

Magnetic depth profiling of the Co/C₆₀ interface through soft X-ray resonant magnetic reflectivity

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Abstract

We have probed the structural and magnetic properties of a ferromagnetic/organic interface constituted by a polycrystalline Co layer deposited on a fullerene thin film through resonant soft x-ray reflectivity measurements. The fitting analysis of the reflectivity indicates the formation of a sharp interface with limited intermixing and a null remanent magnetization in a ~ 1 nm thick region of the Co film at the interface with C₆₀. This information contributes to elucidate the role of organic-inorganic interfaces in the charge and spin transport inside organic spintronic devices.

Index Terms

organic-inorganic interface, cobalt, fullerene, soft X-ray resonant reflectivity, resonant magnetic scattering

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I. INTRODUCTION

THE use of organic materials in spin valves and magnetic tunneling junctions was investigated in depth in recent years for the possibility of combining the potential of molecular electronics and spintronics [1]. Organic materials have low fabrication costs, allow the production of flexible and stretchable device and, above all, present extremely large spin relaxation times (up to a millisecond) thanks to the weak spin-orbit coupling of their light constituting elements. In particular, the behaviour of organic spin valves is largely influenced by the interfaces between the ferromagnetic electrodes and the organic layer [2]. Both the charge and spin injection across the organic-inorganic interface can be largely affected by strong perturbations such as intermixing, chemical reactions or molecular disruption as well as roughness and morphology [3]–[6]. All these phenomena affect the performance of hybrid spintronic devices and complicate the identification of the spin-transport mechanism [7]–[9]. For example, the insertion of a thin oxide barrier between the ferromagnet and the organic revealed to be effective in improving the spin-valve performance [10]. On the other hand, the interaction between organic and ferromagnetic materials has recently attained a huge interest, since it was recognized that the hybridization of organic molecular orbitals and the spin-unbalanced bands of 3d transition metals might constitute a powerful pathway to modify the spin polarization of the interface region [11]–[15]. The electronic structure of the resulting “spinterface” is largely dependent on the strength and character of hybridization as well as on its thickness. This implies the formation of a compound material that, in perspective, could be properly tailored to act as a multifunctional unit for storage and processing [16], [17].

In the plethora of possible organic molecules, the C₆₀ buckminsterfullerene has exhibited a great potential for spintronic applications thanks to its relatively high electron mobility, the weak spin-orbit coupling and the null nuclear magnetic moment of the majority ¹²C isotope which strongly reduces the spin-dephasing mechanisms related to hyperfine coupling. Recent studies demonstrated that at the 3d metallic ferromagnet/C₆₀ interface the hybridization between the metallic 3d_{z²} and the carbon 2p_z orbitals produces unexpected magnetic behaviour at both the ferromagnet and the organic side, as for example the reduction of the magnetic moment of the ferromagnetic layer, the spin reorientation transition from in-plane to out-of-plane magnetization or induced magnetism propagating into the bulk organic C₆₀ layer [18], [19]. Such complex phenomenology can enable spin filtering effects [20] and/or modify the spin polarization of carriers [21] with obvious drawbacks in the functionalities of molecular spintronic

devices.

In this work, we employed soft x-ray resonant magnetic reflectivity (SXRMR) to probe the structural and magnetic properties of a Co/C₆₀ bilayer with the cobalt deposited on top of the organic layer. Investigations of magnetic interfacial configuration in literature mainly refer to the ideal condition of an organic layer on top of a single crystalline ferromagnetic layer, while the opposite configuration, i.e. polycrystalline ferromagnet grown onto an organic layer, has been scarcely investigated. Resonant X-ray reflectivity is a non-destructive photon-in/photon-out synchrotron-based technique that combines spectroscopic information and vertical spatial resolution taking advantage of the interference phenomena. Consequently, this technique is particularly suitable to study the properties of buried interfaces and multilayered heterostructures [22]–[25]. In order to provide depth-resolved information about the compositional and magnetic profile for both C₆₀ and Co, we performed energy- and angle-dependent SXRMR measurements in which the photon energy of the incident x-ray beam ranged across the carbon K (~284 eV) and cobalt L_{2,3} (~778.1–793.2 eV) absorption thresholds. The use of circularly polarized radiation and the analysis of the difference in spectra acquired with opposite helicity and/or magnetization direction provided depth-resolved information on the magnetization distribution [26], [27]. Joint chemical and magnetic information on the buried Co/C₆₀ interface has been obtained through the fitting analysis of the reflectivity measurements. Our results indicate the formation of a well-defined Co/C₆₀ interface with modest chemical roughness, limited intermixing and chemical interaction between the materials. In addition, our measurements describe the magnetic profile of the interface, evidencing the presence of a strongly depressed remanent magnetic moment for the interfacial Co layer.

