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Magnetic properties of the Co/Alq_3 interface

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A method is described for measuring the magnetic integrity of ferromagnetic/organic interfaces that involves measuring the magnetic moment per unit area of bilayers with different ferromagnet thicknesses. The method is first used to determine the thickness of the oxide passivation layer on Co and $Co_{90}Fe_{10}$ (3.0 and 1.6 nm, respectively). The Alq_3/Co interface is rather sharp, with roughness confined to about 3 monolayers of Co at the interface. The Co/Alq_3 interface seems to be much rougher, with a dead layer that is several nanometers thick, However, this layer can be eliminated by capping the Alq_3 layer with Al, so the dead layer is attributed to oxidation of the cobalt surface through the organic. The interface sharpness is improved when a 1 nm layer of LiF is inserted between Co and Alq_3. © *2011 American Institute of Physics*. [doi:10.1063/1.3562504]

There is growing interest in transport of spin-polarized currents through organic conductors. The transport of electron spins through metals and semiconductors, and across narrow insulating tunnel barriers is at the heart of conventional spin electronics. Organic conductors, with their long spin lifetime and low mobility, offer a new set of material properties as compared to the other spin propagation media.[1] Furthermore, organic electronics is an established technology with products such as organic light-emitting diodes for displays and organic field-effect transistors for sensors. The challenge is to add useful magnetic functionality to these devices. Furthermore, the physical processes governing spin transport and lifetime in organic conductors remain matters for discussion.

Recent work on ~10 micron junctions of thin film stacks with an organic layer where the small-molecule semiconductor tris-(8-hydroxyquinoline)Al (Alq_3) acts as a tunnel barrier or a transport layer between ferromagnetic electrodes[2–6] have yielded spin-valve magnetoresistance at room temperature of up to 16%.[6] Experiments at low temperature on nanoscale junctions have yielded magnetoresistance values more than an order of magnitude greater.[7] The large difference in the magnetoresistance for such junctions is likely due to the strong role played by the interface between dissimilar materials. For example, insertion of a thin layer of LiF between an aluminum electrode and Alq_3 can reduce the barrier height and enhance the current injection into the organic layer.[8] It is also advantageous to introduce a thin oxide layer (AlO_x or MgO) between the metallic electrode and the organic layer in spin-valve structures.[3–6] The rationale for this may be (i) the oxide acts as a passivation layer at a point in the fabrication process where vacuum is broken, (ii) by analogy with inorganic semiconductors, the oxide layer may help solve the resistivity mismatch problem,[9,10] or (iii) the oxide acts as a barrier to prevent interdiffusion and chemical reaction between the metal and the organic.

Buried interfaces are not easy to characterize. High resolution transmission electron microscopy (TEM) with atom-scale chemical analysis provided by electron energy-loss spectroscopy is usually the technique of choice, but it does not capture the magnetic character of the interface. TEM images suggest that a rather abrupt interface is formed when ferromagnetic metals are deposited onto Alq_3 films[3,11] with roughness on a 1–2 nm length scale, although other evidence suggests Co penetration up to 50 nm in regions of Alq_3.[12] X-ray spectroscopy suggests a 1 nm reaction layer, and ferromagnetic metallic cobalt at 2 nm and beyond.[11] Here we adopt a simpler method, magnetization measurements on a series of bilayer or capped bilayer systems composed of an organic layer and a ferromagnetic layer of variable thickness. We refer to this as the ferromagnetic film thickness magnetization (FFTM) method.

The principle of the method is illustrated in Fig. 1. A series of bilayer films is prepared on a substrate. The nominal ferromagnetic layer thickness t is varied, and the film moment m in Bohr magnetons per square nanometer is plotted against t. The slope for bulk cobalt, for example, corresponding to the room-temperature cobalt magnetization $M = 1.44$ MA m^{-1} is 154 μ_B nm^{-3}. This is the slope expected for large cobalt thicknesses, but deviations will appear at thicknesses comparable to the interface roughness or interdiffusion layer width, as shown in Fig. 1(b). At a very rough interface, detached islands of ferromagnetic metal may be surrounded by organic material. These may be superparamagnetic at room temperature, but will block with approximately the full cobalt magnetization at low temperature. It has been established that the magnetization of cobalt retains practically its bulk value up to the surface layer.[13] The intercept t_x and the shape of the curve at smaller thickness provides information on the ferromagnetically active interface between the metal and the organic. It must be recognized that the interface is formed of discrete atoms, with roughly five atomic layers per nanometer, so there are bound to be deviations from the high-thickness slope below 1 nm. Furthermore, interfaces are rarely ideally sharp. Roughly speaking, t_x is the magnetic "dead layer" thickness. Thinner films may have a magnetic moment, but it is reduced from the bulk value by roughness, interdiffusion, and/or chemical reaction.

