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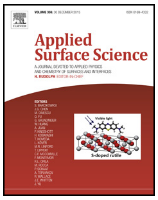

# Investigations of the polymer/magnetic interface of organic spin-valves

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ABSTRACT

This work investigates the top interface of an organic spin-valve, to determine the interactions between the polymer and top magnetic electrode. The polymers studied are regio-regular poly(3-hexylthiophene) (RR-P3HT) and poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene (PBTTT) and the magnetic top electrodes are NiFe and Fe. X-ray photoelectron spectroscopy (XPS) is used to determine the bonding at the interface, along with the extent of how oxidised the magnetic layers are, while atomic force microscopy (AFM) is used to determine the surface roughness. A magneto-optic Kerr effect (MOKE) magnetometer is used to study the magnetic properties of the top electrode. It is shown that at the organic–magnetic interface the magnetic atoms interact with the polymer, as metallic–sulphide and metallic-carbide species are present at the interface. It is also shown that the structure of the polymer influences the anisotropy of the magnetic electrode, such that the magnetic electrodes grown on RR-P3HT have uniaxial anisotropy, while those grown on PBTTT are isotropic.

## 1. Introduction

Organic spintronics studies the spin carrier transportation through organic semiconductors (OSCs). The first organic spin-valve was demonstrated in 2004 by Xiong et al. [1], who achieved a 40% magnetoresistance (MR) at 11 K in the spin-valve structure $La_{0.7}Sr_{0.3}MnO_3$/tris(8-hydroxyquinoline)/Co (LSMO/$Alq_3$/Co). Since then researchers have studied a range of organic spin-valves, where the organic semiconductor spacer layers include $Alq_3$ [1,2], rubrene [3] and regio-regular poly(3-hexylthiophene) (RR-P3HT) [4,5], and the magnetic electrodes include FeCo, NiFe and LSMO [1–5]. It has been found that MRs greater than 20% can be achieved in organic spin-valves at temperatures lower than 100 K [6], but at room temperature the MR has been reduced to ~1% [4]. The reason behind this decrease in the MR with temperature is believed to be due to the interactions between the magnetic electrodes and the organic semiconductor at the interfaces [7].

Thus in recent years, research into organic spin-valves has focussed on understanding and manipulating the interfaces between the magnetic electrodes and the organic semiconductor in order to achieve larger MRs at room temperature. These studies into the organic/magnetic interfaces has allowed for novel organic spin devices to be developed including the organic spin switch [8] and organic spin transistor [9]. For example Majumdar et al. [10] and Morley et al. [11,12] have used X-ray photoelectron spectroscopy (XPS) to studying the bonding between the bottom magnetic electrode and the organic layer. Majumdar et al. [10] found that additional layers such as self-assembling molecules between the magnetic electrode and the organic semiconductor changed the bonding between the organic semiconductor and the magnetic electrode. While Morley et al. [11] found that organic semiconductors chemisorbed stronger onto oxide surfaces compared to non-oxide surfaces. Other work on magnetic–organic interfaces has shown that the interface can act as a spin filter, this includes work by Steil et al. [13] who used time resolved two-photon photoemission to study the spin dynamics of the Co/$Alq_3$ interface. They found that the electrons are trapped at the interface, so causing the interface to act as a spin filter. While Atodiresei et al. [14] and Methfessel et al. [15] used spin-resolved scanning tunnelling spectroscopy along with first principle electronic structure theory to show that the organic molecules on the magnetic surface can act as a spin filter. Zhan et al. [16] studied the $Alq_3$/Co interface using XPS and ultra-violet photoelectron spectroscopy (UPS) to determine how the work function changed from pure Co with the addition of $Alq_3$ on top. They found with the addition of $Alq_3$ the work function decreased from 5 eV for Co to 3.6 eV for the $Alq_3$/Co interface. They concluded this was due to an interfacial dipole forming with the positive charge on the $Alq_3$ side, which shifts the $Alq_3$ valence features towards a higher binding energy. Recent work by Wang et al. [17] has studied the interface between the top

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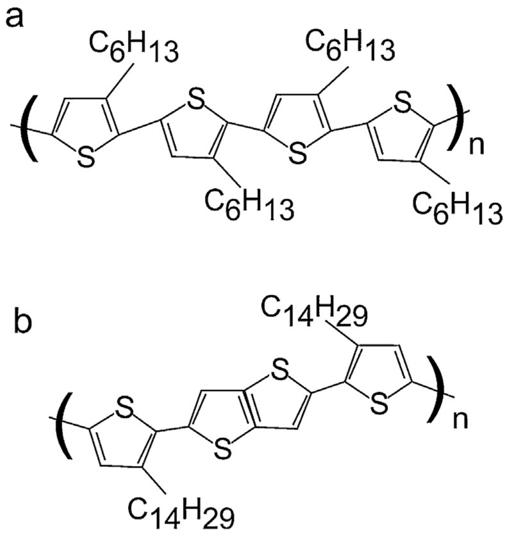

**Fig. 1.** Chemical structure of the polymers (a) RR-P3HT and (b) PBTTT.

magnetic electrode and $Alq_3$ using XPS. They determine that at the interface the FeCo partially reacts with the $Alq_3$ layer to form a metal carbide species. They also determined that the roughness at the interface is one of the reasons why spin-injection can fail in organic spin-valves.