II. EXPERIMENTAL

The SXRMR measurements were performed at the BEAR bending-magnet beamline of the ELETTRA synchrotron [28], [29]. The investigated sample was grown by *in-situ* deposition at room temperature of C₆₀ and subsequently of cobalt by thermal sublimation on a Si(001) substrate covered by native silicon oxide with an expected thickness in the range of 1–3 nm. The deposition rates were 0.4 nm/min for C₆₀ and 0.12 nm/min for cobalt, as indicated by a quartz crystal microbalance. The expected nominal thicknesses for the C₆₀ and Co layers are 42 nm and 8 nm, respectively. A soft x-ray beam with 90% degree of circular polarisation was adopted to perform all the energy and angular measurements. Resonant reflectivity spectra were acquired at room temperature firstly

on the bare C_{60} layer and subsequently, after the deposition of the cobalt layer, on the full Co/C_{60} system. In order to carry out dichroic reflectivity measurements at the C K and Co $L_{2,3}$ absorption thresholds, the in-plane remanent magnetization of the sample was switched through an external magnetic field generated *in situ* by a coil mounted on the sample holder and having a strength of about 40 mT. The magnetization was oriented parallel to the sample surface and in the scattering plane and all the spectra were acquired in remanence. To provide the resonant contribution to the refractive index for both materials, x-ray absorption and x-ray magnetic circular dichroism (XMCD) spectra were measured in total-electron yield mode varying the photon energy across the C K and Co $L_{2,3}$ thresholds and measuring the drain current. From the absorption and XMCD spectra we obtained the imaginary parts of the atomic charge and magnetic scattering factors and the real parts are then calculated through Kramers-Kronig relations [27]. Non-resonant values of the atomic scattering factors are taken from Ref. [30].

The fitting of the experimental reflectivity spectra was carried out with the ReMagX software, which is based on the 4×4 matrix formalism for the propagation of the electromagnetic waves in anisotropic multilayers [23], [27], [31]. The measurements consist of two sets of reflectivity data, one acquired before and the other after the Co deposition. For each of the two configurations, a structural model of the sample, i.e. the concentration depth profiles for the various elements, is provided by the simultaneous fitting of all the acquired angular and energy reflectivity scans. The subsequent fitting of the dichroic reflectivity spectra on the complete sample furnishes the Co magnetization depth profile.

The morphology of the surface of the cobalt layer was probed *ex situ* by atomic force microscopy (AFM) measurements using a Smena vacuum head (NT-MDT[®], Moscow, Russia). Topographic images were collected in air, in semi-contact mode, by using relatively hard cantilevers with resonant frequency of 300 kHz and elastic constant of 15 N/m. *Ex-situ* magneto-optical Kerr effect (MOKE) was used in order to verify the magnetic behaviour of the cobalt layers. Measurements were performed in longitudinal configuration with excitation wavelength $\lambda_{ex} = 632.8$ nm and external applied magnetic field $\mu_0 H_{max} = 0.3$ T directed parallel to the sample surface.

III. RESULTS AND DISCUSSION

θ - 2θ measurements at constant photon energy $h\nu=765.7$ eV obtained before and after the deposition of the Co film over the C_{60} layer are shown in Fig. 1. The curve relative to the Co/C_{60} bilayer is the average of two measurements acquired with opposite magnetization directions in order to cancel magnetic dichroic effects. This dichroic contribution is in any case very small, the used photon energy being 13 eV below the Co L_3 absorption peak. Both curves show clear interference oscillations that confirm the homogeneity of the layers. In particular, the clear interference pattern in the curve relative to the Co/C_{60} bilayer indicates a uniform and homogeneous coverage of cobalt.

