Magnetoresistance in CuPc Based Organic Magnetic Tunnel Junctions

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Abstract. We investigate the magnetoresistance of exchange biased spin valves with hybrid barrier layers, MgO(2 nm)/CuPc (t = 0, 1, 2, nm) where CuPc is the organic semiconductor copper phthalocyanine, which are patterned into micron size tunnel junctions by UV lithography. The stacks are produced by sputtering in a Shamrock tool and the organic layer is subsequently deposited by thermal evaporation. Devices in the first set showed 22 %, 10 % and 5% MR at 300 K for t = 0, 1 and 2 nm, respectively. These values increased up to 33 %, 28 % and 23% for the same junctions at 50 K. From these data we infer that the spin polarization is reduced by CuPc in the barrier and the spin scattering by Cu$^{2+}$ is strongly temperature-dependent. By comparison, if an Alq$_3$ layer is used, where there are no paramagnetic scattering centres, the magnetoresistance is independent of the thickness of the organic layer, at least up to 8 nm.

1. Introduction
Spin injection, transport and dynamics in organic semiconductors are of growing interest as the new field of organic spin electronics begins to take shape. Long spin life times due to the low spin-orbit coupling and weak hyperfine interactions should allow the spin polarized carriers to travel over significant distances in the organic semiconductors despite their small mobility [1]. From the application point of view, cheap and flexible organic electronic devices have been developed for commercial displays OLED and there are prototype organic field effect transistors (OFETs) and organic solar panels. The challenge is to add spin functionality to these organic devices.

A common approach is to look for magnetoresistance in organic based spin valve structures [3-5]. A typical spin valve device consists of two ferromagnetic layers (FM) separated by a nonmagnetic (NM) spacer layer. The operating principle of these devices depends on the relative alignment of magnetizations of the two FM layers in a pseudo spin valve, the two layers have different coercivity so a symmetric, butterfly-like plot of resistance versus applied field is obtained. In an exchange-biased spin valve one of the FM layers is pinned while the other one is free to rotate under external magnetic field. An asymmetric magnetoresistance plot is obtained with switches close to zero field when the magnetization directions of the magnetic layers are antiparallel, the system normally shows high resistance when the two FM layers are made of the same material. When they are aligned parallel, the resistance reaches its minimum value.

The possibility of spin injection into an organic layer (Alq$_3$) was suggested by Dediu et al. [2], but the first successful spin valve structure was reported by Xiong et al. [3]. They reported 40% negative magnetoresistance at 11 K by using La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) and Co FM electrodes with a 120 nm Alq$_3$ organic spacer. The magnetoresistance disappeared when the temperature was increased up to
Another negative magnetoresistance effect was seen by Dediu and his group on the LSMO/Alq₃/AlOₓ/Co/Al structure [4]. They observed nearly 11% negative MR at 20 K but the MR fell to -0.15% at room temperature. Use of an oxide layer between organic layer and a ferromagnetic electrode was suggested by Santos et al. [5]. The oxide layer was intended to overcome the conductivity mismatch problem between the semiconductor and metal layers and assist the electron injection into the semiconductor [6,7]. They used Co and NiFe as FM electrodes with an AlOₓ (1.5nm)/Alq₃ (1-4 nm) hybrid barrier. In this structure 6% positive MR was observed at room temperature. Another group was unable to detect any magnetoresistance with 50-100 nm thick Alq₃ barrier [8]. Later, Szulczewski et al. made lithographically patterned junctions using an exchange biased spin valves structure with MgO(2nm)/Alq₃(0-8nm) hybrid barrier [9]. In this experiment organic Alq₃ layers (0-8nm) were deposited on crystalline MgO barrier and the bottom stack was made with exchange biased CoFeB. They observed up to 16 % MR at room temperature. The remarkable observation was that the MR was independent of Alq₃ barrier thickness in a range where the transport mechanism changed from tunnelling (2nm) to diffusion (8nm). Three quarter of spins preserved their orientations on passing through the 8 nm organic layer.

