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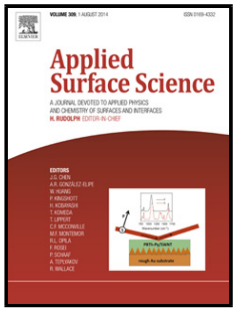

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Study of the magnetic-Alq_3 interface in organic spin-valves

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Abstract

The interface between the organic semiconductor tris(8-hydrixyquinolate) aluminium (Alq_3) and two different magnetic electrodes has been investigated using X-ray photoelectron spectroscopy (XPS), Kelvin Probe, atomic force microscopy (AFM) and Magneto-optic Kerr effect (MOKE) magnetometry. The transition metal magnetic electrode/Alq_3 films were first measured using a XPS, and then washed and remeasured. It was found that Alq_3 still existed on the magnetic electrode after washing. This suggests that the Alq_3 chemisorbs onto the transition metal electrode surfaces. Using MOKE magnetometry, the surface magnetisation of the transition metal electrodes was studied. It was found that the surface magnetisation of the NiFe electrode changed with the Alq_3 layer on top, which was taken to be due to the Alq_3 chemisorption onto the NiFe electrode, so changing the electronic states at the interface.

Keywords: organic spintronics; interfaces; XPS;

Introduction

Organic spintronics studies the behaviour of spin carriers in organic semiconductors, including the transportation using the organic semiconductor as the spacer layer between the two magnetic electrodes in a spin-valve. The advantages of organic semiconductors for spintronic applications include their cost, ease of fabrication and long spin diffusion time, due to the relatively weak spin-orbit coupling and hyperfine interaction [1]. The first demonstration of an organic spin-valve by Xiong et al [2] was a $La_{0.67}Sr_{0.33}MnO_2$ (LSMO)/tris(8-hydrixyquinolate) aluminium (Alq_3)/Co device. They measured a magnetoresistance (MR) of ~ 40% at 11K, but no MR was measured at temperatures above 150K. Since then one of the main focuses of research into organic spin-valves has been on achieving room temperature magnetoresistance, with a range of magnetic electrodes (e.g. LSMO, Co, FeCo, NiFe [3-6]) and organic semiconductors (e.g. Alq_3, P3HT, rubrene [3-10]). To date, the highest MRs achieved at room temperature for the organic semiconductor layer thicker than 50nm are MR= -0.15% for LSMO/100nm Alq_3/Co [11], MR= 3% for LSMO/100nm P3HT/Co[7] and MR= -0.45% for CoPt/TIPS-pentacene/Co [12].

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Research has also focussed on how the interface between the magnetic electrode and the organic semiconductor influences the spin injection and detection of the charge carriers into/from the organic semiconductor. It has been suggested [13] that the organic semiconductor strongly bonds to the surface of the bottom electrode, such that it changes the electronic structure of the electrode, and hence changes the interfacial properties. The bonding can occur due to two different processes [13], the first is physisorption, where the molecule's electron cloud "pushes" the metal's surface wavefunction, causing the work function to be lowered, and there is no overlap of the wavefunctions. The second is chemisorption, where charge transfer occurs between the metal and the molecule, which may form a strong interface dipole, thus a strong electronic coupling. Barraud et al [14] put forward the spin-hydridization-induced polarised states (SHIPS) model which hypothesises that the first molecular layer on the magnetic electrode changes the spin polarisation states at the surface of the magnetic electrode, thus changing the MR of the device. Steil et al [15] demonstrated these hybrid interface states using two-photon photoemission on a Co/Alq_3 interface. They found that the electrons are trapped in these hybrid states, allowing the interfaces to act as spin filters. These hybrid states form due to the Alq_3 chemisorbing into the Co, so that there is an interaction between the molecular orbitals of the Alq_3 and the metallic bands of Co. Majumdar et al [16] showed that using self assembling molecules (SAMS) between the bottom electrode and RR-P3HT could annihilate the MR measured, by destroying these interface sates. Morley et al [17] have shown that the RR-P3HT bonded strongest to LSMO, while exhibiting weaker bonding to the transition metal electrodes. It was also found that the bonding depended on the electrode surface roughness and the solvent used to spin-coat the polymer.

