Magnetic Response of an Ultrathin Cobalt Film in Contact with an Organic Pentacene Layer

Yuet-Loy Chan,[1] Ya-Jyuan Hung,[1,2] Chia-Hao Wang,[1,2] Ying-Chang Lin,[1] Ching-Yuan Chiu,[1] Yu-Ling Lai,[1]
Hsu-Ting Chang,[1,2] Chih-Hao Lee,[1,2] Y. J. Hsu,[1,3,*] and D. H. Wei[1,†]

[1]*National Synchrotron Radiation Research Center, 30076 Hsinchu, Taiwan*
[2]*Department of Engineering and System Science, National Tsing Hua University, 30013 Hsinchu, Taiwan*
[3]*Institute of Electro-Optical Science and Engineering, National Cheng Kung University, 70101 Tainan, Taiwan*
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To emulate the interfacial regimes of a Co/Pc/Co spin-valve structure, we fabricated ultrathin pentacene/cobalt (Pc/Co) and cobalt/pentacene (Co/Pc) bilayers. Through measurement of the magneto-optical Kerr effect, we found the Co layer has its magnetic properties depend strongly upon the order of deposition. Further x-ray spectroscopy and microscopy investigation indicated Co/Pc was chemically stable, whereas Pc/Co was reactive and exhibited complex magnetization pattern. The different chemistry and magnetic configurations at interfaces could cause additional complication for spin injection.

The feasibility of incorporating organic materials into spintronic devices has received intensive investigation [1–3]. Composed of atoms of small atomic number Z and therefore exhibiting weak hyperfine and spin-orbit interactions, the conducting polymers or molecules are considered as promising materials capable of preserving electron spins over a distance in the order of tens of nanometers. However, when the tris(8-hydroxyquinolinato) aluminum (Alq_3) served as a spacer in a vertical pseudo-organic spin-valve (OSV) structure, Xiong *et al.* discovered that the magnetoresistance (MR) ratio of $LaSrMnO_3/Alq_3/Co$ trilayers decreased rapidly with increasing temperature [4]. As a rationalization of this unexpected dependence on temperature, the ferromagnetism of half-metallic $LaSrMnO_3$ film at the bottom electrode was first considered to exhibit the undesired temperature dependence, whereas, after the $LaSrMnO_3$ layer was replaced with a Fe film whose Curie temperature is 1043 K, the structure still failed to yield an observable MR ratio at 300 K. The presence of polarized carriers in bulk electrodes apparently failed to circumvent the MR anomaly in the vertical OSV structure, and a modified mechanism for spin injection at the Fe/Alq_3 interface was thus suggested [5].

To establish efficient spin injection from a ferromagnet (FM) into an organic semiconductor (OSC), one must suppress the equilibration between the chemical potentials of two spin channels at FM-OSC interfaces [6] and circumvent the large mismatch of electric conductivity between FM and OSC [7]. Electron tunneling [8] and transport through interfacial gap states [9] are two of the mechanisms that meet the criteria above, but neither is known to posses such a temperature dependence that can produce a substantial change of MR ratio found in the $Fe/Alq_3/Co$ structure. The factor(s) affecting spin injection at a FM-OSC interface consequently remains a focus of current research [10–14]. In this work, our attention was devoted to a highly relevant but less discussed objective—namely,

how a FM film adjusts its characteristic properties when it is in direct contact with a conjugated OSC layer. Because two interfaces exist in a FM/OSC/FM trilayers, to better distinguish the possible difference between two interfaces our investigation involved structures in two series fabricated in reverse order of deposition: pentacene ($C_{22}H_{14}$, Pc) on cobalt (Co/Pc) and cobalt over pentacene (Pc/Co). Furthermore, films of thickness a few nm were retained in all structures to emulate the interfacial regime of a real trilayer structure of which the thickness of an individual layer is typically 30 nm or larger. The magnetic properties of a Co film were examined macroscopically with the magneto-optical Kerr effect (MOKE) and microscopically with an x-ray photoemission electron microscope (PEEM). A prospective correlation between magnetism and chemistry was investigated with additional x-ray photoemission spectroscopy (XPS).