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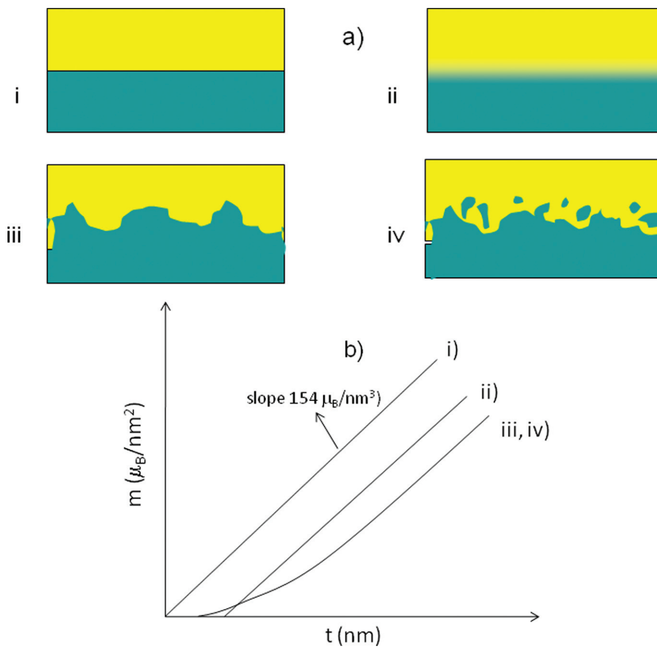

FIG. 1. (Color online) Schematic illustration of different magnetic interfaces: (i) sharp, atomically flat interface, (ii) diffuse interface with a reacted interlayer where the metal is no longer all ferromagnetic, (iii) a rough but sharp interface, and (iv) a very rough, but sharp interface. The magnetic moment is plotted as a function of the nominal thickness of ferromagnetic metal, *t*, in the lower panel.

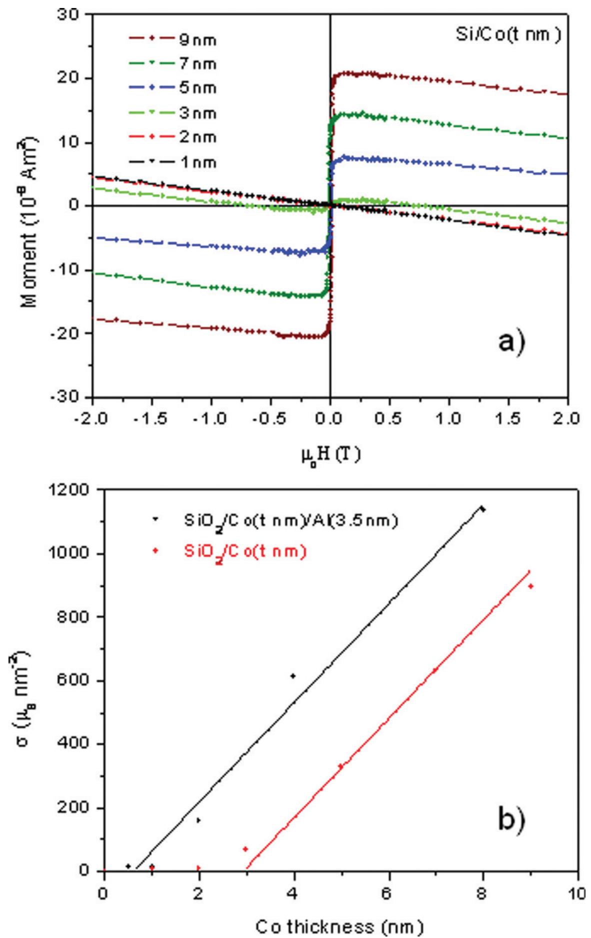

FIG. 2. (Color online) (a) Room-temperature magnetization curves for cobalt layers of different nominal thickness deposited on Si/SiO_2. (b) FFTM plot of the data, showing the effect of introducing a 3.5 nm Al cap layer.

