Characterizing ferromagnetic oxide/organic semiconductor interfaces using a spin-polarized metastable helium beam

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Here we give an overview of how a spin-polarized metastable helium beam may be used to characterize surfaces and interfaces relevant to spin injection from a ferromagnetic (FM) electrode to an organic semiconductor (OSC). Taking advantage of the extreme surface sensitivity of this technique, we show how information regarding the electronic and magnetic properties of FM/OSC interfaces may be obtained. We demonstrate how the spin polarization at the surface of a FM oxide—Fe$_3$O$_4$(001)—may be drastically enhanced through atomic adsorption. We also investigate the adsorption of copper phthalocyanine (CuPc) on Fe$_3$O$_4$(001) revealing that the CuPc molecular orbitals are spin polarized due to the magnetic interaction with the substrate, even for a relatively thick film of 5 nm.

**Key words:** spin polarization, molecular spintronics, organic semiconductors, Fe$_3$O$_4$, copper phthalocyanine, spin-polarized metastable helium

1. Introduction

Recently, the importance of surface and interfacial states in determining the efficiency of spin injection from a ferromagnetic (FM) metal into a non-magnetic solid has become increasingly clear\(^1\)-\(^6\). Bulk properties expected to provide advantages for spintronic applications, such as half-metallic ferromagnetism, often disappear at the surface of a material as reconstruction and relaxation of the atomic structure lead to modifications in the spin-resolved densities of state\(^6\). Furthermore, in molecular spintronic devices, hybrid interface states that form due to the strong chemical interaction of organic semiconductors (OSCs) with FM substrates may significantly compromise the spin-filtering mechanism and therefore device performance\(^6\),\(^7\).

In order to fully characterize a ‘spinterface’, an understanding of the spin-resolved valence band electronic structure is required and for this task, ultraviolet photoemission spectroscopy (UPS) is usually employed. However, even low-energy He I photons (h\(\nu\) = 21.2 eV) penetrate somewhat below the topmost surface so that the resulting ejected electron spectrum contains a contribution from the bulk of the substrate. Here, we briefly demonstrate how the use of a spin-polarized beam of metastable helium (He $^23S$) atoms may provide complementary information to UPS but with a much greater surface sensitivity (Fig. 1)\(^9\),\(^10\). This sensitivity arises from the large surface interaction cross-section of He $^23S$ which means that deexcitation takes place several angstroms above the outermost surface. Hence, spin-polarized metastable deexcitation spectroscopy (SPMDS) is a very applicable technique for investigating the electronic and magnetic properties of FM/OSC interfaces.

Firstly, we describe how the surface spin polarization of Fe$_3$O$_4$(001) thin films may be greatly enhanced by atomic adsorption, in this case through hydrogen termination. We then investigate the adsorption of Cu phthalocyanine (CuPc) on Fe$_3$O$_4$(001) focusing on the spin polarization induced in the CuPc molecular orbitals (MOs) due to the magnetic interaction with the substrate.
2. Experimental Details

FeO₃(001) thin films were prepared by depositing ~20 nm of Fe onto single crystal MgO(001) substrates under a local oxygen atmosphere of 3 × 10⁻⁴ Pa, generated using a gas-dosing line. Clean MgO surfaces were obtained using a novel UHV ozone dosing system (to be described elsewhere) in which the sample is annealed at 700 °C in a constant flow of low-concentration (<15%) ozone. Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to verify surface order and cleanliness. In the deposition of Fe, 99.99% pure Fe rods were heated by an electron-beam evaporator (Omicron EFM3) with deposition rates of ~1 Åmin⁻¹ and sample temperature during exposure was 350 °C. This growth procedure is known to lead to high-quality FeO₃(001) films, as described previously¹⁻¹². Purified CuPc (Sigma Aldrich) was deposited by heating to 350 °C using a homemade thermal evaporation source with deposition rates of ~1 Åmin⁻¹, as measured using a water-cooled quartz crystal microbalance. Before the acquisition of SPMDS spectra, samples were pulse-magnetized to magnetic saturation in the in-plane direction, with measurements taken at remanence.

The details of the apparatus used to generate a spin-polarized beam of metastable helium atoms have been described in detail elsewhere¹¹,¹³. Briefly, He²⁺S atoms emerging from a pulsed nozzle-skimmer discharge source are normally incident on a sample surface. Electrons emitted due to He²⁺S de-excitation are then detected by a retarding field analyzer mounted to the sample normal.

3. Results and Discussion

In SPMDS, spin-dependent ejected energy spectra are acquired with the He²⁺S electron spin direction aligned either parallel (↑) or anti-parallel (↓) to the sample magnetization direction. This then allows the asymmetry in the intensity of emission for parallel, (positive) spin asymmetry corresponds to a negative magnetization direction. This then allows the described elsewhere) in which the sample is annealed at 700 °C in a constant flow of low-concentration (<15%) ozone. Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to verify surface order and cleanliness. In the deposition of Fe, 99.99% pure Fe rods were heated by an electron-beam evaporator (Omicron EFM3) with deposition rates of ~1 Åmin⁻¹ and the sample temperature during exposure was 350 °C. This growth procedure is known to lead to high-quality FeO₃(001) films, as described previously¹⁻¹². Purified CuPc (Sigma Aldrich) was deposited by heating to 350 °C using a homemade thermal evaporation source with deposition rates of ~1 Åmin⁻¹, as measured using a water-cooled quartz crystal microbalance. Before the acquisition of SPMDS spectra, samples were pulse-magnetized to magnetic saturation in the in-plane direction, with measurements taken at remanence.

