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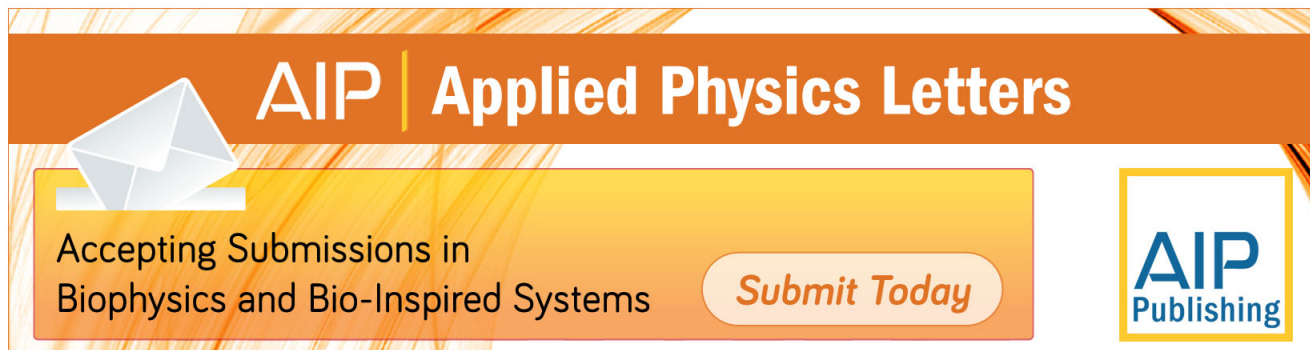
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Interface effects on an ultrathin Co film in multilayers based on the organic semiconductor Alq₃

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The effect of the AlO_x barrier thickness on magnetic and morphological properties of Ta/Co/(AlO_x)/Alq₃/Si hybrid structures was systematically studied by means of atomic force microscopy, superconducting quantum interference device magnetometry, and nuclear magnetic resonance (NMR). All used techniques pointed out that the barrier thickness of 2 nm is required to obtain a magnetically good cobalt layer on top of Alq₃. ⁵⁹Co NMR measurements revealed that the AlO_x barrier gives rise to the formation of an interface layer with “defective” cobalt favoring growth of “bulk” cobalt with good magnetic properties. © 2010 American Institute of Physics. [doi:10.1063/1.3505495]

Spin injection and transport in organic semiconductors (OSs) have been attracting much attention since the demonstration of the magnetoresistive effects in lateral devices¹ and the spin valve (SV) effect in the vertical configuration.² These hybrid structures provide tunable electronic properties combined with low-cost production, efficient spin-injection, and long spin diffusion length.³ A crucial point to take into account in the case of vertical architecture of SVs is the quality of the top ferromagnetic (FM) electrode that is deposited on the OS layer. As expected, the magnetic properties and their reproducibility are strongly affected by the underlayer roughness.^{4–6} Furthermore, it has been shown that deposited Co, both as clusters or atoms, can penetrate into the Alq₃, causing pinholes and Co inclusions over a distance of ~100 nm.² On the other hand, transmission electron microscopy revealed an abrupt interface between Co and Alq₃ with minimal intermixing.⁷ Therefore, the insertion of a buffer layer between the FM top electrode and the OS has been widely adopted to reduce possible interface disorder.⁸ Following this approach, examples of efficient device performance are reported in Ref. 8 where the good quality of the Alq₃ layer without Co inclusions and with significantly better SV effect was demonstrated in Co/tunnel barrier/Alq₃/La_{0.67}Sr_{0.33}MnO₃ (LSMO) structure after insertion of a thin Al₂O₃ tunnel barrier. Since magnetic and transport properties of FM/OS/FM junctions are strongly dependent on interface roughness or compositional intermixing, a deep comprehension of the interface quality is essential to understand the device performance and operation conditions.