The interface between the top electrode and the organic semiconductor has also been studied, by investigating different interface layers between them. Schulz et al [18], Dhandapani et al [5] and Szulczewshi et al [19] all investigated using LiF as an interface layer between Alq_3 and the top electrode. Dhandapani showed that it improved the MR of FeCo/Alq_3/NiFe spin-valves, while Schulz showed that the presence of LiF reversed the net extracted spin polarisation at the NiFe cathode, which resulted in the change in sign of the MR. This was argued to be due to the electric dipole moments of the LiF modifying the vacuum level of the Alq_3, thus changing the NiFe band that was relevant for hole extraction Szulczewshi showed that the LiF layer lowered the work function of the top magnetic electrode used by 1.4eV, confirming the explanation of MR sign reversal by Schulz et al. Another study used Al_2O_3 as the interface layer between the ferromagnetic electrode and organic semiconductor, which acted as a tunnel barrier to the spin carriers being extracted from the organic semiconductor, and it was argued to also reduce the penetration of the top electrode into the organic semiconductor [11]. Using Al_2O_3, Dediu et al [10] achieved a room temperature MR *ca.* -0.15% for a LSMO/Alq_3/Al_2O_3/Co spin-valve.

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Thus understanding the bonding at the interfaces between the magnetic electrodes and the organic semiconductor is important, so that the magnetic-organic interface models presented, (such as SHIPS [14]) can be verified, as well as improving the development of spin device designs. In this letter we report a study of the interface between Alq_3 and two different magnetic transition metal alloys, to determine the type of bonding present at the interface, and whether any change in the electronic states caused by the interfacial bonding can be observed.

Experimental Procedure

We studied two different magnetic electrodes with the organic semiconductor Alq_3 on top, plus for comparison two plain magnetic electrodes were also studied. The samples were fabricated on glass substrates, which were cleaned using acetone and IPA. The $Fe_{50}Co_{50}$ (FeCo) and $Ni_{81}Fe_{19}$ (NiFe) films were grown onto the glass substrates using RF sputtering from 150mm diameter alloy targets with known compositions (50:50 FeCo and 81:19 NiFe). The 40nm FeCo films were grown at a pressure of 4.5mTorr and a power density of $2kWm^{-2}$ and the 40nm NiFe films were grown at a pressure of 4.5mTorr and a power density of $1kWm^{-2}$. On top of each of the magnetic electrodes was thermally evaporated a 10nm Alq_3 film, in a vacuum system with a base pressure of $\sim 10^{-7}$ mbar. The deposition rate was between 0.1nm/s and 0.2nm/s. The Alq_3 purchased from Sigma Aldrich (99.995% purity) was further purified by train sublimation in a vacuum of $\sim 10^{-6}$ mbar before being used. The first series of samples characterised were 40nm FeCo, 40nm NiFe, 40nm FeCo/10nm Alq_3 and 40nm NiFe/10nm Alq_3. After the initial MOKE measurements, which demonstrated a change in the magnetisation hysteresis loop for the NiFe/Alq_3 film compared to the NiFe film, a second series of samples were fabricated to further investigate this result. The samples fabricated had different thicknesses of NiFe layers (10nm, 20nm and 40nm) with a 10nm Alq_3 layer grown on top.

To characterise the interface of the magnetic-organic samples, four different techniques were used: X-ray photoelectron spectroscopy (XPS), Kelvin probe, atomic force microscopy (AFM) and magneto-optic Kerr effect (MOKE) magnetometry. The XPS spectra were analysed using a Kratos Axis Ultra DLD photoelectron spectrometer, incorporating a 165 mm radius analyser using monochromatic Al source operating at 144 W (12 mA x 12 kV), at a pass energy of 40 eV for high resolution scans (energy resolution measured to be 0.76 eV on silver for pass energy employed) and 160 eV for survey scans and operating in the hybrid spectroscopy mode, covering an analysis area of approximately 700x400 μm. Four samples (FeCo film, NiFe film, FeCo/Alq_3 film and NiFe/Alq_3 film) were investigated using a XPS to determine the affect of Alq_3 on the magnetic electrodes. The first set of XPS measurements obtained spectra for the as-prepared samples. The samples were then taken from the XPS and washed using acetone and then chloroform in order to remove the Alq_3 from the electrode surfaces. This method was used by Majumdar et al [16] in their study of the LMSO/RR-P3HT interface and Morley et al [17] in a previous study of magnetic electrode/RR-P3HT interface. If the Alq_3 is strongly bonded (chemisorbed) to the magnetic electrode surface, then a layer of Alq_3 may still be on the surface after washing. If the Alq_3 is weakly or non-bonded (physisorbed) to the magnetic electrode, then