All experimental structures were prepared in two separated, but connected, ultrahigh vacuum (UHV) chambers equipped with electron beam evaporators (OMICRON EFM-3) or a miniature Kunden cell evaporator (ADDON low temperature cells). On transfer of samples between the chambers for metallic and organic deposition, bilayers in two series—Co/Pc and Pc/Co—were thermally evaporated over either a Si(100)/Cr (3.4 nm) (introduction of Cr is to improve the Co adhesion) or a naturally oxidized Si(100) substrate, respectively; their film thicknesses were calibrated with either the intensity oscillations of a medium-energy electron diffraction pattern (Co) or a thin-film thickness monitor (Pc). The rates of deposition were 0.2 nm/min for Co and 0.1 nm/min for Pc, and Auger spectroscopy confirmed that the film homogeneity was better than 5% within an area of 6 mm in diameter. After fabrication, the structures were transferred into a chamber for polar and longitudinal (along a fixed [0$\bar{1}$1] direction) MOKE measurements. For x-ray spectral and microscopic investigations, the UHV systems were con-

nected to 09A2 beam line and 05B2 PEEM station at Taiwan Light Source, respectively. Except for the azimuthal anisotropy, which was independently determined by *ex situ* MOKE, and one Co/Pc structure, which was briefly removed from the UHV condition to adjust its position for maximized contrast of magnetic image, all structures were kept under UHV condition at all times.

The first structure investigated was a thin Co bottom film exposed to Pc molecules. Monitored by both *in situ* and *ex situ* MOKE, the Co film was found to maintain an in-plane magnetization and an easy axis oriented azimuthally along the $[0 \; \frac{-1-\sqrt{3}}{4} \; \frac{-1+\sqrt{3}}{4}]$ direction before and after the Pc deposition. In fact, as illustrated in Fig. 1(a), the most significant impact of bringing Pc onto a Co film was an immediate decrease ($\sim 5\%$) of *in situ* measured coercivity (H_c) after adsorbing only 0.1 nm of Pc. As H_c is a measure of anisotropy strength, the decrease of its magnitude implies that the anisotropy of Co film was softened upon adsorption of Pc. The concern was whether the softening would lead to a non-negligible perturbation toward the spin-polarized carriers transporting through it. In principle, the presence of an adsorbate would invariably disturb a substrate, but the strength of such disturbance is related closely to whether the adsorption resembles chemisorptions or physisorption. Chemisorption involves bond formation, and therefore charges transfer between the adsorbate and the substrate; chemisorption consequently generates not only an electric-dipole field at the interface but also the opposite binding energy (BE) shifts between electron donation and reception states. In contrast, for physisorption the dominant force holding both parts together is the van der Waals force originating from a rearrangement of the electron cloud between the adsorbate

and the electron tail protruding from the substrate surface [15]. Because only charge redistribution, not bond formation, is involved, physisorption introduces a dipole field at the interface but causes no shift of binding energy. According to Fig. 1(b), the binding energy of the C 1*s* level gradually decreases following an accumulation of Pc molecules on the Co surface, whereas the binding energy of the Co 2*p* level maintained at a constant value within our detection limit. Because the energy shift occurred on C 1*s* only, the interface is believed to be chemically stable, and the binding energy shift on C 1*s* is likely to associate with other physical processes within the Pc layer itself, such as the thickness-dependent molecular orientation which resulted from the competition between Co-Pc and Pc-Pc interactions [16,17]. With the Pc adsorption resembling physisorption, the magnetic properties of the Co bottom layer is not expected to be significantly altered, and the weak thickness-dependent coercivity change is ascribed to the formation of nucleation centers upon Pc adsorption.

