Soft is Good, but Beware the Interfaces

This report features the work of Pei-Yu Cheng, Der-Hsin Wei and their co-workers published in Appl. Phys. Lett. ***104****, 043303 (2014), and the work of Jhen-Yong Hong, Minn-Tsong Lin and their co-workers published in Appl. Phys. Lett.* ***104****, 083301 (2014).*

Organic electronics attract much media attention. For example, by mounting electronic units on a flexible substrate, it is now practicable to construct lightweight, or even wearable, products, so that digital information can be accessed in ways that were previously unimaginable. A prerequisite of flexible electronics is, however, that the components residing on the substrates be just as flexible. Soft materials such as organic semiconductors (OSC) were hence introduced to work alongside metallic electrodes. Following successful use of layered metal-OSC hybrid structures to control charged carriers, scientists subsequently began to explore whether similar structures might be used to manipulate another property of electrons—spin.[1,2] Writing in *Applied Physics Letters*, Pei-Yu Cheng and collaborators at the NSRRC identified a potential problem in hybrid devices due to the presence of metal diffusion from the top electrode deeply into the OSC underlayer.[3] Jhen-Yong Hong and collaborators at National Taiwan University demonstrated a significant improvement in the magnetoresistance of a hybrid spin valve after the insertion of an ultrathin oxide layer at every ferromagnet-OSC (FM-OSC) interface.[4] These findings not only deepen our knowledge of what occurs at metallic-organic interfaces, but also pave the way for the construction of functional organic spin valves.

Controlling charged particles while minimizing their power consumption is one mission of electronic devices. The difficulty of the task is compounded when maintaining the spin polarization of carriers is also necessary. Considering that spin-orbit interactions (SOI) are what depolarize the spin current in non-magnetic materials, the use of OSC layers, which are known to exhibit small SOI, is expected to relieve such a concern, but the advantage of small SOI might be cancelled by the charge

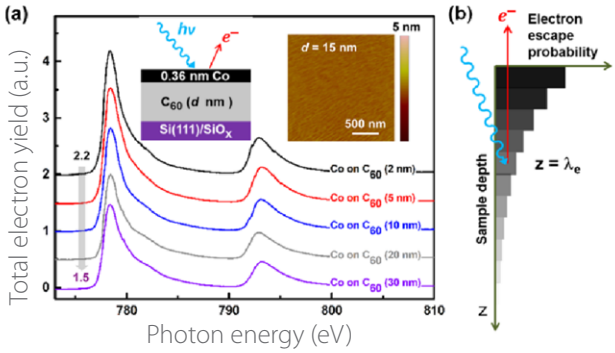

Fig. 1: (a) Co L-edge spectra taken from C_{60} (*d* nm)/Co (0.36 nm), *d* = 2–30. Reduced spectral intensity was found from structures with C_{60} of increased thickness. (b) An electron emitted at depth $z = \lambda_e$ within a C_{60} film has probability e^{-1} to reach $z = 0$. (Reproduced from Ref. 3)

traps present in OSC. In Cheng's work, the original aim was to understand why the Co electrode deposited on a fullerene (C_{60}) layer showed retarded development in its ferromagnetic (FM) order. Their research indicated, however, that the suppression of magnetic long-range order in the Co top electrode is associated with diffusion of metal into the C_{60} underlayer. Employing near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at **BL05B2** to examine the electronic structures of C_{60}/Co bilayers, the team found that not only were the π* resonances at the C K-edge sensitive to the presence of Co, but also the intensity of the Co L-edge varies systematically with the thickness of the C_{60} film. Figure 1 illustrates that the spectral intensity of Co at a fixed amount is inversely proportional to the thickness of the C_{60} film in the bilayers. After experimentally determining the inelastic mean free path of electrons in a C_{60} film, Cheng performed a model analysis on the data, which indicates that the interfacial region containing a mixture of

C_{60} and Co clusters has thickness at least 18.5 nm. Spin-polarized carriers are expected to experience enhanced scattering and depolarization when traveling through this mixed OSC-FM.