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it is more likely that significantly more, if not all of the Alq_3 layer will be removed by washing. After washing, the samples were then reloaded into the XPS, and the spectra remeasured. Due to the solvent washing, all the samples were calibrated to the C(1s) signal at 285eV consistent with the XPS of any organic residues that may remain. All the calibrated XPS spectra were curve-fitted using CasaXPS using a Gaussian-Lorentzian mixed lineshape [20], which allowed all the peaks to be identified. Further studies of the electrode surface were made using atomic force microscopy (AFM), using a Digital Instruments Dimension 3000 force microscope, in tapping mode. These measurements gave the surface roughness, as well as 3D images of the surfaces. The work function (WF) of each surface was measured using a Kevin Probe (ASKP200200). The 5mm diameter stainless steel tip was lowered close to the surface until a WF gradient of >300 was achieved. Each sample was then grounded from the top surface using a copper clamp, and 300 points were measured to determine the mean WF. The WF of the tip was first calibrated by measuring the WF of two known samples, gold (Au) and aluminium (Al). The normalised magnetisation loops of the magnetic electrodes were measured on a MOKE magnetometer, from these loops the anisotropy field (H_k), coercive field (H_c) and remenant magnetisation (M_R) were determined [21].

Results and Discussion

For each sample, a "wide" XPS spectrum was taken, this was to determine the main elements present at the surface of each scan. It also allowed any differences between the as-grown and washed samples to be identified. From Figure 1, it is observed that the transition metal electrode surfaces had a thin oxide layer present. This occurred as the growth of the magnetic electrode and the Alq_3 occurred in different deposition systems, such that the magnetic electrode surface was exposed to atmosphere. The percentage of oxygen on the surface of the FeCo was 80%, while for NiFe the percentage was 50%. Thus the FeCo electrode has a thicker oxide layer compared to the NiFe and was further confirmed by x-ray reflectivity (XRR) data [22]. It is also observed that the FeCo/Alq_3 (as-grown and washed) and the NiFe/Alq_3 (as-grown and washed) spectra have a small peak for N(1s) due to the Alq_3, while the FeCo and NiFe electrode spectra do not. The ratio of the elements present at the surface can be determined from the wide spectrum. It was found that for the FeCo electrode the composition was Fe=44% and Co=56% so slightly richer in Co than expected and for the NiFe electrode the composition was Ni=61% and Fe=39%, so richer in Fe than the growth composition, but consistent with other measurements of the surface [17, 22].

As Alq_3 contains nitrogen and aluminium, the N(1s) and Al(2p) peaks were investigated using XPS. From Figure 2a, it is observed that the N(1s) spectra for the FeCo electrodes (as-grown and washed) has two peaks at 397.4eV and 400.1eV, with the 397.4eV peak being larger than the 400.1eV peak. These peaks correspond to metal nitrides and C-N bonds respectively. For the FeCo/Alq_3 (as-grown) has one large peak at 399.7eV, which is due to Alq_3 film, as it contains C-