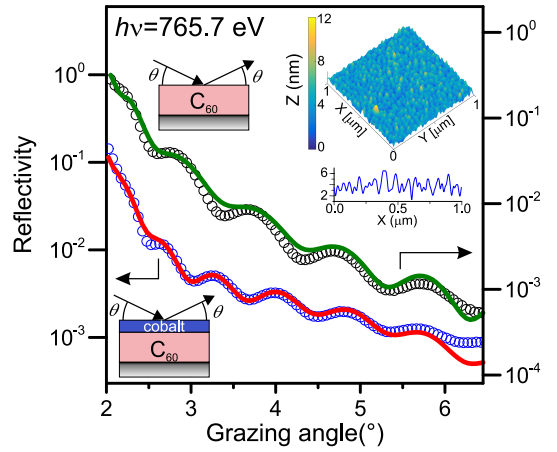


Fig. 1. θ - 2θ scans at the photon energy $h\nu=765.7$ eV acquired before (black circles) and after (blue circles) the *in-situ* deposition of the Co layer compared to their fittings (green and red curve, respectively). The scan for the bare C_{60} layer is shifted vertically to avoid superposition and for a better readability. Inset: Topographic AFM image for a $1 \mu\text{m} \times 1 \mu\text{m}$ region of the Co/C_{60} system. The colorbar matches the range of the height in the AFM image. A typical line profile is reported at the bottom. The root-mean square roughness (RMS) of the surface is 1.0 ± 0.2 nm.

In Fig. 1 we also report the best-fitting curves for the two θ - 2θ scans. The most relevant fitting parameters, which give a structural model that must reproduce all the angular and energy reflectivity scans, are the thickness, roughness and mass density of the various layers. The second set of measurements, acquired on the complete sample, is sensitive to the characteristics of both the C_{60} and Co layers and of their interface. The obtained parameters relative to the organic film are confirmed by the fitting of the first set of scans, performed immediately after the deposition of the fullerene film. We find that the actual thickness of the layers is 6.3 ± 0.5 nm for cobalt and 45 ± 1 nm for C_{60} . These values are very close to the expected nominal thicknesses of 42 nm and 8 nm, respectively. The thickness of the organic layer is large enough to ensure that the morphology of the surface is not conformal to the one of the substrate. The density of the C_{60} resulted 1.64 ± 0.07 g/cm³, indicating the formation of a densely packed molecular layer [32]–[34]. In the structural model obtained from the analysis, the root-mean square (RMS) roughness of the Co/C_{60} interface results 0.4 nm indicating the presence of a rather sharp interface, while a RMS roughness of 1.0 nm is found for the surface of the Co layer. For what concerns the Co/C_{60} interface, we are not sensitive enough to distinguish between a simple rough profile or a graded interface. However, considering the metal-on-organic nature of the Co/C_{60} bilayer, we guess that a thin intermixed region could reasonably have been formed. The thickness of this region can be estimated as 0.9 ± 0.3 nm (i.e. the full width at half maximum roughness of the interface), suggesting that the diffusion of cobalt inside the organic layers is rather limited. A small interdiffusion between Co and fullerene is often experienced [18], [21], even though in some studies intermixing regions up to 18 nm were observed [35]. The penetration of the Co atoms is found to be higher for slow deposition rates, however it can be reduced through depositing on a highly textured C_{60}

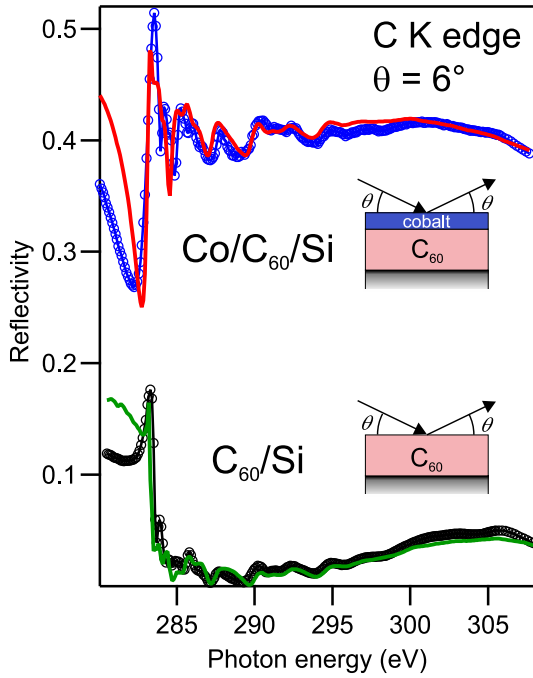


Fig. 2. Resonant reflectivity energy scans measured across the C K edge for the grazing angle $\theta=6^\circ$ before (black circles) and after (blue circles) the deposition of the Co layer. The fittings of both curves are reported as green and red line, respectively.

