

Tuning the electron injection barrier between Co and C₆₀ using an Alq₃ buffer layer

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Introduction:

- Since the first reported organic spintronic device based on carbon nanotubes in 1999,¹ devices fabricated from a variety of organic materials have been extensively investigated.^{2,3} The application of π -conjugated organic semiconductors into spin valves has aroused much interest because they possess several advantages: being inexpensive, processability at lower temperatures with less toxic waste, chemical tuning of electronic functionality and easy thin film fabrication. Most importantly, due to their extremely weak spin-orbit interaction and hyperfine interaction, exceptionally long spin diffusion lengths can be expected.^{2,3}
- C₆₀ is a promising n-type organic semiconductors, with ionization potential of ~ 6.3 eV and band gap of ~ 2.3 eV. Furthermore, room temperature C₆₀-based organic spintronic devices has been successfully demonstrated.⁴
- Interface is critical as it determines the injection efficiency of spin-polarized currents. Therefore it is of great significance to figure out ways to decrease the carrier injection efficiency at the interface between ferromagnetic electrodes and organic transporting layer. Herein we successfully reduce the electron injection barrier between Co and C₆₀ using an Alq₃ buffer layer.

Methodology

❖ Thin film growth:

Co: MBE

Organic semiconductors: Home-made double-head K-cell

❖ Interface property characterization: XPS and UPS

All the experiments are carried out at SINS beam line in SSSL

Results and Discussion

UPS study of Alq₃/Co interface

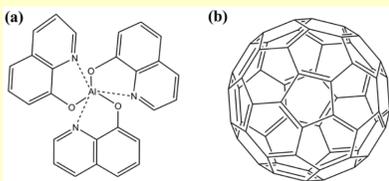
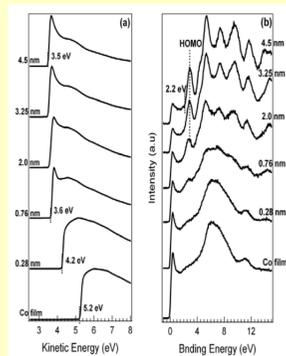


Fig.1 The chemical structural schematics of (a) Alq₃ and (b) C₆₀

Fig.2 The evolution of (a) secondary electron cutoff and (b) valence band spectra as a function of Alq₃ thickness on Co substrate. All the spectra are taken with a photon energy of 60 eV. A -5 bias is applied to the sample during the measurements of secondary electron cutoff and an offset of -0.6 eV have been made to each spectrum in (a).



• From Fig. 2 it can be seen a large interface dipole is formed between Alq₃ overlayer and Co substrate, which is contributed by two aspects: The Pauli repulsion at the interface (about several tenths of eV) and the intrinsic interface dipoles of Alq₃ molecules (about 1.0 eV). This is the reason why we choose Alq₃ to decorate the surface of Co substrate in the pursuit of decreasing the electron injection barrier between Co and the subsequent deposited organic semiconductors

XPS study of Alq₃/Co interface

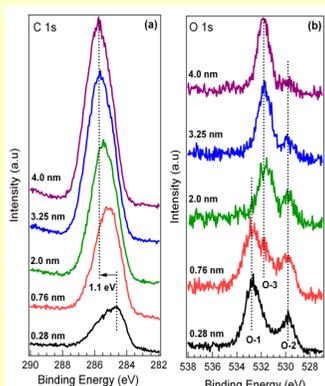


Fig.3 The evolution of (a) C 1s and (b) O 1s as a function of Alq₃ thickness on Co film. The C 1s and O 1s spectra were taken at photon energies of 350 eV and 650 eV, respectively.

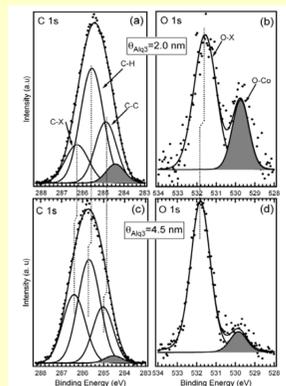


Fig.4 A fit to core level of C 1s (a), (c) and O 1s (b), (d) at normal thickness of 2.0 nm and 4.5 nm Alq₃, respectively, for Alq₃ growth on Co thin film. Solid lines through the experimental data points demonstrate the results of least-squares fitting.

- Interfacial chemical reactions occur between Alq₃ molecules and Co atoms: breaking of the C-X (X: Nitrogen or Oxygen) bonds and formation of Co-O bonds.^{4,5}
- The electronic gap states may produced in the interfacial chemical reaction between Alq₃ and Co, which could facilitate the injection of electron at the interface.