In this letter, we study magnetic and morphological properties of Co/(AlO_x)/Alq₃ interfaces with various AlO_x barrier thickness probed by means of zero-field ⁵⁹Co nuclear magnetic resonance (NMR), superconducting quantum interference device magnetometry (SQUID), and atomic force microscopy (AFM). The interfaces under study represent the

top electrode of vertical organic SVs layers of Co/Alq₃/LSMO where the insertion of a buffer layer of aluminum oxide was essential for devices operation.

50-nm-thick Alq₃ films were deposited at room temperature (RT) by organic molecular beam deposition in UHV conditions (10⁻⁹–10⁻¹⁰ mbar) on naturally oxidized Si substrates. The Alq₃ layer was covered by AlO_x tunnel barrier (0–5 nm) grown by channel spark ablation from a polycrystalline stoichiometric target. The 15-nm-thick Co top layer was deposited by magnetron sputtering in Ar atmosphere. Finally, a 2-nm-thick Ta capping overlayer was added in order to prevent Co oxidation. These systems lack the bottom LSMO electrode in order to perform a magnetic characterization but 50 nm OS film thickness ensures that the Alq₃ surface morphology is independent from the substrate (both Si or LSMO) and the Co/Alq₃ interfaces can be compared with the analogous ones in the full operating devices.

The sample Co/Alq₃/LSMO without AlO_x barrier demonstrates a quite inhomogeneous morphology with different surface microstructures examined by AFM (Nanoscope III/A Multimode) in tapping mode. Some part of the sample has a nanograined morphology resembling the typical microstructure of cobalt deposited on ordinary substrates, e.g., Si [see Fig. 1(a)]. The other part of the sample, however, bears clear resemblance to the morphology of recrystallized Alq₃ [see Fig. 1(b)]. We note that the bare Alq₃ thin films is amorphous with root-mean-square (rms) roughness of about 1.5 nm (data not shown) but exposure to air is known to induce the formation of Alq₃ crystalline structures increasing thus the overall film roughness.⁹ The estimated rms roughness of Co/Alq₃/LSMO is higher in zones where Co decorates Alq₃ with peak-to-peak (PP) of about 10 nm, as compared with the continuous Co regions where PP is less or equal to 2 nm. This large contrast confirms the morphological indication that Co adhesion depends on the crystallinity of Alq₃. The absolute value of the roughness may however be influenced by Ta capping layer, since tantalum atoms tend to fill the small gaps between large cobalt particles, smoothing the

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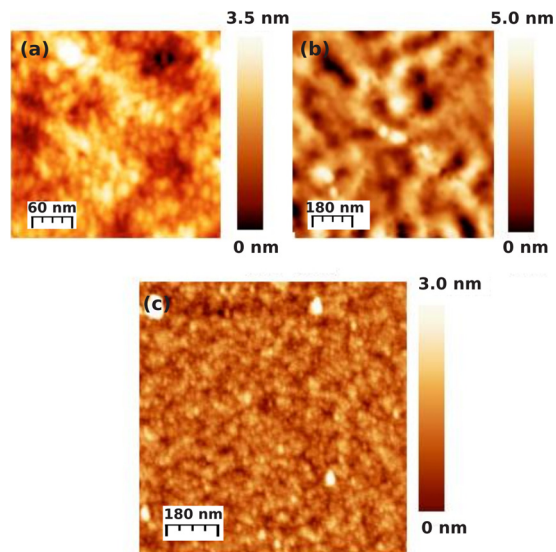


FIG. 1. (Color online) AFM Images (height topographic signal) for the sample Ta/Co/Alq₃/Si (top panel): (a) example of a typical Ta/Co morphology (zoom from the original size 5 × 5 μm); (b) example of Alq₃ recrystallization when the Co barely decorates the Alq₃ structure underneath (zoom from the original size 5 × 5 μm), and (c) Ta/Co/1 nm AlO_x/Alq₃/Si (bottom panel).

measured surface.¹⁰ The average grain size in the smoother areas is 30–40 nm.