To manipulate the organic–magnetic interface, additional layers have been added between the organic semiconductor and the magnetic electrode, including $AlO_x$ [18], which was found to decrease the interface roughness and increase the spin carrier extraction from the organic semiconductor into the magnetic electrode. They claimed that the roughness at the interface acted as sites where the spin carrier could be spin-flipped, thus reducing the number of majority polarised spin carriers being extracted at the top electrode. By reducing the roughness, the number of these spin-flip sites were reduced, hence a higher number of majority spin polarised carriers were extracted from the top magnetic electrode. Another thin layer added between the organic semiconductor and the top magnetic electrode was LiF [19], which was found to change the density of states at the interface, thus changed the sign of the MR of the device from positive with no LiF layer to negative with the LiF layer. Shi et al. [20] investigated how the interface layer 11,11,12,12-tetracyanonaptho-2,6-quinodimethane (TNAP) between Co and $Alq_3$ changed the hybrid interface states using UPS and XPS. They found that using a 0.8 nm thick TNAP layer produced hybrid interface states due to the chemical interactions between the Co and TNAP. These states resulted in the reduction of the hole injection barrier energy level.

Most of the research has studied the bottom electrode–organic interface to understand the bonding between the layers [10–15]. This paper uses a range of techniques (XPS, atomic force microscopy (AFM), Magneto–optic Kerr effect (MOKE) microscopy) to study the interface between the polymer and top magnetic electrode used in organic spin devices, thus allowing further understanding of the bonding that occurs at this interface. The organic semiconductors investigated are the conjugated polymers regio-regular poly(3-hexylthiophene) (RR-P3HT) (Fig. 1a) and poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene (PBTTT) (Fig. 1b), both of which have shown promising results in spin-valves [5] and organic spin transistors [9] due to their high mobility, plus both contain sulphur atoms in the polymer backbone. The top electrodes studied were the transition metals NiFe and Fe, as NiFe has been regularly used as the top electrode [5,9,19] and Fe is studied as a comparison to NiFe.

## 2. Experimental procedure

In this paper, 12 different bilayer samples were studied, these consisted of either one of the polymers (RR-P3HT or PBTTT) as the bottom layer and either $Ni_{81}Fe_{19}$ (NiFe) or Fe as the top layer. Different thicknesses of the top layer were studied to determine how this influences the interfaces and top electrode magnetic properties.

The bilayer structures were fabricated on glass substrates (1.5 mm × 1.5 mm), which were cleaned using acetone followed by IPA within an ultrasonic bath. For RR-P3HT 10 mg/ml was dissolved into 1,2-dicholorobenzene for 1 h at 70 °C, followed by hot filtering (0.45 μm PTFE) and hot spincasting at 2000 rpm for 1 min. For PBTTT, 7 mg/ml was dissolved in 1,2-dicholorobenzene for 1 h at 70 °C, followed by hot filtering (0.45 μm PTFE) and hot spincasting at 5000 rpm for 1 min. Both polymers were then annealed at 110 °C for 45 min. The magnetic electrodes were then evaporated onto the polymer. The chamber was baked out to a pressure of $2 \times 10^{-7}$ mbar. The NiFe and Fe layers were deposited at a rate of 0.4–0.6 Å/s. The thickness of the magnetic layers were 3, 5 and 10 nm, as measured using the calibrated thickness monitor on the system. A 1.3 micron thick RR-P3HT film was also measured on the XPS, to compare the S 2p and C 1 s peaks with those of the polymer/magnetic samples.

The bonding at the interface was studied using X-ray photoelectron spectroscopy (XPS). XPS was performed on an AXIS Nova (Kratos Analytical, Manchester, UK), utilising a monochromatic Al $K_\alpha$ source (1486.6 eV) operated at 225 W (15 kV, 15 mA). Samples were mechanically mounted onto the instrument plate using copper plates. The analysis area was 700 × 400 μm (Field of View 1, slot aperture) for all analyses. Survey spectra were collected at a pass energy of 160 eV and were the average of 3 sweeps, while high resolution spectra were collected at a pass energy of 40 eV and were the average of 10 sweeps. Charge neutralisation was used throughout the analysis, and the energy scale was corrected during post-processing such that the main component of the C 1s peak was set to 285 eV. All the spectra were collected in fixed analyser transmission mode. For the S 2p spectra, due to the weak signals measured, the average of 3 different XPS spectra were taken. This improved the signal to noise ratio (SNR) by a factor 2, thus improving the resolution of the spectra. All the XPS spectra were analysed using the CasaXPS software [21]. For all the atomic percentages calculated, the measured peak areas were first corrected for the relevant elements Relative Sensitivity Factor (RSF) from within CasaXPS [21]. For the Kratos Axis Nova, the CasaXPS database uses the Schofield sensitivity factors.

Atomic force microscopy (AFM) was used to determine the surface roughness of the magnetic layer. A Digital Instruments Dimension 3000 force microscope was used in tapping mode to image the surfaces. A Magneto-optic Kerr effect (MOKE) magnetometer was used to study the magnetic behaviour of the magnetic layer as a function of thickness. For each sample one edge was defined as 0°, so that the magnetic hysteresis loops as a function of angle between the magnetic field and this defined edge were measured. From the magnetisation hysteresis loops measured as a function of field direction it was possible to observe how the magnetic properties (anisotropy field ($H_k$), coercive field ($H_c$), remnant magnetisation ($M_R$)) changed with magnetic film thickness on the polymer. Hence the anisotropy present in the magnetic films was determined.

## 3. Results and discussion

Fig. 2 shows the wide XPS spectra for the 13 different samples. The S 2p peak can be observed at 165 eV for the thinnest top electrode layers and the P3HT film, while the peak disappears as the