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N bonds [23]. For the FeCo/Alq_3 (washed), two peaks again are observed in the N(1s) spectrum at 397eV and 399.9eV, with the 399.9eV peak being larger than the 397eV peak. As the 399.9eV is due to the C-N bond in Alq_3 and the peak is larger than the 397eV, this means there is still Alq_3 present on the surface of the FeCo. A similar behaviour is observed in the NiFe/Alq_3 spectra, where for the NiFe (washed and as-grown) electrodes, the two peaks occur at 397.5eV and 399.9eV, with the 397.5eV peak being the largest peak. For the NiFe/Alq_3 (as-grown) N(1s) spectrum one peak was measured at 399.7eV due to the Alq_3 film [23]. Then after washing the NiFe/Alq_3 (washed) N(1s) spectrum had two peak at 397.6eV and 399.9eV, with the later having a larger concentrating, indicating Alq_3 remains present on the NiFe surface after washing. For the Al(2p) spectra (Fig. 3), it is observed that the FeCo/Alq_3 (as-grown) and the NiFe/Alq_3 (as-grown) surfaces have a peak at 74.1eV, which corresponds to the Alq_3 film [24]. For the FeCo/Alq_3 (washed) surface, the peak at 74.1eV is observed, although as expected the peak magnitude is reduced, due to the removal of most of the Alq_3 after washing. For the NiFe/Alq_3 (washed) surface, no Al peak is observed as a consequence of the overlapping Ni(3p) region, which dominates the Al(2p) signal (Fig. 3). For the NiFe/Alq_3 (as-grown), a much smaller Ni(3p) peak was measured, due to the Alq_3 film thickness of ~10nm dominating the XPS spectra, meaning that the Al(2p) peak is observed the measured spectra. For consistency, the O(1s) peaks (Figs. 4) were studied for all four samples (as-grown and washed). For the transition metals electrodes (washed and as-grown), the two peaks occur at binding energies (B.E) of 529.3eV and 531.1eV, which correspond to metal oxides and hydroxides present at the surface and are typical of transition metal oxides. The NiFe electrode also has an additional shallow peak at 534eV. For the FeCo/Alq_3 (as-grown) and NiFe/Alq_3 (as-grown) films, it is observed that the largest peak is at 531.4eV, which is due to the Alq_3 film [23] with a smaller one at 529eV and a very small peak above 534.5 eV. The latter peak is likely to be either due to Na Auger electrons or an O(1s) resonance. For the FeCo/Alq_3 (washed) surface, the two oxide peaks are back to the same ratio and same B.E.s as the FeCo (washed) surface O(1s) peaks. This suggests that after washing, if any Alq_3 is still present on the surface of the FeCo, the O(1s) 531.4eV peak is too small to be detected using XPS compared to the metal oxide peaks. While for the NiFe/Alq_3 (washed) surface the two main peaks are of similar height, which is different from both the NiFe/Alq_3 (as-grown) and NiFe(as-grown and washed) surfaces. This suggests that there is still Alq_3 present on the NiFe surface, as the spectra is not the same as the NiFe electrodes, but the majority of the Alq_3 has been removed. The O(1s) and N(1s) core levels values are in good agreement, with other studies of Alq_3 on surfaces such as Al [24, 25] and CaF_2 [26].

Comparing all the XPS spectra, it is observed that there is still Alq_3 present after washing meaning that the Alq_3 has more strongly bonded to the magnetic surface. This suggests that the bonding is achieved via chemisorption rather than the much weaker physisorption [13]. It is also observed that the Alq_3 bonds stronger to the FeCo electrode compared to the NiFe electrodes. This is concluded as the peaks associated with Alq_3 in the N(1s) and Al(2p) are larger in magnitude for the FeCo/Alq_3 (washed) surface compared to the NiFe/Alq_3 (washed) surface.

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This could be due to the FeCo surface being ~80% oxide compared to the ~50% oxide for NiFe and the Alq_3 chemisorbing stronger to an oxide rather than the transition metal.

The sample surfaces were imaged using an AFM, from which growth mechanism and mean surface roughness of each surface can be determined. The 3D AFM images are shown in Figure 5 for the different FeCo and NiFe films (bare-electrode (washed), Alq_3 (as-grown) and Alq_3 (washed)). It is immediately clear that all the films involving FeCo are extremely flat, with a rms surface roughness of 1.004 nm for the FeCo (washed) film, while the FeCo/Alq_3 (as-grown) rms surface roughness was 1.932 nm and the FeCo/Alq_3 (washed) rms surface roughness was 1.003 nm.