Knowing that ill-defined interfaces can deteriorate the performance of organic spin valves, Hong decided to decrease the orbital hybridization and metal diffusion in the device by inserting a thin oxide layer between every FM-OSC interface. Instead of constructing a FM/OSC/FM trilayer, Hong's device consisted of a soft bottom layer (NiFe/Co bilayers), an ultrathin AlO_x film, an organic spacer (3,4,9,10-perylene-teracarboxylic dianhydride; PTCDA), a second AlO_x film, and a hard top layer (Co). With this architecture, Hong's device delivered 13.5% tunneling magnetoresistance at room temperatue. To ensure that the introduction of an oxide layer did not alter the fundamental properties of the PTCDA layer, Hong carefully measured the molecular orientations of PTCDA through polarization-dependent and angle-resolved NEXAFS spectra in a series at **BL05B2** and **BL11A1**, respectively. The team concluded that, regardless whether it was deposited on a Co or an oxide surface, the PTCDA molecular plane (both perylene and anhydride groups) is essentially oriented lying-down. Moreover, the presence of the oxide layer served to minimize orbital hybridization. As seen in Fig. 2 in which X-ray photoemission electron spectroscopy (XPS) are shown at the C *1s* and O *1s* regions from Co/PTCDA and Co/AlO_x/PTCDA at **BL09A1**, the team found that the PTCDA layer shows significantly more molecular features when adsorbed on the oxide surface. An AlO_x layer (thickness 0.6 nm) is sufficient to eliminate any hybridization between Co and PTCDA.

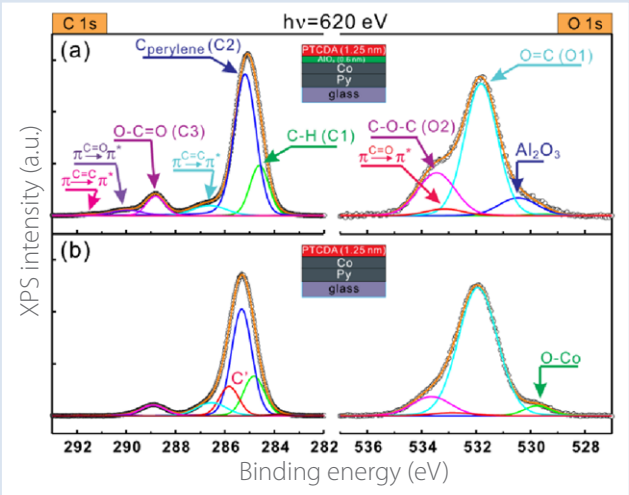

Fig. 2: XPS spectra of C *1s* and O *1s* recorded from a PTCDA film (1.25 nm) deposited onto (a) Co/AlO_x/ and (b) Co. (Reproduced from Ref. 4)

The identification of metal diffusion at OSC/FM bilayers implies that what separates the OSC spacer and FM electrode is not a two-dimensional surface but a region of thickness 10-20 nm comprising a mixture of metal clusters and organic molecules. Increasing the applied voltage can in principle push charged carriers through this ill-defined region, but the enhanced scattering and non-negligible SOI are expected to destroy the spin coherence among carriers. The improvement observed from devices with an oxide layer inserted between the OSC and FM layers demonstrates how critical the interface is, but constructing a functional organic spintronic device while minimizing or possibly eliminating any hard metallic layers remains a challenge.

References

1. V. Dediu, M. Murgia, F. C. Matacotta, C. Taliani, and S. Barbanera, Solid State Commun. **122**, 181 (2002).
2. Z. H. Xiong, D. Wu, Z. V. Vardeny, and J. Shi, Nature **427**, 821 (2004).
3. P. Y. Cheng, M. R. Chiang, Y. L. Chan, Y. J. Hsu, P. C. Wang, and D. H. Wei, Appl. Phys. Lett.**104**, 043303 (2014).
4. J. Y. Hong, K. H. Ou Yang, B. Y. Wang, K. S. Li, H. W. Shiu, C. H. Chen, Y. L. Chan, D. H. Wei, F. H. Chang, H. J. Lin, W. C. Chiang, and M. T. Lin, Appl. Phys. Lett. **104**, 083301 (2014).