The role of aluminum oxide buffer layer in organic spin-valves performance

Yiqiang Zhan, Xianjie Liu, Elin Carlegrim, Fenghong Li, I Bergenti, P Graziosi, V Dediu and Mats Fahlman

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Spin injection and transport in organic semiconductors have been gathering much attention since the demonstration of the magnetoresistive effects in lateral devices \(^2\) and the spin valve (SV) effect in vertical devices \(^1\). One of the main issues in the vertical architecture of SVs is the quality of the top ferromagnetic (FM) electrode that is deposited on the organic film. For example, in the device discussed in Ref. \(^2\), the Co electrode was deposited on top of 8-hydroxyquinoline aluminum (Alq3) layer. It is well known that the FM properties of the top layer very much depend on the roughness of the substrate, \(^3,4\) and of course the interaction with the substrate as well. It has been frequently reported that the roughness of organic surface is rather high, \(^5\) which would affect the quality of FM electrode above it. Furthermore, our recent results \(^6\) have shown that Co atoms (or clusters) penetrate into the Alq3 layer upon vapor deposition. The penetrated Co atoms and the Co atoms at the interface will chemical react with Alq3 molecules. \(^5\) Not only does this chemical interaction create uncertainty in terms of how (and if) it affects the spin injection, but also the quality of Co film itself is crucially related to the interface. \(^6\) In conventional organic electronics, inserting a buffer layer in between the top electrode and the organic layer \(^2,9\) has been widely adopted to improve device performance. Following this approach, an organic SV with a thin layer of aluminum oxide inserted between the organic and top electrode recently has been demonstrated showing improved SV behavior. \(^10\)

In this letter, ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) results on Co/Al2O3/Alq3 interfaces are reported in comparison with the Co/Alq3 interface. The energy level alignment at the Co/Al2O3/Alq3 interfaces is discussed as well. Reasons for the improvement of the Co electrode upon inclusion of an Al2O3 buffer layer are presented based on our XPS and x-ray magnetic circular dichroism (XMCD) results.

The experiments were carried out using a Scienta® ESCA 200 spectrometer. The vacuum system consists of an analysis chamber and a preparation chamber. XPS and UPS were performed in the analysis chamber at a base pressure of \(10^{-10}\) mbar, using monochromatized Al(Kα) x-rays at \(hν=1486.6\) eV and He I radiation at \(hν=21.2\) eV, respectively. The experimental conditions were such that the full width at half maximum of the Au 4f\(_{7/2}\) line was 0.65 eV. The binding energies were obtained referenced to the Fermi level with an error of \(±\) 0.1 eV. Sputtering and material depositions were done in a preparation chamber with a base pressure of \(10^{-10}\) mbar. The Alq3 was purchased from Sigma-Aldrich. Alq3 was deposited in situ from a simple Knudsen cell with a flux rate of about 5 Å/min (estimated from the attenuation of the core level signals of the bottom layer). Co was deposited using a UHV e-beam evaporator (Omicron EFM3) at a deposition rate of about 3 Å/min. The aluminum oxide layer was deposited ex situ directly by channel spark method. \(^11\) In order to investigate the buried Co/Al2O3/Alq3 interface, first a 15 nm thick Alq3 film was deposited on a sputter-cleaned Si-substrate, followed by deposition of about 2 nm Al2O3 buffer layer and 20 nm Co. Afterward, the sample was take out from vacuum and a simple ex situ peel-off technique was adopted to turn over the sample. A clean Si-substrate attached to a two-sided UHV-compatible conductive carbon tape was pressed onto the Co/Al2O3/Alq3/Si sample in atmosphere. After separating the two Si-substrates, the Co/Al2O3/Alq3/ sample was peeled off from the Si-substrate and attached to the carbon tape. More detailed information of the peel-off technique can be found in Ref. \(^6\).

The inverted sample, now Alq3/Al2O3/Co, was transferred back into vacuum and analyzed by XPS (also angle-resolved XPS) and UPS. The inverted Alq3/Co was made in the same way for comparison. The take-off angle noted in the figure is defined as the angle between the direction of the detected electrons and the surface of the sample, i.e., a 90° take-off angle means that the electrons are detected leaving perpendicular to the surface (parallel to the surface normal).