film [36]. The structural features of the interface are largely dependent on the fabrication procedure which, in our case, promotes the growth of a smooth, compact C_{60} layer [34]. Thus, the formation of small clusters at the surface is likely more favoured than the interdiffusion of sparse atoms. This mechanism prevents the diffusion of cobalt atoms into the organic layer, similarly to the deposition on top of Alq_3 thick films, for which the formation of cobalt clusters was observed [37]. The achievement of a small metal-on-organic interface region for organic spin valves containing Alq_3 molecules is essential to increase the magnetoresistance of these devices at room temperature through improving the spin current injection and detection [7]. Our results indicate that this structural improvement can be obtained also for devices incorporating the Co/C_{60} bilayer.

The surface topographic image of the cobalt layer, probed by *ex-situ* AFM, is shown in the inset of Fig. 1. The cobalt film displays an homogeneous distribution of grains with an averaged radius of 20 ± 2 nm [38]. The surface is very smooth, with a RMS roughness of 1.0 ± 0.2 nm. Noticeably, the surface roughness of the cobalt provided by AFM agrees perfectly with the value obtained through the fitting of the reflectivity measurements.

Reflectivity scans as a function of the photon energy were acquired spanning the regions of the C K and Co $L_{2,3}$ absorption thresholds while keeping the angular geometry fixed. The energy scans performed across the C K edge at a grazing angle $\theta=6^\circ$ before and after the deposition of the Co layer are shown in Fig. 2 with their respective best-fitting curves. After the deposition of the Co layer we acquired dichroic SXRMR measurements with two opposite remanent-

magnetization directions. In Fig. 2 we show the average of these two measurements. It is worth noting that the resonant reflectivity at the C K edge is larger for the sample with the cobalt layer on top of C_{60} rather than for the bare organic film. This is an apparent contradiction motivated by the experimental geometry because, in the energy range of the C K edge, the grazing angle $\theta=6^\circ$ is smaller than the critical angle of cobalt for total external reflection (about 9°) [39]. The cobalt layer therefore contributes significantly to reflect most of the incident radiation. Nevertheless, the penetration depth of the incident radiation for $\theta=6^\circ$ is about 6 nm [40]. This value is large enough to let the radiation pass through the cobalt layer and be scattered also by the underlying molecules, thus providing the resonant contribution of the C_{60} to the reflectivity.

The good agreement shown in Fig. 2 between the numerical calculations and the experimental results confirms the rather limited interaction between the metal and the organic material. All the spectral features of the resonant contribution are reported correctly, and there is no evidence of changes which might be assigned to the orbital hybridization of the molecules with the metal. In particular, in case of hybridization the spectral term at about 283.5 eV, which is related to the lowest occupied molecular orbital (LUMO), should be depressed with respect the other features of the resonant region. This behaviour is expected in close similarity to what has been observed through soft X-ray absorption spectroscopy of the Co/C_{60} interface for which the formation of spin-polarised molecular states was observed for thicker metal-organic intermixing regions [18], [35]. In our case, the structural characterization indicates a boundary region of about 1 nm, i.e. of the order of one molecular layer, hence the $Co-C_{60}$ chemical interaction should concern primarily the top layer of C_{60} molecules. We notice that no dichroism was observed for the SXRMR spectra at the carbon K edge. This is likely due to the thermal state of our sample, that was kept at room temperature. In analogous bilayers consisting of Co deposited onto a C_{60} layer, Cheng et al. [35] found a clear XMCD signal on the C K edge at 125 K and no dichroism at room temperature. On the reversed bilayer, i.e. C_{60} film deposited on Co, Moorsom et al. [18], combining XMCD and polarized-neutron reflectivity (PNR) measurements performed in an applied magnetic field and at low temperature (100 K), found for the fullerene close to the interface a small magnetic moment of about $1.2 \mu_B$ per cage with a direction opposite to the bulk Co magnetization. A fullerene magnetization opposite to that of the interfacial transition metal was also found by Tran et al. in a C_{60}/Fe bilayer [41]. A lower temperature and/or the application of a magnetic field during the measurements are probably needed to highlight a net magnetization of the molecules at the interface, as is the case with the experiments mentioned above [18], [35].