The second structure under investigation had the same Co and Pc layers but fabricated in a reverse order of stacking over a Si(100) substrate covered with its nature oxide. Because the Pc layer is known to undergo a fractal mound growth mode on a SiO_2 surface [18], the Co film was practically grown over a rough Pc surface. Low energy electron diffraction and *ex situ* MOKE investigations indicated that the bilayers have no structural long-range order, and examination on a Pc (6.4 nm)/Co (5.4 nm) structure revealed an in-plane anisotropy with its easy axis oriented azimuthally along the [011] direction. Similar growth induced anisotropy has been found in Alq_3/Co bilayers [19,20]. What was unexpected was the need of relatively high Co coverage for Pc/Co bilayers to show a ferromagnetic order. As depicted in Fig. 2(a), the *in situ* hysteresis measurements acquired on Pc (6.4 nm)/Co (x nm) near 300 K, with $x = 0.1$–12.2, showed no observable hysteresis before the Co adlayer reached a nominal thickness of 3.3 nm. Increasing the Co coverage produced progressively increased magnitudes of remanence (M_r) and H_c, but the magnitude of H_c never exceeded what was measured at Co/Pc bilayers. In addition, the critical thickness was found to depend on temperature. As illustrated in Fig. 2(b), the Pc (6.4 nm)/Co (1.5 nm) showed an enhanced ferromagnetic order when it was cooled down to 198 K. Repeating the same room temperature measurements on other bilayers with 10.8 nm thick Pc layers arrived at similar thickness dependences and a critical thickness of 1.6 nm as indicated in Fig. 2(c). For an ultrathin film having its magnetic properties evolving with thickness, the finite-size effect has to be taken into account [21]. However, unless the Co top layer has somehow retain its size- and temperature-dependent properties through a process like the penetration of metal clusters [22], the finite-size effect which occurs at the ultrathin regime should not be the dominant factor affecting the properties of structures with large film thicknesses. To see if there are other non-
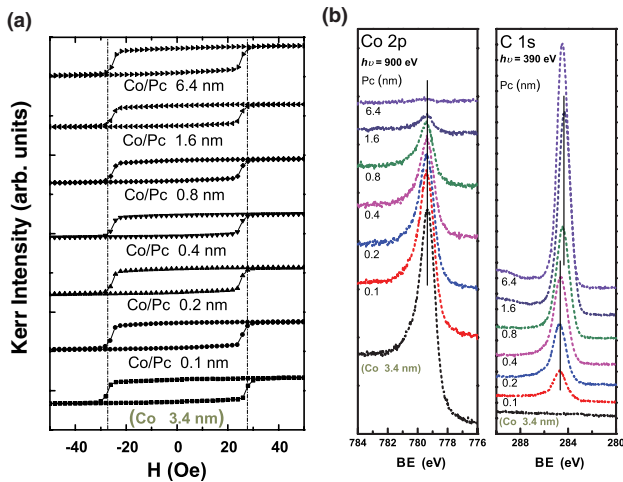

FIG. 1 (color online). MOKE and XPS measurements of Co (3.4 nm)/Pc bilayers recorded for various thickness of Pc. In (a), the hysteresis of the Co bottom layer measured along [011] shows little alteration upon the presence of a Pc adlayer. For core-level spectra illustrated in (b), the absence of opposite energy shifts between the binding energies of Co 2*p* and C 1*s* indicates the adsorption of Co onto Pc resembles physisorption.
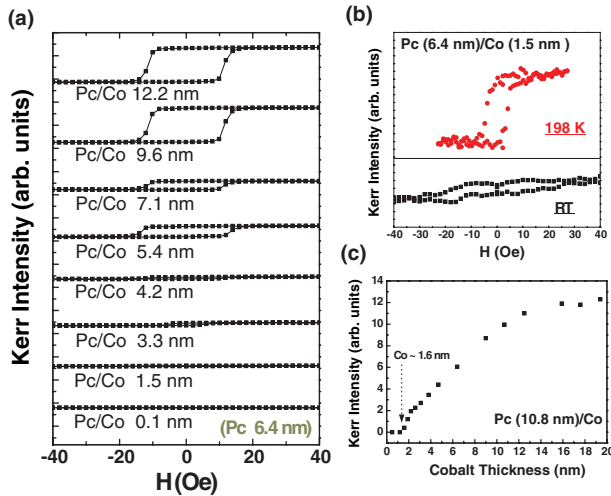
FIG. 2 (color online). MOKE measurements of Pc (6.4 nm)/Co bilayers with various thicknesses of Co. In (a), the hysteresis of Co overlayer taken at room temperature displayed clear thickness dependence. In (b), the hysteresis loops of Pc (6.4 nm)/Co (1.5 nm) structure have their Y axis zoomed in by a factor of 50. An enhanced ferromagnetic order was observed at 198 K. Hysteresis responses recorded at room temperature indicated the Pc (10.8 nm)/Co bilayers exhibited similar thickness dependence as depicted in (c). The Kerr intensity recorded in (c) corresponds to the remanence of each hysteresis loop.
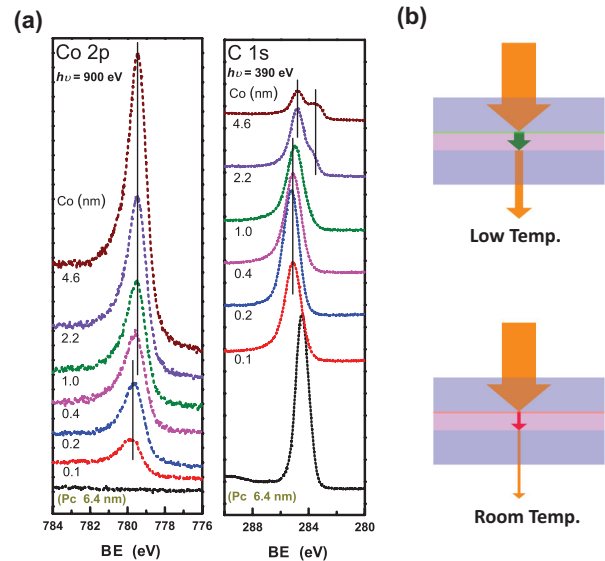