Inserting an AlO_x barrier makes the morphology of the Co film and Ta capping layer fairly homogeneous [see Fig. 1(c)]. In the sample with 1-nm-thick AlO_x barrier the surface is smooth with an rms roughness of 0.33 ± 0.02 nm, PP height of 3.5 ± 0.2 nm, and an average grain size ~30 nm. However further thickening of the AlO_x spacer does not change the surface morphology of the samples significantly. Figure 2(a) displays the rms roughness and PP variation in the topographic height versus thickness of the AlO_x barrier, in the range 1–5 nm. Both parameters are nearly constant albeit for a small increase with thickness as expected for an overall thicker film. These AFM measurements draw us to the conclusion that the AlO_x barrier of 1 nm is already sufficient to guarantee a smooth and morphologically homogeneous Co film.

The AlO_x barrier improves also the magnetization of the heterostructures. All samples, measured by a Quantum Design MPMS-XL 5T SQUID, reproduce a FM behavior at RT (data not shown). The saturation magnetization from $M_S \approx 850 \pm 20$ emu/cm³ for the sample without barrier increases with the AlO_x thickness [Fig. 2(b)] recovering the best value $M_S \approx 1100$ emu/cm³ obtained by deposition of Co on Si substrate. This recovery is achieved for barrier thickness of 2 nm or more determining a critical thickness for AlO_x barrier required to obtain Co film of a good quality. This value is consistent with the threshold for a continuous Co film obtained from AFM. The low coercive field value, $\bar{H}_C \approx 15$ Oe, suggests the nanocrystalline nature of these films with ferromagnetically weakly coupled Co nanograins and strongly reduced anisotropy,¹¹ and the absence of variation with AlO_x thickness nicely correlates with the almost constant roughness of Fig. 2(a).

A threshold barrier thickness of ~2 nm is also found in zero-field ⁵⁹Co NMR measured at $T = 1.6$ K with home-built broadband NMR spectrometer¹² and a tuned probe circuit.

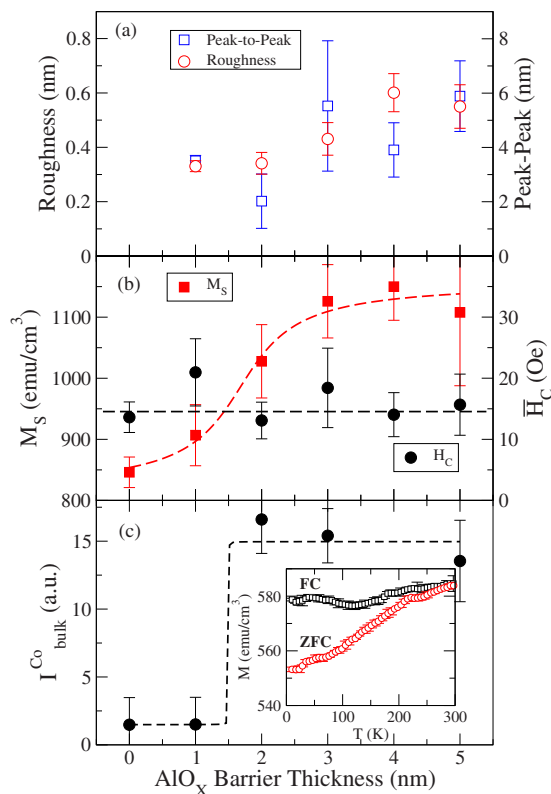


FIG. 2. (Color online) The AlO_x barrier thickness dependence of (a) rms roughness (circles) and PP height (squares); (b) saturation magnetization M_S (squares) and coercive field H_C (dots); (c) ⁵⁹Co NMR integrated intensity of bulk cobalt (dots). Lines are guides for eyes. Inset: temperature dependence of the magnetization measured in the sample without barrier ($H = 10$ Oe, in-plane).