X-ray absorption spectroscopy (XAS) and XMCD measurements were performed at beamline D1011 of the MAX-II storage ring, located at the MAX-Laboratory for Synchrotron Radiation Research in Lund, Sweden. For both the XAS and XMCD measurements, the angle of incidence...
of the photon beam was set to 75° relative to the sample normal. For XMCD, the in-plane magnetization of the Co films was set by applying a magnetic field pulse of about 500 G. The XMCD spectra were recorded with a fixed helicity of the light and opposite magnetization directions.

The UPS spectra of both Alq3/Al2O3/Co and pure Co are shown in Fig. 1, denoted by “inverted” and “cobalt,” respectively. It can be clearly seen that the work function of the inverted structure, Alq3/Al2O3/Co, is 3.7 eV, as estimated from the secondary electron cutoff, while the work function of the as-deposited Co film was deduced as 5.0 eV, which is in good agreement with previously published value.12 In the inset of Fig. 1, the Alq3 features clearly are present in the UPS spectrum of the inverted sample in the range of 2–13 eV, although there is an overlap with the tail of the huge secondary electron cutoff for the higher energies.

The value of the highest occupied molecular orbital (HOMO) onset is 2.0 eV higher than the zero point, where the Fermi edge of pure Co sits.

From the data obtained from inverted structure (Alq3/Al2O3/Co), the energy level alignment at the interface of Co-on-Al2O3-covered-Alq3 can be constructed as shown in inset of Fig. 1. Since the onset of Alq3 HOMO is 2.0 eV below the Fermi level and the secondary electron cutoff is 3.7 eV below the vacuum level, the ionization potential can be deduced as 5.7 eV, which is consistent with previous values.6,13 The work function of Co is 5.0 eV, so the vacuum level offset at the interface between Alq3 and Co is 1.3 eV, obtained by subtracting the work function of the inverted sample Alq3/Al2O3/Co (3.7 eV) from that of Co. This offset, caused by a strong interface dipole, rigidly shifts the valence features of Alq3 toward higher binding energy, increasing the hole-injection barrier and decreasing the electron-injection barrier compared to the case of vacuum level alignment to a 5.0 eV work function electrode. A similarly sized dipole-induced vacuum level offset (1.4 eV) was found at the Co-on-Alq3 interface.6

In addition to the above described energy level alignment, the XPS core level spectra of both Alq3 and Co were measured to study the differences between the Alq3/Co interface with and without Al2O3 buffer layer. Figure 2 describes the O(1s) spectra of the inverted Alq3/Co and Alq3/Al2O3/Co, where the O(1s) spectrum of pure Alq3 is shown as a reference. The appearance of an additional peak (529.6 eV) in the inverted Alq3/Co system has been ascribed to a strong interaction between Co and the phenoxide part of Alq3.6 This additional peak disappears when the Al2O3 buffer layer is inserted between Alq3 and Co. There is only one peak in the spectrum of O(1s), which matches very the peak of the pure Alq3.

The angle dependent Co(2p)3/2 XPS spectra of both the Alq3 and Co interfaces with and without an Al2O3 buffer layer are shown in the top and bottom parts of Fig. 3, respectively. The Co(2p)3/2 XPS spectra measured with different takeoff angles are denoted as the values of the angles. In the Alq3/Co system, a clear new peak appeared at the position of 781 eV.6 When decreasing the takeoff angle, the ratio between this peak and the main peak (778 eV) increased, which indicates that an interaction between Alq3 and Co occurred at the interface. However, in the Alq3/Al2O3/Co system, as shown in the bottom part of Fig. 3, all the spectra have the same intensity.
the inserted Al$_2$O$_3$ buffer layer separates the Alq$_3$ and Co and low takeoff angles. The absence of the new peak indicates helicity of the circularly polarized light. Figure 4 with in-plane magnetization parallel and antiparallel to the obtained by taking the difference between the XAS spectra after each step at room temperature. The XMCD curves were step and the Co thickness of the Co film was increased step by step and the Co film deposited on top of Alq$_3$ film. The XMCD measurements confirm that the Co film deposited on top of Al$_2$O$_3$ buffered has better quality than the one on bare Alq$_3$. This high quality Co layer gives the possibility of operation of buffered vertical SVs at room temperature.