FIG. 3 (color online). XPS measurements of Pc (6.4 nm)/Co bilayers with various thicknesses of Co. In (a), the dependence of energy shifts on coverage observed for Co $2p$ and C $1s$ indicates the presence of a reactive interface. The additional shoulder appearing near 283.5 eV in C $1s$ spectra indicates the formation of Co carbide. Considering the Co-C composite has a low saturation magnetization and a low Curie temperature, it is possible for the spin-polarized carriers (orange arrows) to exhibit distinct temperature-dependent transmission probabilities as illustrated in (b).

trivial interface effect(s) that would persist its (their) impacts to the magnetic properties of Pc/Co structures, we recorded core-level electron spectra to examine the responses of Co and C at ultrathin Pc/Co bilayers. As depicted in Fig. 3(a), for Co deposited on Pc, we observed not only a shift of C $1s$ and Co $2p$ core levels to greater and lesser binding energies, respectively, but also a spectral feature corresponding to cobalt carbide [23]. While our study could not distinguish if the Co atoms or clusters diffusion had occurred, the spectra above did agree with an earlier report [24] that the interface at Pc/Co is chemically less stable than that at Co/Pc. Along with the possibility of metal diffusion, we anticipate that the Pc/Co structure has an ill-defined interface that mixes with Co clusters and cobalt carbide. Since the Co-C composite film is known to exhibit temperature dependence in its magnetic properties [25,26], the spin-polarized carriers crossing a Co-C composite interface are expected to show a temperature-dependent transmission probability as schematically illustrated in Fig. 3(b). The presence of ill-defined interfacial regimes also provided a reasonable explanation for the need of high Co coverages to turn on ferromagnetism in Pc/Co bilayers.

Understanding that reversing the deposition order of Co and Pc layers produced significantly modified hysteresis behavior and interfacial chemistry, the next concern was if the interface morphology would deliver other perturbation to the polarization of carriers. To clarify such a concern, we investigated the micromagnetic behavior of as-deposited