However, it is very clear from Fig 5e that the Alq_3 grows in island formations on NiFe, which is quite different from the growth mechanism on top of the FeCo electrode. For the NiFe (washed) electrode the rms surface roughness was 0.858nm and the NiFe/Alq_3 (washed) rms surface roughness was 0.821nm, also very flat. We note that the Alq_3 films were grown under nominally identical conditions – the Alq_3 growth rate for both was kept to between 0.1nm/s and 0.2nm/s, and the growth was in the same chamber at the same vertical position, with the same substrate stage rotation, from the same crucible (without being refilled between growths), with a load-lock system used to perform the sample manipulation (such that the main-chamber was not vented to atmosphere between growths). The substrates used for the ferromagnetic growth were from the same batch and treated in the same way prior to growing the ferromagnets and the Alq_3.
The growth mechanism of Alq_3 can be altered by a number of different methods, including the substrate wettability [27], deposition rate [28], and light condition [29]. The substrate wetting is how well the Alq_3 bonds to the surface, this includes a wetting layer, which is an amorphous layer that forms, before the grain growth of the Alq_3, it depends on the surface chemistry, including the bonding and roughness [27]. It has also been found that a low evaporation rate (<0.2nm/s) for Alq_3 gives randomly oriented crystals with 10-30nm gaps between them, while high evaporation rates (>0.4nm/s) gives a dense uniform film with no pinholes [28]. Growing Alq_3 in light (using a 100W tungsten filament lamp) and dark also influences the growth. For the Alq_3 films grown in light, islands were observed with surface roughness of 4.6nm, while growth in the dark produced homogenous films with surface roughness of 2.1nm [29]. As the Alq_3 films were grown in the same conditions, it is likely that the surface energy of the NiFe electrode is markedly different to the FeCo electrode, possible due to the presence of Ni or the lower oxide coverage, which leads to the different growth mechanisms in Fig. 5 [27].

For neither electrode it is not possible to detect any individual molecules of Alq_3 still attached to the surface of the electrode after washing, which the XPS N(1s) and Al(2p) data show are present. This is likely to be due to the resolution of the AFM not being sufficient to detect the Alq_3 molecules on the electrode surface, due to the molecules either being widely scattered across the surface (i.e. not a continuous layer) or being in a continuous layer.

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The work function of the different surfaces were measured to compare the WF of NiFe and NiFe/Alq_3 (washed) surfaces to see if these is any difference due to the Alq_3 being chemisorbed onto the NiFe. For the NiFe surface the WF= 5.20 ± 0.01 eV, while for the NiFe/Alq_3 surface before washing the WF = 5.23 ± 0.01 eV and after washing the WF = 5.20 ± 0.01 eV. Thus there is no difference in the WF between the NiFe surface and the NiFe/Alq_3 (washed) surface, this could be due to the measurement being done over a wide area (5mm^2), leading to the NiFe dominating the measurements, as there is a too small amount of Alq_3 chemisorbed onto the surface of the NiFe for the Kelvin Probe to detect. The WF measurements suggests that the Alq_3 is not a continuous layer on the surface after washing.

As there is evidence of a strong bonding between the Alq_3 and the transition metal electrodes from the XPS data (Figures 2-4), the work of Baurrad et al [14], suggests that the electronic interface states should change with this bonding. From the SHIPS model, the first organic layer on the electrode, changes the polarisation states, so changing the MR of the device. While Steil et al [13], showed that the hybrid interface states exist due to the chemisorption of the Alq_3 onto the electrode, causing the molecular orbitals and metallic bands to interact. Thus to investigate this change in the electronic interface states, the surface magnetisation of the magnetic electrodes was measured using a MOKE magnetometer. This is because the magnetisation of a material is related to the spin polarisation and density of states of the material, i.e the electronic states are linked to the magnetisation. The principle of MOKE is that the polarised laser interacts with the magnetisation within the thin film [30]. As the magnetic electrodes are transition metals, the laser will only penetrate a certain distance, known as the skin depth into the magnetic film. The skin depth of a material is given by:

$$\delta = \sqrt{\frac{2\rho}{2\pi f \mu_o}} \tag{1}$$

Where ρ is the bulk resistivity of the material and f is the frequency of the light source. For the MOKE set-up, the wavelength of the laser was 635nm, thus the frequency was 4.7×10^{14}Hz. The bulk resistivity of FeCo is 79nΩ.m and NiFe is 69.3nΩ.m. Thus the skin depth of FeCo is 6.5nm and NiFe is 6nm. This means that the majority of the magnetisation loop measured on the MOKE magnetometer is from the surface magnetisation, rather than the magnetisation of the whole film (t~40nm). Initial MOKE measurements on the first samples showed that there was no difference in the magnetisation loops measured for the FeCo electrode and the FeCo/Alq_3 sample. For the NiFe electrode and NiFe/Alq_3 sample, a difference in the magnetisation loops was measured. It was found that the NiFe/Alq_3 magnetisation loop along the hard axis had a larger coercive field compared to the NiFe electrode hard axis loop. To confirm that it was the Alq_3 causing the change in the magnetisation loop, and not other factors, such as a change in the polariser or analyser angle, the alignment of the sample in the MOKE, a second set of NiFe/Alq_3 samples were fabricated, with different thicknesses of NiFe. After the growth of the NiFe film, the substrate was split in half, so that one half was kept as a NiFe electrode and the other half had

