situ, were used as substrates. The Si/SiO₂ substrate was grown on the cleaned

Si by using an UV-ozone treatment to oxidize the Si surface. The substrate layers were obtained by the deposition of 5 nm of MoO₃ (Sigma-Aldrich) and Cs₂CO₃ deposited on Si substrate. Subsequently, 6T (Tokyo Chemical Industry) and SubPc (Sigma-Aldrich) were deposited step-by-step in a deposition chamber (<5.0x10⁻⁹ Torr), until a thickness of 5 nm was reached. UPS and XPS spectra were measured using photon energies of 30 eV for the UPS and 200 and 235 eV for the XPS to obtain Cl 2p and S 2p peaks, respectively. The heterostructures were annealed for 60 s at 150 °C in the analysis chamber. The modifications on the morphology due to the annealing was investigated using the compact scanning transmission X-ray microscopy (STXM) at PF, KEK, Japan. [4]

3. Results and discussion

Figure 1 shows the molecular structure of SubPc and 6T and the schematic illustration of the two studied systems before the contact.

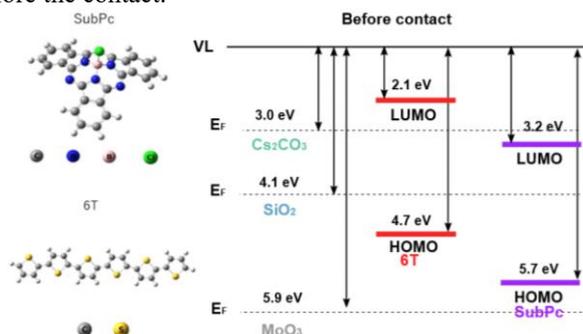


Fig. 1 Molecular structure of SubPc and 6T and schematic illustration of the two studied systems before contact with the measured values of the WF of the substrates and ionization potential (IP) and the electron affinity (EA) of the organic thin films. The EA was obtained from the literature. [5]

After the contact, we observed a rearrangement in the energy levels. For the MoO₃, the binding energy (BE) of HOMO onsets were measured as 0.55 eV and 0.86 eV for 6T and SubPc, respectively. On the other hand, due low WF of Cs₂CO₃, the HOMO onsets of the organic materials move away from the Fermi level to 1.16 eV and 1.14 eV for 6T

and SubPc, respectively. For the SiO₂, the HOMO onsets were measured as 0.73 eV and 1.24 eV for 6T and SubPc, respectively. When the first organic layer is deposited for high WF substrate, the charge was transferred from 6T to the substrate to obtain the equilibrium and equalize the Fermi level position, which moves closer to HOMO. For the low WF substrate, however the charge was transferred from the substrate to the 6T layer, hence the Fermi level located closer to LUMO. And for the SiO₂, since the WF is localized close to the equilibrium position the 6T HOMO is located in an intermediate position compared to others substrate. The easiness to donate or accept an electron gives to 6T an ambipolar property that could act as donor or acceptor character by changing the substrate WF. [6] However, after deposition of SubPc the information about the charge transfer and band bending at the OOH interface could not be extracted in the same way.

To estimate qualitatively the charge accumulated at the OOH interface deposited the substrates, we analyzed the evolution of S 2p and Cl 2p peaks position, which are associated with 6T and SubPc, respectively. Figure 2 shows the peak shift of S 2p and Cl 2p (straight lines), which exhibits the same tendency as described above by the UPS measurement.