Co/Pc bilayers with a synchrotron-based x-ray microscopy, PEEM. Introducing the polarized photon along the direction of [011] and using the x-ray magnetic circular dichroism (XMCD) as its contrast mechanism, the x-ray image in Fig. 4(a) showed no observable magnetic contrast for Pc (1.8 nm)/Co (1.1 nm) near 300 K, a trend similar to the preceding hysteresis measurement on a thicker Pc film. The magnetic contrast became visible at a Co coverage 2.2 nm, and exhibited a ripplelike configuration as shown in Fig. 4(b). Because polarized electrons must respond to the magnetization vectors along their transport path, a spin-polarized current flowing through a medium filled with randomly oriented domain structures would suffer a decreased coherence due to the presence of extra spin-dependent scattering and reflection [27]. Close examination revealed that the magnetic image contains essentially two superimposed patterns as indicated in Figs. 4(c) and 4(d): a small range (~1 μm) of intensity variation spread across the entire image and a scattered variation patterns with larger lateral dimension (approximately tens of micrometers). To rationalize the information conveyed by x-ray images, our basis is that the intensity of the XMCD-based image (I) is proportional to the inner product of the magnetization vector in the ferromagnetic film (M) and the polarization vector of the photon (σ), $I \propto M \cdot \sigma$ [28]. Because the photons arrive at the surface at a 65° of angle of incident, the magnetic image acquired under a constant photon helicity contained con-
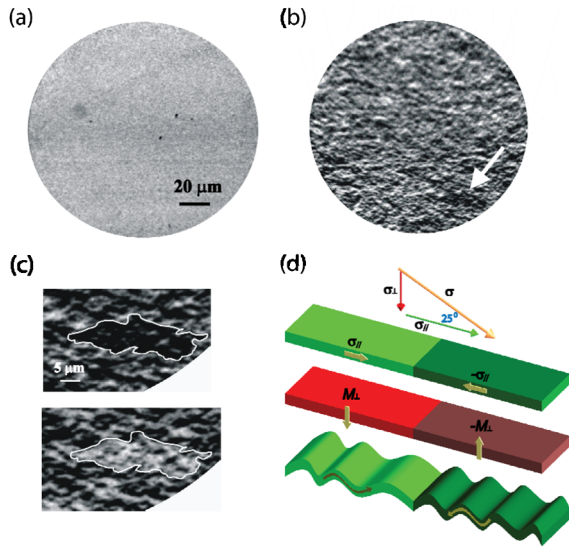
(a)   (b)

(c)   (d)

FIG. 4 (color online). (a),(b) XMCD ferromagnetic images of a Co film (thicknesses 1.1 and 2.2 nm, respectively) deposited on a Pc layer (thickness 1.8 nm). A thick Co layer is required to successfully observe magnetic contrast with microdomains. No morphology contrast is observed here in the XMCD-based image. Images in (c) are enlarged images of the region pointed out in (b). Images illuminated by photon beam with opposite helicities have inverted shades. Such microdomains in a single image are believed to have arisen from energy minimization and the film roughness as illustrated in (d).

tributions from both parallel ($M_\parallel \cdot \sigma_\parallel$) and perpendicular ($M_\perp \cdot \sigma_\perp$) components. Assuming the simplest case that M and σ lie on the same plane of incident photons as illustrated in Fig. 4(d), we estimate the relative image intensity according to this equation:

$$I(M; \sigma) \propto M_\parallel \cdot \sigma_\parallel + M_\perp \cdot \sigma_\perp.$$

Accordingly, the varied $I(M; \sigma)$ observed under fixed photon helicity can only come from a varying magnetization vector M. Unless the magnitude of Co magnetization depends on position, the display in a PEEM image is a map of included angles between localized magnetization vectors and the polarization vector of an incident photon. To explain what possible sources could make the magnetization vector vary in such an atypical manner, we first recall that the presence of multiple domains could reduce the magnetostatic energy of Co film. In addition to the energetic requirement, the profile of the bottom Pc layer morphology is expected to introduce a localized perpendicular modulation on top of the existing planar domain configuration in Co film, especially at ultrathin film thickness. Consequently, the ripplelike magnetization pattern recorded on PEEM is likely to be the result of a multidomain Co film standing on top a rough surface. An interface exhibiting multiple magnetizations states as described above is expected to cause extra spin-dependent scattering for polarized carriers traveling through it.

In summary, we have examined the responses of an ultrathin ferromagnetic Co film in contact with an organic Pc layer to investigate the modifications occur at FM-OSC junctions. According to our work, the Pc molecules adsorb on a Co film (thickness 3.4 nm) in a manner resembling physisorption, whereas the structure fabricated in reversed order has cobalt carbide formation as well as possible Co cluster penetrations at the interfacial regime. Depending on the magnetic nature of the interface, we expect that a spin-polarized current flowing through such a hybrid structure would have to adjust its spin coherence and spin injection efficiency accordingly. Furthermore, as the micromagnetic image reveals complicated domain configurations at Pc/Co bilayers, the spin-polarized current is expected to experience enhanced spin-dependent scattering.

*yjhsu@nsrrc.org.tw
†dhw@nsrrc.org.tw

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