An awkward feature of thin films is that they have two sides! We have to know how one side behaves in order to deduce something about the other. A judicious choice of substrate and capping layer in a series of different stacks is required to exploit the FFTM method. Here we discuss the cobalt/Alq_3 interface. Alq_3 is a popular tunnel barrier or transport layer in organic spin-valve structures. All the thin film structures were prepared without breaking vacuum in a chamber with a base pressure of 5×10^{-8} Torr. Cobalt was deposited on a Si/SiO_2 substrate or Alq_3 films by using an electron-beam evaporation technique. The source–substrate distance was 250 mm. The Alq_3 and Al cap layers were deposited by thermal evaporation. Film thicknesses were monitored using a quartz crystal monitor during deposition. All magnetization measurements were made in a 5 T SQUID magnetometer.

Initially, we investigated a cobalt layer deposited on Si wafers that were subsequently exposed to air. The cobalt is known to form a monolayer of Co–O–Si phase at the interface[14] and the upper surface is oxidized on exposure to air to yield a 2–3 nm passivation layer of CoO.[15] Since CoO is an antiferromagnet, with a Néel temperature of 291 K, it makes no contribution to the ferromagnetic moment. Fitting the data in Fig. 2, to a line with slope 154 μ_B nm^{-3} gives a thickness $t_x = 3.0$ (1) nm, which may be identified with the thickness of the CoO passivation layer at the surface, provided the SiO_2/Co interface is flat and sharp. The high-field diamagnetic slope is due to the silicon substrate. The effect of adding a 3.5 nm Al cap layer is shown in Fig. 2(b). It reduces t_x to 0.5 (3) nm, which reflects the combined magnetic roughness of the top and bottom interfaces.

Turning now to the Co/Alq_3 interface, the cobalt layer can be either above, or below the Alq_3. When it is on top, it is necessary to use a cap layer in order to prevent the formation of CoO. The plot for Alq_3/Co/Al stacks is shown in Fig. 3(a). The value of t_x is small, 1.0 nm, indicating the cobalt–organic interface is quite well defined when the cobalt is on top, with possible formation of a metalorganic complex.[16] If the Al cap layer is omitted, the value of t_x rises to 3.4 nm, which represents the sum of the CoO passivation layer thickness and the Alq_3/Co interface. The rms roughness of the 40 or 10 nm Alq_3 layer is 0.19 or 0.32 nm, respectively, much less than the dead layer thickness.

The situation seems to be different when Alq_3 is deposited on cobalt. Then the value of t_x is 3.3 nm, which suggests an extremely diffuse interface. This would appear to justify the practice of incorporating a thin protective layer of AlO_x (Refs. 3–6) or MgO (Ref. 6) at the surface of the bottom cobalt electrode in an organic spin-valve stack. However, a surprising result was found when an Al cap layer was deposited on the Alq_3. The characteristic thickness t_c then fell to just 1.0 nm. It seems that the Co/Alq_3 interface is oxidizing through the Alq_3, and that it is *not* intrinsically very rough. Since fairly large magnetoresistance values are achieved at room temperature for stacks that have a direct Alq_3/Co top interface, it seems likely that similar results may be possible with a direct Co/Alq_3 bottom interface as well, at least insofar as the organic acts as a tunnel barrier.

In Al-capped Co on Alq_3, t_x was reduced from 0.6 nm at room temperature to 0.3 nm at 4 K. The disconnected regions

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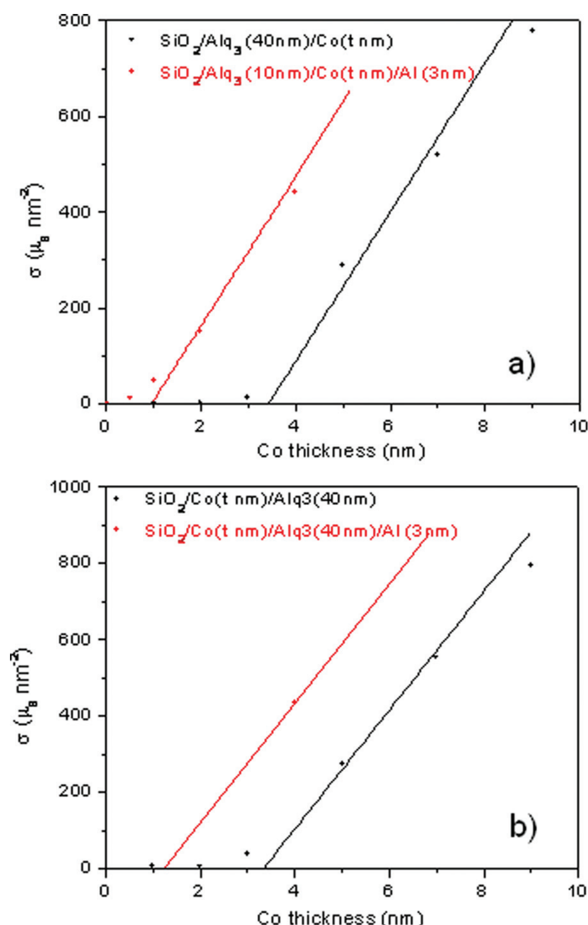