All spectra (see Fig. 3), obtained on the same set of samples, show the presence of a main Gaussian resonance line centered in the usual Co metal range, at a frequency of ~220 MHz. The full width at half maximum is ~10 MHz, i.e., the line is much broader than in perfect, epitaxial films but it can still be attributed exclusively to “bulk” Co nuclei, surrounded by the full set of $z = 12$ nearest neighbor (nn) Co.¹³ The width is due to the presence of smaller perturbations, such as a mixture of fcc Co (~217.4 MHz), hcp Co (~224 MHz), and a large amount of stacking faults (distributed between fcc and hcp phases).¹³ However, the samples without and with 1-nm AlO_x barrier reveal the much lower NMR signal intensity $I_{\text{bulk}}^{\text{Co}}$ than samples with the thicker barrier [see Figs. 3 and 2(c)]. Since the observed NMR signal arises from domain walls (DWs) (as evident by the large detected DW enhancement),¹³ the reduction in $I_{\text{bulk}}^{\text{Co}}$ for barrier thickness below 2 nm may be due to the formation of very small single domain cobalt particles (grains) disconnected magnetically. Therefore, such an effect in the samples with the barrier thinner than ~2 nm may be responsible for the reduced M_S values [compare Figs. 2(b) and 2(c)].

This assumption is supported also by the temperature dependence of the magnetization measured in the junction without barrier at $H = 10$ Oe. The inset of Fig. 2(c) shows that for this film zero field cooling (ZFC) and field cooling (FC) $M(T)$ curves, both measured on heating, split below ~220 K. The observed behavior could be interpreted as the superposition of a clusterlike contribution and a normal FM one. We suppose that at interface with Alq₃ small Co clusters

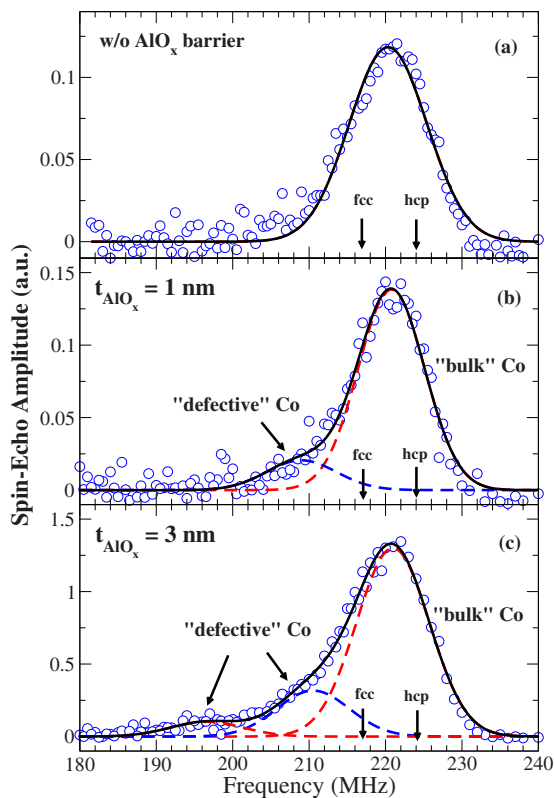


FIG. 3. (Color online) Zero-field ^{59}Co NMR in Ta/Co/(AlO_x)/ Alq_3 /Si (a) without, (b) with 1-nm-thick, and (c) with 3-nm-thick AlO_x barrier measured at $T=1.6$ K. All spectra were corrected by corresponding enhancement factor.

are present, likely interacting both with other clusters and with the continuous film rising above. In that situation a collective behavior is expected and accordingly the temperature at which divergence between ZFC and FC curves occurs indicates the onset of cooperative freezing of interacting magnetic clusters.¹⁴ It is important to notice that for the samples with the AlO_x barrier the measured temperature dependence of FC/ZFC curves is clearly different.¹⁵ While we cannot exclude the presence of a few Co clusters even in the case of samples with the oxide barrier, as some voids or defects in the AlO_x layer are likely, we think that these clusters should be larger with respect to the case of bare Alq_3 , or strongly interacting, as they appear to be blocked up to RT. Hence the presence of a 2-nm-thick AlO_x barrier is sufficient to grow magnetically well connected FM Co layer on top of Alq_3 .