The crossover from tunnelling to diffusive (or hopping) transport has also been studied by Yoo et al. with rubrene [10]. Schoonus et al. studied spin valves with on AlOₓ(1.5nm)/Alq₃(0-4nm) hybrid barrier [11]. In the tunnelling regime (t = 1nm) they observed 12 % room temperature MR but there was a significant reduction when t ≥ 2 nm which they identify as a two-step tunneling where the largest contribution to the current comes from tunnelling via a site in the AlOₓ/Alq₃ interface. Another study was done by Drew et al. on the FeCo/TPD/Alq₃/LiF/NiFe vertical stack, where the Alq₃ is 200 nm thick, by low-energy muon spin rotation technique [12]. They observed that spin diffusion length at low temperature is nearly 35 nm, but MR is less than 0.2 %.

After these promising experiments on Alq₃, investigations have spread to other organic semiconductors. Another widely used material is copper phthalocyanine (CuPc), a prototypical p-type organic semiconductor, also used in OLEDs. The possibility of spin injection into CuPc was first demonstrated by Cinchetti et al. [13]. Their approach was using spin-resolved two-photon photoemission spectra to inject the spins into CuPc from Co/CuPc interface. By using this technique they successfully injected the spins into a CuPc layer and spins retained their polarization up to 16 monolayers (~ 5nm) of CuPc. Another experiment was done by Liu et al. to show the possibility of injection of spin polarized carriers into the CuPc [14]. In their experiment they used Fe and Co as FM electrodes and 100 nm CuPc as a spacer layer. Their result showed 6.4% MR at 40 K but it disappeared at room temperature.

Here we focus on the CuPc based magnetic tunnel junctions with a hybrid MgO/CuPc barrier. We prepared lithographically patterned junctions of various sizes using a bottom-pinned exchange biased stack.

2. Experimental methods and materials

The CuPc layers were deposited in a bell jar system with a base pressure of ~5x10⁻⁶ mbar. CuPc was supplied from Sigma Aldrich in a powder form and it was purified by heating at 300°C under an Ar flow. The CuPc was evaporated from an alumina crucible which is heated by tungsten filament. Firstly, we made a series of singe CuPc layers on SiO₂ substrate to study the surface morphology by atomic force microscopy (AFM). One of the key elements in organic spin valves is the roughness of ferromagnetic/organic interfaces which is directly related to the spin injection from FM layer so we have also studied the structural and magnetic characterization of FM/organic interfaces by TEM and SQUID, respectively.

For the magneto transport measurements, the following multilayer stack Si/SiO₂(500)/Ta(5) /Ru(30)/Ta(5) /NiFe(5) /IrMn(10) CoFe(2.5)/Ru(0.9)/CoFeB(3) /MgO(2) was prepared by sputtering in the Shamrock tool which has a base pressure of 2x10⁻⁸ torr (the numbers in parenthesis are in nanometer). Then, vacuum was broken and samples were transferred to an annealing furnace. Here they were annealed at 350°C in a field of 800 mT during 1 hour to set the exchange bias and to get crystallize the
CoFeB layer. After that, samples were transferred to the bell jar organic evaporation system, where the base pressure is \(~5\times10^{-6}\) mbar, to deposit the CuPc organic layers (0-2 nm). After the organic depositions, the samples were transferred to Shamrock tool to deposit top FM electrode (CoFe 3nm) and capping layers (Ta 5nm/Ru5nm). These completed stacks were patterned by a three step UV lithography technique with junction sizes ranging from 4x4 µm² to 50x150 µm². Positive photoresist (S1813) was spun on the samples and exposed to define a dog bone structure. Then, the samples were Ar ion milled down to substrate and covered with 90 nm SiO₂ to protect the organic layer from any solvents. Then, SiO₂ layer was removed from the dog bone structure by lifting off. Due to pure yield after lift off we did not succeed to make devices with an organic layer thicker than 2 nm. The junction areas were defined by the second lithography process. The positive photoresist was spun again on the samples and exposed to UV with a metal mask defining the mesas. Later, they were Ar ion milled down to MgO barrier and 50 nm SiO₂, which was removed from mesas by lifting off, deposited to isolate the bottom stacks. A final exposure and development step creates strips for the top and bottom contacts. Here, Ta(5nm)/Cu(50nm) bilayer was sputtered to form the top contacts and the lithography was successfully finished by the last lift off step. We made two sets of samples. The thickness of the organic layers is 0, 1, 2 nm and 0, 2 nm for the first and second set, respectively.