In Fig. 3 we show the SXRMR energy scans acquired for the bilayer system at the grazing angles 3° and 6° . The spectra in the top panels were averaged over the two opposite orientations of the sample magnetization. The dichroism correspondent to these measurements, defined as the difference between the reflectivity curves acquired with opposite sample

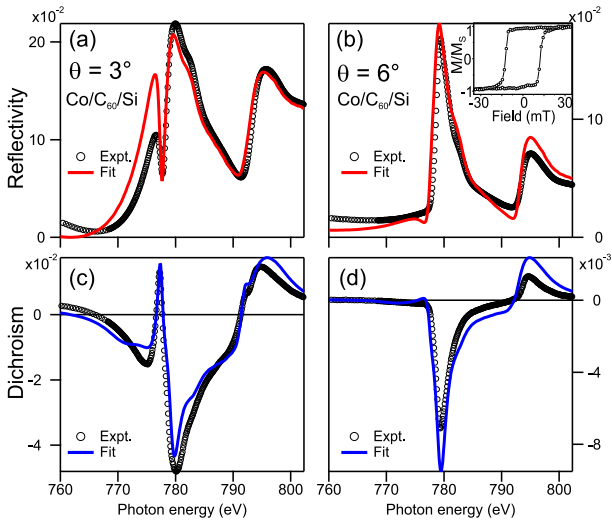


Fig. 3. (a)-(b) Energy-dependent average resonant reflectivity (black dots) and fitting curves (red lines) across the Co $L_{2,3}$ absorption edge at the constant grazing angles $\theta=3^\circ$ and 6° , respectively. In the inset of panel (b) we report a typical hysteresis loop measured by longitudinal MOKE. The coercive field is 12 ± 1 mT. (c)-(d): Dichroism of the resonant reflectivity (black dots) and best fitting (blue line) for the two angular geometries

magnetization, is reported in the bottom panels. In the inset of panel (b) we also show the magnetic hysteresis loop of the sample acquired through *ex-situ* Kerr rotation measurements. The hysteresis loop is typical for a ferromagnetic metallic cobalt layer, with a coercive field of about 12 mT. It is worth to notice that the shape of the averaged reflectivity spectra and the corresponding dichroism curves exhibit a clear dependence on the angular geometry. The resonant spectrum at 3° resembles the real part of the refraction index for the region of the cobalt absorption threshold, while at 6° the reflectivity is closer to the typical profile of the absorption spectrum for a metallic cobalt layer, which is strictly related to the imaginary part of the refractive index [42].

As explained above, the reflectivity scans across the Co $L_{2,3}$ edges were fitted together with the average angular scans and the energy scans across the C K edge acquired after the Co deposition, providing the structural parameters of the complete sample. The resonant charge and magnetic atomic scattering factors for the energy region of the Co $L_{2,3}$ absorption thresholds were retrieved from the soft X-ray absorption and magnetic circular dichroism spectra (XAS/XMCD) acquired just after the cobalt deposition. The best-fitting curves are shown in the panels (a) and (b) of Fig. 3, comparing them with the experimental data. A fitting analysis of the dichroic energy scans at 3° and 6° is performed in order to individuate the vertical distribution of the Co magnetic moments. The obtained best-fitting curves are reported along with the experimental dichroic scans in the panels (c) and (d). The good agreement with the fitting curves confirms the reliability of our results for the magnetization profile of the cobalt layer. In the fitting of the dichroic measurements, we fixed the structural parameters previously obtained by the analysis of the average angular and energy scans. Considering z as the vertical axis perpendicular to the sample surface and oriented along the growth direction,

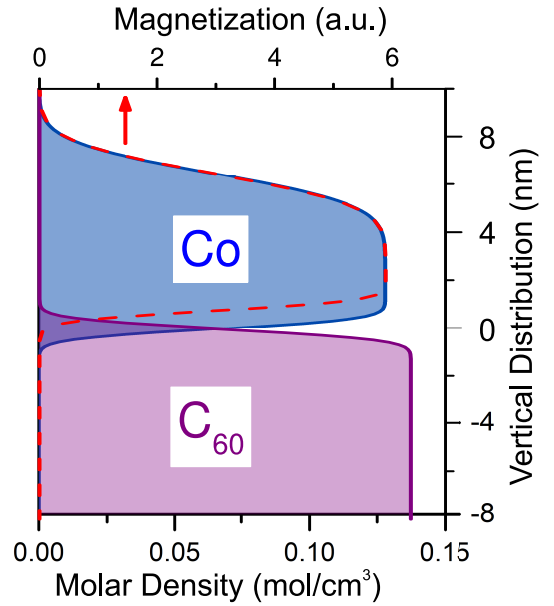


Fig. 4. Depth profiles of C molar density (violet solid line), Co molar density (blue solid line) and Co remanent magnetization (red dashed line) in the top portion of the sample obtained from the fitting analysis. The zero in the vertical distribution corresponds to the center of the interface region.