In addition the spectra obtained on samples with AlO_x barrier contain a distinct, structured lower frequency shoulder (see Fig. 3) attributed to the “defective” cobalt. Such a defective cobalt have one or more either missing or substituted nn Co (e.g., with Al ion). The replacement of one nn Co atom by a nonmagnetic atom or defect removes a hyperfine contribution at the cobalt nucleus producing a shift in the resonance ^{59}Co frequency by about 12–22 MHz depending on substituent.¹³ Therefore inserting the AlO_x barrier results in the formation of $\text{Co}_{1-c}\text{X}_c$ alloy (c is the concentration of the defects X) presumably located close to the interface. This observation and the fact that the thick enough AlO_x barrier substantially improves the magnetization and NMR intensity $I_{\text{bulk}}^{\text{Co}}$ [see Figs. 2(b) and 2(c)] allow to conclude that the formation of an interface layer with defective Co ($\text{Co}_{1-c}\text{X}_c$ random alloy) is important to obtain a good quality FM bulk cobalt on top of Alq_3 layer.

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¹V. Dediu, M. Murgia, F. C. Matocotta, C. Taliani, and S. Barbanera, *Solid State Commun.* **122**, 181 (2002).

²Z. H. Xiong, D. Wu, Z. Vally Vardeny, and J. Shi, *Nature (London)* **427**, 821 (2004).

³V. A. Dediu, L. E. Hueso, I. Bergenti, and C. Taliani, *Nature Mater.* **8**, 707 (2009).

⁴I. Bergenti, A. Riminucci, E. Arisi, M. Murgia, M. Cavallini, M. Solzi, F. Casoli, and V. Dediu, *J. Magn. Magn. Mater.* **316**, e987 (2007).

⁵C. Pernechele, I. Bergenti, M. Solzi, M. Ghidini, F. Casoli, and V. Dediu, *J. Magn. Magn. Mater.* **322**, 1251 (2010).

⁶Y. Liu, S. M. Watson, T. Lee, J. M. Gorcham, H. E. Katz, J. A. Borchers, H. D. Fairbrother, and D. H. Reich, *Phys. Rev. B* **79**, 075312 (2009).

⁷W. Xu, J. Brauer, G. Szulczewski, M. Driver, and A. N. Caruso, *Appl. Phys. Lett.* **94**, 233302 (2009).

⁸V. Dediu, L. E. Hueso, I. Bergenti, A. Riminucci, F. Borgatti, P. Graziosi, C. Newby, F. Casoli, M. P. De Jong, C. Taliani, and Y. Zhan, *Phys. Rev. B* **78**, 115203 (2008).

⁹H. Aziz, Z. Popovic, S. Xie, A.-M. Hor, N.-X. Hu, C. Tripp, and G. Xu, *Appl. Phys. Lett.* **72**, 756 (1998).

¹⁰C. Clavero, L. Martínez, A. García-Martín, J. M. García-Martín, Y. Huttel, N. D. Telling, G. van der Laan, A. Cebollada, and G. Armelles, *Phys. Rev. B* **77**, 094417 (2008).

¹¹G. Herzer, *IEEE Trans. Magn.* **25**, 3327 (1989).

¹²G. Allodi, A. Banderini, R. De Renzi, and C. Vignali, *Rev. Sci. Instrum.* **76**, 083911 (2005).

¹³P. Panissod, in *Frontiers in Magnetism of Reduced Dimension Systems*, edited by V. G. Bar'yakhtar and P. E. Wigen (Kluwer Academic, Netherlands, 1998), Vol. 49, p. 225.

¹⁴S. Bedanta and W. Kleeman, *J. Phys. D: Appl. Phys.* **42**, 013001 (2009).

¹⁵See supplementary material at <http://dx.doi.org/10.1063/1.3505495> where zero-field-cooling vs. field-cooling magnetization data suggests that the AlO_x barrier reduces the formation of non interacting magnetic clusters.