3. Results and discussion

Figure 1 shows the AFM image of SiO₂/CuPc(2nm) single layer and the RMS roughness of CuPc layers in a range of 2-8 nm. The RMS roughness of the 2 nm CuPc layer is found to be 0.39 nm and it is nearly independent of thickness. This low roughness in the CuPc layer allows us to make very smooth organic barrier in our devices.

Another key element of the spin injection into an organic is the chemical nature of the organic /FM interface. The chemical reaction between the Co or Fe and CuPc has been reported by Aristov et al. [15]. Figure 2 shows the magnetic moment measurements of the bilayers with and without CuPc. It is very clear that inserting CuPc between SiO₂ and Co results in a significant reduction of the magnetic moment of Co layer, by nearly 40%. The reason for this significant reduction might be the formation of magnetic dead layer due to chemical reaction at the organic/FM interface, which can influence carrier injection into the organic. The figure 3 shows the TEM image of one unpatterned stack. The CoFeB and MgO layers seem to have a good crystalline structure and a sharp interface but the CuPc/CoFe interface seems to be rougher which might lead to spin scattering at the interface. This rough CuPc/CoFe interface is a critical issue for the spin injection into the CuPc layer.
The figure 4a and 4b show the TMR characteristics of the first set of CuPc based MTJs at 300 K and 50 K, respectively. Here, the junction sizes are 50x150 µm². In the case it is obvious that TMR strongly depends on the thickness of the CuPc layer as well as temperature. At room temperature, inserting 1 nm CuPc layer between MgO and CoFe layer destroyed nearly 10% MR in the tunnelling regime. The further increase of the thickness of CuPc layer (t = 2 nm) caused to lose another 7% MR. We infer that this is due to the spin scattering from the paramagnetic Cu²⁺ ions in CuPc.

Figure 5a shows the temperature-dependent resistance behaviour of the devices. When t is 1 nm, the resistance is nearly independent of temperature as expected for the tunnelling. However, when t is 2 nm, resistance changes nearly by a factor of 2 over the temperature range suggesting the onset of a parallel conduction channel due to diffusion through the thicker CuPc layer. Figure 5b shows a plot of resistance area product (RA) versus the square root of area of the MgO(2nm)CuPc(0nm) samples. RA changes with area, unlike the second set where RA was nearly constant. We attribute this difference to a non-uniform barrier in the first set of samples.
Figure 6a and 6b show MR characteristics of second set of CuPc based junctions. Here, the junction sizes are 10x10 µm$^2$ and 50x50 µm$^2$ for the MgO(2nm)/CuPc(2nm) and MgO(2nm)/CuPc(0nm) samples, respectively. In this set, the MR values are bigger than for the first set and the RA is approximately 1 MΩµm$^{-2}$ for $t = 0$ nm, regardless of junction area. There is still a significant reduction of the MR nearly 10% at 300 K, when 2 nm CuPc is inserted between MgO and CoFe.

From these results we can deduce that the spin diffusion length in CuPc may be 3-4 nm at room temperature and that depends strongly on two factors which are the paramagnetic nature of CuPc and the CuPc/CoFe interface. One can compare these results with Alq$_3$ based MTJs. Spin diffusion length is more than 8 nm for Alq$_3$ at room temperature while it is less in CuPc.

4. Summary
Lithographically patterned and exchange-biased CuPc based vertical junctions show useful room-temperature magnetoresistance. The room temperature spin scattering length in the CuPc inferred to be ~ 3-4 nm and it is depended on the paramagnetic scattering centres in the CuPc and the CuPc/CoFe interface. We believe that spin diffusion length can be improved by using a fabrication process that
does not break vacuum. Our results suggest that it is possible to inject and recover spin polarized electrons to the organic layer.

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