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Alq_3 deposited on top. This allows further measurements of the NiFe electrode to be carried out to make sure that any changes measured are due to the Alq_3 rather than degradation. Also the magnetisation loops of the NiFe electrode were measured before the Alq_3 was deposited and then after the Alq_3 was deposited. Figure 6 shows the normalised magnetisation loops for NiFe electrodes and the NiFe/Alq_3 samples. It is observed that for all three NiFe thicknesses, the hard axis hysteresis loop changes once the Alq_3 has been deposited on top. This suggests that the strong bonding at the interface between the NiFe and Alq_3 does change the electronic states and hence the surface magnetisation. It is observed that for all three samples, the coercive field of the loops increases, with the Alq_3 on top. The difference in coercive field for all three NiFe thicknesses was ~0.25kA/m (Figure 7), which suggests the same influence has caused the change in the surface magnetisation. From Figure 7, it is observed that the coercive field of NiFe linearly decreases with thickness, and this decrease occurs for both the NiFe electrode and the NiFe/Alq_3 sample. It is also noted in Figure 6, that the NiFe/Alq_3 hard axis magnetisation loops are less sharp compared to the NiFe electrode loops. The effect was probably not observed in FeCo, as the coercive field of the FeCo electrode was 10kA/m, which is a factor 10 larger than the NiFe electrode coercive field, so a change of ~0.25kA/m in the coercive field would be lost within the error of the measurement. This is because a larger applied field (100kA/m) was required to saturate the FeCo electrode, so the error on each field was ± 0.75kA/m, while a smaller applied field (20kA/m) was required to saturate the NiFe electrode, leading to an error of ±0.2kA/m on each field. Hence the difference is observed in NiFe as the coercive field of the NiFe is <1kA/m, so a change of ~0.25kA/m is large enough to make a difference to the magnetisation measured. As the MOKE magnetometer is a surface sensitive technique rather than a bulk technique, the absolute magnetisation is not known, but the change in the surface magnetisation of the NiFe electrode and the NiFe/Alq_3 (washed) samples can be taken as the difference in the change in light intensity when the film is measured. Thus doing this measurement for the NiFe electrode the change in voltage was 0.0578V, while for the NiFe/Alq_3 (washed) electrode the change in voltage was 0.049V. This gives a ~15% decrease in the surface magnetisation due to the chemisorptions of the Alq_3 onto the NiFe electrode. As the skin depth is ~6nm, this suggests that the Alq_3 has chemisorbed into the top 1nm of the NiFe.

The XPS spectra and the MOKE data show that the Alq_3 is strongly bonded to the bottom electrode, and that this bonding changes the surface magnetisation. There are two possible ways that the Alq_3 could bond to the surface, the first is by chemically bonding onto the electrode surface (chemisorption) via charge transfer, such as organic-metal oxide complexes and the second is by physisorption via van der Waals forces [13, 24]. It is likely that the Alq_3 chemisorbed onto the magnetic surfaces, as Alq_3 was still present after cleaning, which shows there was a strong bond between the Alq_3 and the magnetic surface. This chemical bonding will alter the density of states at the interface, by forming hybrid interface states [15], which will change the spin polarisation and thus the surface magnetisation. This is the principle behind the

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SHIPS model given by Baurrad et al [14]. If the Alq_3 physisorbed onto the surface of the magnetic electrode, it changes the electronic structure by lowering the work function [13], although this may not change the spin polarisation of the electrode. As van der Waals forces are relatively weak, it is likely that cleaning the Alq_3 layer with chloroform would remove the Alq_3 from the surface. This would suggest that it is more likely that the Alq_3 chemisorbed onto the magnetic electrodes, as there was still a layer present after cleaning with chloroform.