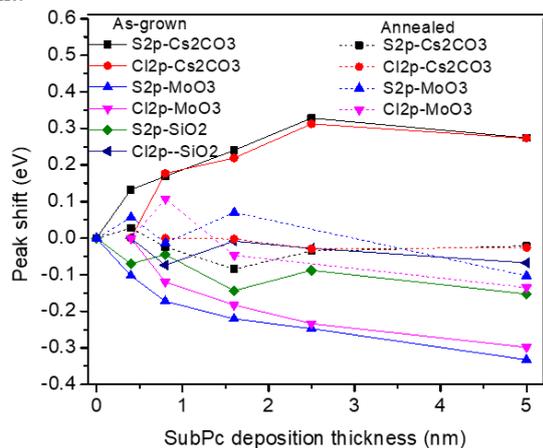


Fig. 2 Energy shift in function of the SubPc thickness deposited on 6T (5 nm)/ MoO₃, on 6T (5 nm)/ SiO₂ and on 6T (5 nm)/ Cs₂CO₃ for the as-grown film (straight line) and for the annealed film (dashed line).

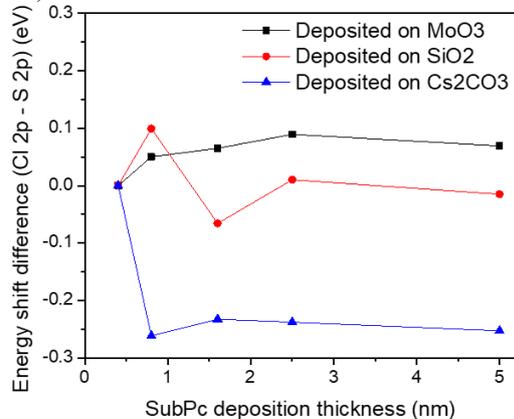


Fig. 3 Energy shift difference (Cl2p-S2p) for the organic stack layer deposited on MoO₃, Si/SiO₂ and Cs₂CO₃ in function of the SubPc thickness.

The band bending in SubPc can be extracted by the Cl 2p – S 2p peak shift, displayed in Fig. 3. Although there is a big shift for lower BE for the thin SubPc layer deposited on 6T/Cs₂CO₃, due to the substrate influence, the following deposition showed that the band bending occurred in upward direction. For the SubPc/6T deposited on SiO₂, due to measurement fluctuations is difficult to conclude. The upward band bending suggests that an electron is accumulate at the SubPc interface due to the acceptor property. After annealing the stack layers, we observed a drastic reduction of the core-level shift at the organic films, as displayed at Fig. 2 (dashed lines), which could be explained as reduction of the density of the SubPc tail states that controls the band bending at the OOH interface by better molecular stacking due to the annealing, which reduces the available states to charge transfer to achieve the equilibrium. The influence of structural properties of SubPc on its electrical properties will be discussed in our presentation using STXM.

3. Conclusions

We studied the SubPc/6T system deposited on MoO₃, SiO₂ and Cs₂CO₃. We observed the electronic states using UPS and XPS and we conclude that different values of the WF of the substrates can modify the direction of the charge transfer at 6T/Substrate due to its ambipolar property in order to align the Fermi level with the substrate and achieve the equilibrium. Upon the deposition of SubPc, the OOH formation generates the charge transfer from 6T to SubPc due to the acceptor property of SubPc. For the SiO₂ substrate, we could not observe a clear evidence of charge transfer effect at both interfaces. We also demonstrated that modification in the film structure, by annealing, can control the charge transfer and charge accumulation at the OOH interface due to the reduction of the density of tail states. We conclude that the selection of the substrate WF and the film modifications can be used to control the electrical properties of OOH.

Acknowledgements

The first author acknowledges the Japanese Government for providing financial assistance to conduct this work through Monbukagakusho (MEXT) scholarship. This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2016G584 and 2016S2-002).

References

- [1] K. Cnops et al., Nat. Commun. **5** (2014) 3406.
- [2] J.-P. Yang et al., J. Phys. D: Appl. Phys. **50** (2017) 423002.
- [3] A. L. Foggiatto and T. Sakurai, Jpn. J. Appl. Phys. **57** (2018) 03EE01.
- [4] Y. Takeichi et al., Rev. Sci. Instrum. **87** (2016) 013704.
- [5] J. Endres et al., Chem. Mater. **28** (2016) 794.
- [6] T. Sakanoue et al., J. Appl. Phys. **103** (2008) 094509