FIG. 3. (Color online) FFTM plots for the Alq_3/Co interface showing the effect of the Al cap layer on (a) the bilayer with cobalt on top and (b) the bilayer with Alq_3 on top.

of cobalt metal shown in Fig. 1(a) (iv) are blocked, increasing the ferromagnetic volume and decreasing its roughness.

In almost all of the FFTM plots, there is a nonzero cobalt moment at thicknesses that are just less than t_x. This shows clearly that t_x is an upper limit on the thickness of the magnetic dead layer. For example, the data in Fig. 3(a) show a moment $m = 47\ \mu_B\,\mathrm{nm}^{-2}$ for a thickness of 1 nm. This would be consistent with a corrugation of the Co/Alq_3 interface in which half of the area at this depth is composed of cobalt atoms that are connected to the bulk of the film. Such a corrugated surface may help to promote spin injection into the organic, whereas an interface where paramagnetic cobalt is dissolved in the organic is likely to destroy the spin polarization of injected electrons by spin-flip scattering.

Finally, we investigated the effect of introducing a thin interlayer of LiF between the Co and Alq_3. The LiF is expected to promote injection of electrons into the band derived from the lowest unoccupied molecular orbital (LUMO) of Alq_3. In a sandwich structure with two cobalt electrodes, the current flowing across the device at low bias increases by three orders of magnitude when the LiF is introduced [Fig. 4]. The effect of LiF at the Co interface is to reduce t_x from 0.6 to 0.3 nm. However, no magnetoresistance

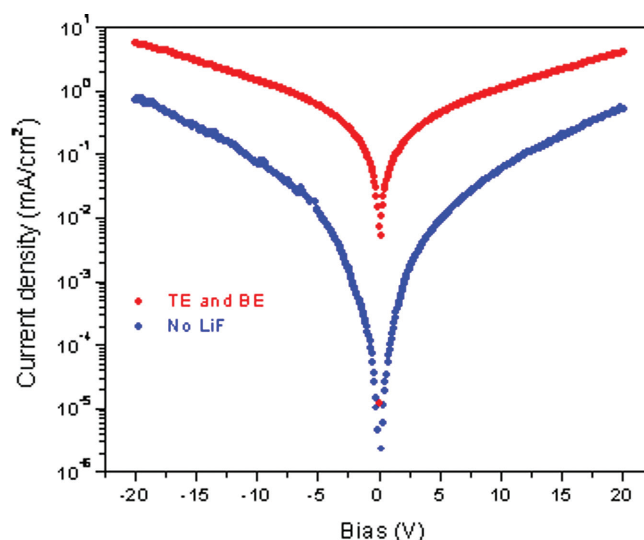

FIG. 4. (Color online) *I*:*V* characteristics of a Co/Alq_3/Co structure with and without a 1 nm LiF interlayer at the top (TE) and bottom (BE) interfaces.

was observed in spin valve stacks with a LiF interlayer. This suggests that spin is not preserved for electrons injected into the LUMO. Any tunnel magnetoresistance in the stacks is swamped by the effect of the unpolarized electron current.

In conclusion, the FFTM method helps to characterize the magnetic integrity of ferromagnetic/organic interfaces. These interfaces are surely critical for developing organic spintronics, but they are not well understood. For example, it is not clear why we can inject or recover spins across a Co/Alq_3 interface in a mode where they hop or diffuse through the organic,[6] when it is difficult to do the same at a Co/Si interface.[17] The development of "spinterface science" should eventually clarify these issues, but it will need new experimental probes and protocols to explore the critical buried interfaces.

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