This change in the surface magnetisation due to the adsorption of molecules into magnetic films, has been studied for the adsorption of H onto ultrathin Co films [31], where they found that the hydrogen forms strong H-Co bonds, which reduced the surface magnetisation when all the Co atoms were bonded to H, but enhanced the surface magnetism, when there was partial H coverage. Similarly, it has been shown that there is an electronic interaction between the C_{60} π electrons and the Fe_3O_4 3d electrons, which lead to an induced magnetic moment in the interfacial electronics states [32]. Density functional theory also predicted that benzene adsorbed onto Fe(100) have a spin-polarisation induced onto it by the Fe(100) interface, whose sign is determined by the distance of the benzene from the Fe surface [33]. As these studies demonstrate that adsorption of small molecules into magnetic surfaces change the surface magnetisation and the spin polarisation, this means the change in the magnetisation of the NiFe/Alq_3 films can be attributed to the Alq_3 molecules chemisorption into the NiFe surface.

These previous measurements techniques such as x-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) have shown that the electronic properties are modified by the chemisoption of organic molecules onto magnetic surfaces [32]. These technique probe different element using high energy x-rays, and from the data it is possible to determine whether interfacial magnetic moments are induced in the organic semiconductor and whether the spin polarisation changes at the surface. They have shown that the spin polarisation is sensitive to the magnetic and electronic structure of the interfaces. From our measurements we are able to state the surface magnetisation changes with the chemisorptions of Alq_3, and the surface magnetisation reduces. This corresponds well with other measurements which have shown a decrease in the magnetic moment with the addition of an organic semiconductor to the surface [31, 32]. From this other work it can also be deduced that it is likely that the Alq_3 is likely to have an induced spin polarisation, due to the chemisorptions. It is also likely that the spin polarisation does not change sign with the chemisorptions of Alq_3 onto the transition electrode surface, as from previous MR measurements [5,18], the MR measured without any interface layers is always positive, as expected.

Conclusions

The XPS spectra and MOKE data show that the Alq_3 strongly bonds to the surface of the transition metal electrode. This bonding is likely to be due to chemisorptions of the Alq_3 onto the metal surface, as there is still Alq_3 on the surface after washing. This chemisorption changes the surface magnetisation of the electrode, which in principle will change the spin polarisation of the

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magnetic electrode, which is consistent with the SHIPS model. This means that the interface between the bottom electrode and the organic semiconductor is very important in organic spin-valves. The XPS spectra show that Alq_3 bonds stronger to the FeCo electrodes compared to the NiFe electrodes, which is probably due to the FeCo having a higher percentage oxide compared to NiFe. This also could be related to the different growth mechanism of Alq_3 on the FeCo and NiFe. Indeed, it is worth noting that using NiFe as the bottom electrode in an Alq_3 spin-valve is unfavourable, as the Alq_3 islands could yield make the magnetoresistance difficult to interpret or, in the worst-case, the two electrodes shorting. The AFM and WF measurements demonstrate that the Alq_3 present on the NiFe surface after washing is not a continuous layer.

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Figure Captions

Figure 1. The wide XPS spectra for (a) the FeCo and FeCo/Alq_3 films and (b) the NiFe and NiFe/Alq_3 films. The data is offset along the y-axis.

Figure 2. The N(1s) spectra for (a) the FeCo and FeCo/Alq_3 films and (b) the NiFe and NiFe/Alq_3 films. The dashed lines are the fitted peaks to the spectrum.

Figure 3. The Al(2p) spectra for the FeCo/Alq_3 films and NiFe/Alq_3 films. The dashed lines are fitted peaks to the data.

Figure 4. The O(1s) spectra for (a) the FeCo and FeCo/Alq_3 films and (b) the NiFe and NiFe/Alq_3 films. The dashed lines are the fitted peaks to the spectrum

Figure 5. AFM images of (a) the FeCo (washed) film, (b) the FeCo/Alq_3 (as-grown) film (c) the FeCo/Alq_3 (washed) film, (d) the NiFe (washed) film (e) the NiFe/Alq_3 (as-grown) film and (f) the NiFe/Alq_3 (washed) film. The scan area was 10 x 10 μm. The z-axis height for a, c, d and f is 100nm, for b is 60nm and for e is 300nm.