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Figure 2 shows the spin asymmetry obtained from the surface of a clean and hydrogen-terminated FeO₃(001) thin film. The spin asymmetry measured at high electron energies (>14.5 eV) corresponds to emission from around the Fermi level, \(E_F\). The spectra confirm our previous measurements from single-crystal FeO₃(001)⁰⁰ and FeO₃(001) thin films subjected to high magnetic fields⁰⁰ and indicate that the spin polarization at the Fermi level, \(P(E_F)\), for the clean surface is close to zero. Considering theoretical predictions of half-metallicity and a value for \(P(E_F)\) of ~100% in the bulk of FeO₄, this is a very surprising result. However, as we have previously discussed⁰⁰,¹⁰, it arises due to the presence of surface dangling bonds which lead to a significant DOS appearing in the bulk majority band gap around \(E_F\). Termination with hydrogen quenches these dangling bonds and shifts the associated surface electronic states to a deeper binding energy, as verified by DFT calculations¹⁴. This leads to a drastic increase in the spin polarization at \(E_F\) as observed in Fig. 2. It is interesting to note that a similar recovery of a high \(P(E_F)\) is not observed when the (111) surface is hydrogen terminated⁰⁶, indicating that the (100) orientation may be a better candidate for device applications and that the surface spin polarity of FM oxides is an intrinsic value that can differ greatly from the bulk.

The ability to enhance and tailor the surface electronic structure of FeO₄, and possibly other FM oxides, offers a means to improve the performance of spintronic and molecular spintronic devices. In the latter case, the modification of the surface density of states (DOS) caused by the adsorption of an OSC molecule can greatly affect the spin injection process¹³⁻¹⁴. To provide a deeper understanding of spin injection, it is therefore necessary to investigate the changes in magnetic and electronic properties that occur upon the formation of an OSC/FM interface.

Figure 3 shows the spin-summed MDS spectra obtained from a clean FeO₃(001) and for CuPc
coverages of 1.6 and 5.0 nm, representing monolayer and multilayer coverages, respectively. The relatively featureless spectrum acquired for the clean surface arises due to deexcitation of He 2$^2$S atoms taking place predominantly through resonance ionization followed by Auger neutralization. As this mechanism is a two-electron process, the spectrum essentially reflects a self-convolution of the Fe$_3$O$_4$(001) surface DOS.

After deposition of 1.6 nm of CuPc, distinct features emerge at mid-to-high kinetic energies. These features are even more apparent for a multilayer coverage of 5 nm and arise due to emission from the MOs of the deposited CuPc. The distinct nature of the peaks, labelled A-E in Fig. 3, is due to the occurrence of the one-electron He 2$^2$S deexcitation mechanism of Auger deexcitation, which typically takes place at organic surfaces. Based on previous MDS studies of CuPc adsorption on HOPG and Fe, peaks A and B may be assigned to emission from $\pi$ MOs located on the inner phthalocyanine ring. C and D arise from a combination of $\pi$ MOs distributed over the four outermost benzene-like rings with a contribution from $\sigma$ MOs. The deepest binding energy peak, E, is due to emission from $\sigma$ MOs only.

Figure 4(a) shows spin-resolved spectra from a 5 nm coverage of CuPc on Fe$_3$O$_4$(001) focusing on emission from MOs closest to the Fermi level which occurs where the count rate falls to zero. A clear difference in emission is seen for parallel (↑) and anti-parallel (↓) spin configurations leading to the spin asymmetry displayed in Fig. 4(a). The spin asymmetry for a 1.6 nm coverage, shown in Fig. 4(b), is similar in form to that for the clean Fe$_3$O$_4$(001) surface (Fig. 2) although with greater emission at lower kinetic energies (< 8 eV). Additionally, after rapidly reducing to almost zero at around 14 eV, the spin asymmetry suddenly increases again to a strong positive value. The energetic location of this rise overlaps with the position of peak A in Fig. 4(a) which corresponds to the highest occupied molecular orbitals (HOMOs) of the CuPc layer. Hence, as spin asymmetry and spin polarization are anti-correlated, this result indicates that the interaction with the Fe$_3$O$_4$(001) surface induces a negative spin polarization in the HOMOs of the adsorbed CuPc layer. In similarity to metal phthalocyanine adsorption on Fe(100), the polarity of the induced spin polarization is the same as for the free substrate. Adsorption-induced charge transfer is likely to account for the measured asymmetry with the main contribution being from electron transfer to the CuPc macrocycle rather than to the central Cu atom.

An appreciable spin asymmetry is still detected for a CuPc coverage of 5 nm indicating that the spin
polarization induced by charge transfer at the CuPc/Fe$_3$O$_4$ interface has a secondary effect on the overlying CuPc film. Interestingly, clear peaks in the spin asymmetry are observed which correspond to the peaks observed in the MDS spectra of Fig. 3. It is possible that the molecular geometry changes as the CuPc layer thickness increases, leading to greater overlap between $\pi$ MOs and higher-binding-energy $\sigma$ MOs and thus induced spin polarization in the latter. For CuPc on Fe(100), a 1 monolayer film adsorbs with the molecular plane parallel to the Fe surface, with thicker films leading to increased disorder.

In summary, we have briefly shown how a spin-polarized metastable helium beam may be used to characterize the surface and interfacial properties of FM/OSC heterojunctions relevant to molecular spintronics. Taking advantage of the surface sensitivity of this technique, information on the surface spin polarization, hybrid interface states, and the substrate-adsorbate magnetic interaction may be obtained, as we have shown here for a clean Fe$_3$O$_4$(001) surface and CuPc/Fe$_3$O$_4$(001) interfaces. Once characterized, these surface and interfacial properties may be tailored to improve device performance, as demonstrated through simple hydrogen termination of a FM oxide.

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