the positions z_1 and z_2 of the lower and the higher boundaries of the rectangular distribution of the magnetic moments were treated as free fitting parameters. In this way the fitting procedure can investigate the possible presence of a layer with null or reduced net remanent magnetization in the Co film at the surface and/or at the interface with the fullerene film or, conversely, an extension of the distribution of the Co magnetic moments inside the fullerene layer. This second possibility is very unlikely because the investigation of the structural characteristics of the film revealed a quite abrupt interface between the Co and fullerene layers but it is important not to confine the lower boundary z_1 in the Co layer to verify the reliability of the fitting procedure. The boundaries of the rectangular magnetic moment distribution were not forced to be sharp but possessed a distinct broadening parameter for the two borders. The Co magnetization depth profile obtained from this fitting procedure is reported in Fig. 4, which also shows the density profile of the Co and C_{60} layers previously provided by the fitting analysis of the average angular and energy reflectivity scans.

Noticeably, comparing the concentration and magnetization profiles of cobalt reported in Fig. 4 we find the presence of a thin Co layer lacking a net remanent magnetic moment close to the buried interface. The thickness of this layer is about 0.8 ± 0.3 nm, which is comparable to the thickness of the interface. The occurrence of a non-magnetic interface layer has been reported for several systems such as (Fe)Co-Alq₃ or Co-Pc, for which the ferromagnetism is observed only once the nominal thickness of the metallic overlayer is larger than 1.5 nm [4], [6], [43]. The presence of a transition-metal layer with reduced magnetization at the interface with fullerene was also reported for C_{60}/Fe systems [41], [44]. In the case of C_{60} deposited on cobalt single-crystal substrates, the adsorption

geometry of the molecule with respect to the surface crystallographic orientation of the magnetic layer is the critical parameter for determining the overall magnetic behavior [18], [45]. The present study deals with the opposite configuration of Co polycrystalline layer onto the organic C_{60} substrate, thus in our case the nature of intermixed interfacial layer and the interface roughness play a very critical role. The reduction of the Co remanent magnetization in the interface region can be tentatively ascribed to the weakening of exchange interaction among Co atoms due to the presence of C_{60} . It is possible that this depleted exchange interaction leads to a paramagnetic Co interface region. However, our measurements probe only the magnetization component in the direction parallel to the sample surface and to the scattering plane, thus we cannot rule out that ferromagnetic Co domains are actually present at the Co/ C_{60} interface but disordered or oriented differently at remanence. In any case, our results indicate that the decrease of cobalt magnetization is spatially limited to the thin interface region.

The presence of this layer with reduced remanent magnetization will have detrimental effects on the spin transport across the interface and the nature and thickness of this region must be taken into account in the modeling of the magnetoresistive response of spintronic devices [46], [47]. Thus, the structural and magnetic optimization of the Co/ C_{60} interface might contribute substantially to the magnetoresistive response of spintronic devices based on these materials. For example, the introduction of an ultra-thin oxide layer between the metal and the organic material should be effective in preventing the formation of the layer with depressed magnetization and in improving the spin injection from the ferromagnetic to the organic film, as demonstrated for similar systems in literature [10], [18].

IV. CONCLUSIONS

We have probed the interface occurring in a Co/ C_{60} bilayer through resonant and non-resonant soft x-ray magnetic reflectivity. This system is typical of the top interface of organic spin valves having the C_{60} layer sandwiched among ferromagnetic electrodes. We show that the SXRMR results provide consistent structural, chemical and magnetic information on the buried organic-inorganic interface. In particular, we demonstrated the presence of a limited roughness, intermixing and chemical interaction at the Co/ C_{60} and the presence of a ~ 1 nm thick buried interfacial Co region lacking net remanent magnetization, in accordance with what was already observed in the reversed bilayer and other similar systems. These results indicate that for the deposition of ferromagnetic metal onto the organic layer, any effect correlated with the formation of a spinterface is limited to this thin region. The magnetoresistive response of devices including Co as top contact over the C_{60} layer will likely benefit from the optimal fabrication of this interface.

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