UPS study of C₆₀/Co, C₆₀/multilayer-Alq₃/Co and C₆₀/monolayer-Alq₃/Co structures

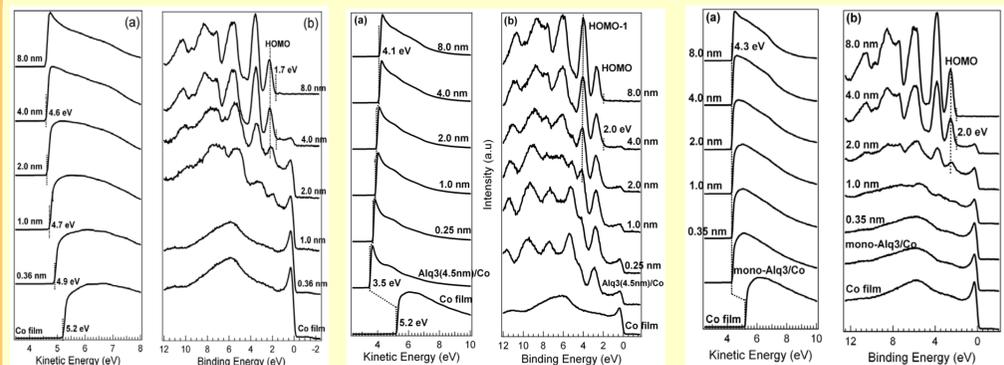


Fig.5 The evolution of (a) secondary electron cutoff and (b) valence band spectra as a function of C₆₀ thickness on Co substrate.

Fig.6 The evolution of (a) secondary electron cutoff and (b) valence band spectra as a function of C₆₀ thickness on 4.5 nm Alq₃/Co substrate.

Fig.7 The evolution of (a) secondary electron cutoff and (b) valence band spectra as a function of C₆₀ thickness on monolayer Alq₃/Co substrate.

- In Fig. 5, the hole injection barrier Δ_h (the distance from HOMO onset to FL) is 1.7 eV for C₆₀ grown on bare Co. Note that the energy gap of C₆₀ is 2.3 eV, therefore the interfacial electron injection barrier Δ_e (the distance from LUMO onset to FL) is about 0.6 eV.
- In Fig. 6 and 7, after the insertion of Alq₃ buffer layer sandwiched between Co and C₆₀, Δ_h enlarges to 2.0 eV, thus Δ_e is reduced to about 0.3 eV. Moreover, it is found that the tuning effect of Δ_e is not dependent on the thickness of mediated Alq₃ film.

The energy level alignment diagrams of C₆₀/Co, C₆₀/multilayer-Alq₃/Co and C₆₀/monolayer-Alq₃/Co structures

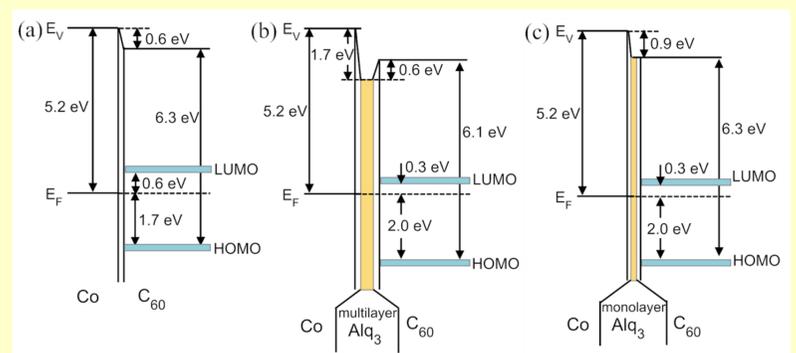


Fig.8 The energy level alignment diagrams for Co on (a) bare Co film, (b) multilayer Alq₃/Co substrate and (c) monolayer Alq₃/Co substrate.

- As shown in the illustrations, the insertion of an Alq₃ buffer layer between C₆₀ and Co reduces the electron injection barrier from 0.6 eV to 0.3 eV. However, increasing the thickness of Alq₃ cannot bring down Δ_e further. It seems that the Fermi level after the growth of C₆₀ is pinned at 0.3 eV below the fullerene LUMO

Conclusions

- The insertion of Alq₃ buffer layer between C₆₀ and Co can effectively reduce the interfacial electron injection barrier by almost half, from 0.6 eV to 0.3 eV
- The tuning effect of Δ_e is independent on the thickness of Alq₃ buffer layer, which means the monolayer Alq₃ film could tune Δ_e as effectively as that of multilayer film.

Reference:

1. K. Tsukagoshi, et. al, *Nature* **401**, 572 (1999)..
2. V. Dediu, et. al, *Solid State Commun.* **122**, 181 (2002).
3. Z. H. Xiong, et. al, *Nature* **427**, 821 (2004).
4. T. W. Pi, et. al, *Physical Review B* **71**, 205310 (2005)..
5. T. W. Pi, et. al, *J. Appl. Phys.* **101**, 043704-7 (2007).