Figure 6. Normalised magnetisation loops of the NiFe and NiFe/Alq_3 as a function of applied magnetic field

Figure 7. Coercive field as a function of NiFe thickness for the NiFe and NiFe/Alq_3 films. The solid lines are a linear fit to the data.

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Highlights

Alq_3 chemisorbs onto magnetic transition metal surfaces
Alq_3 changes the surface magnetisation of the NiFe film
Alq_3 chemisorbs stronger onto the oxide rich FeCo surface

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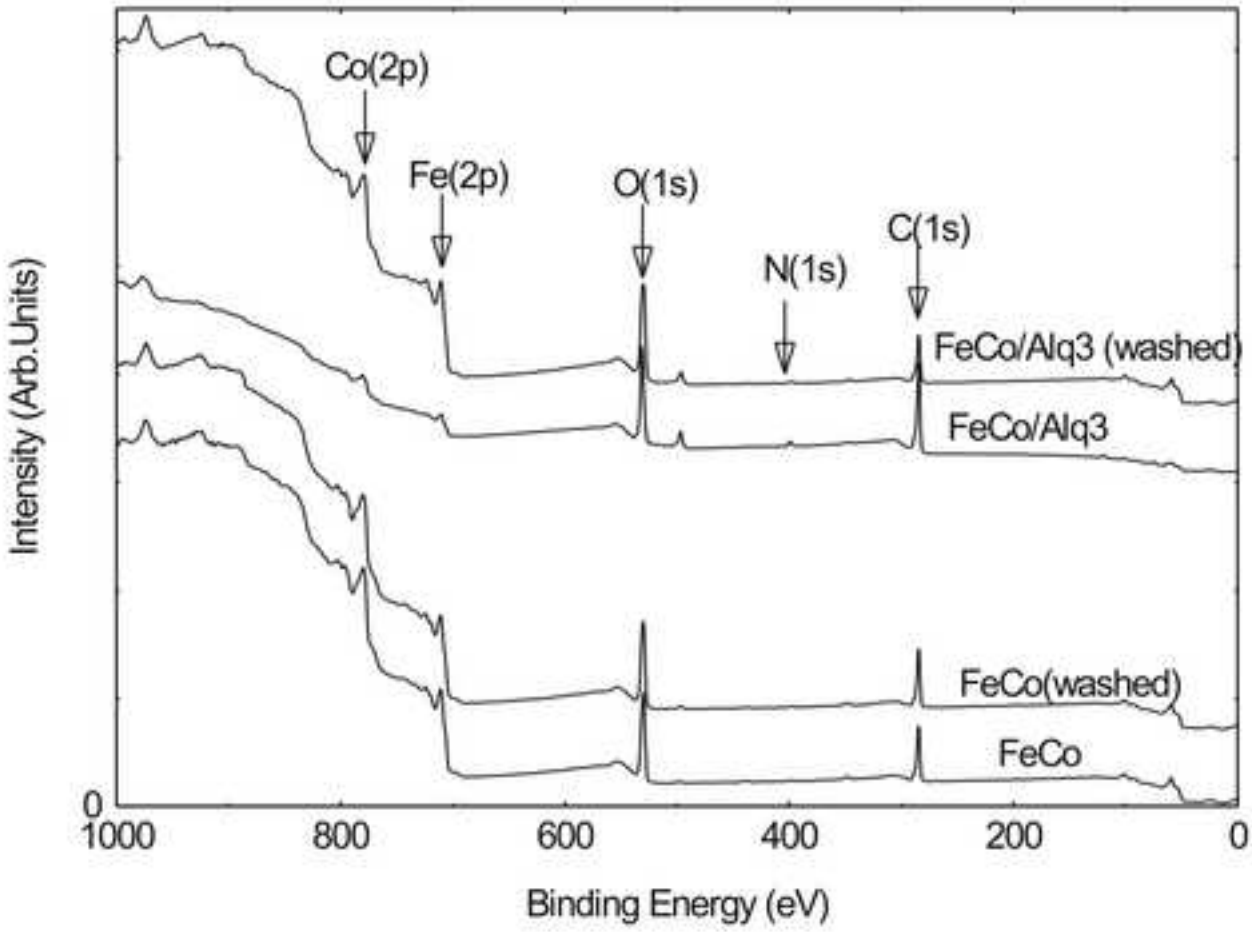

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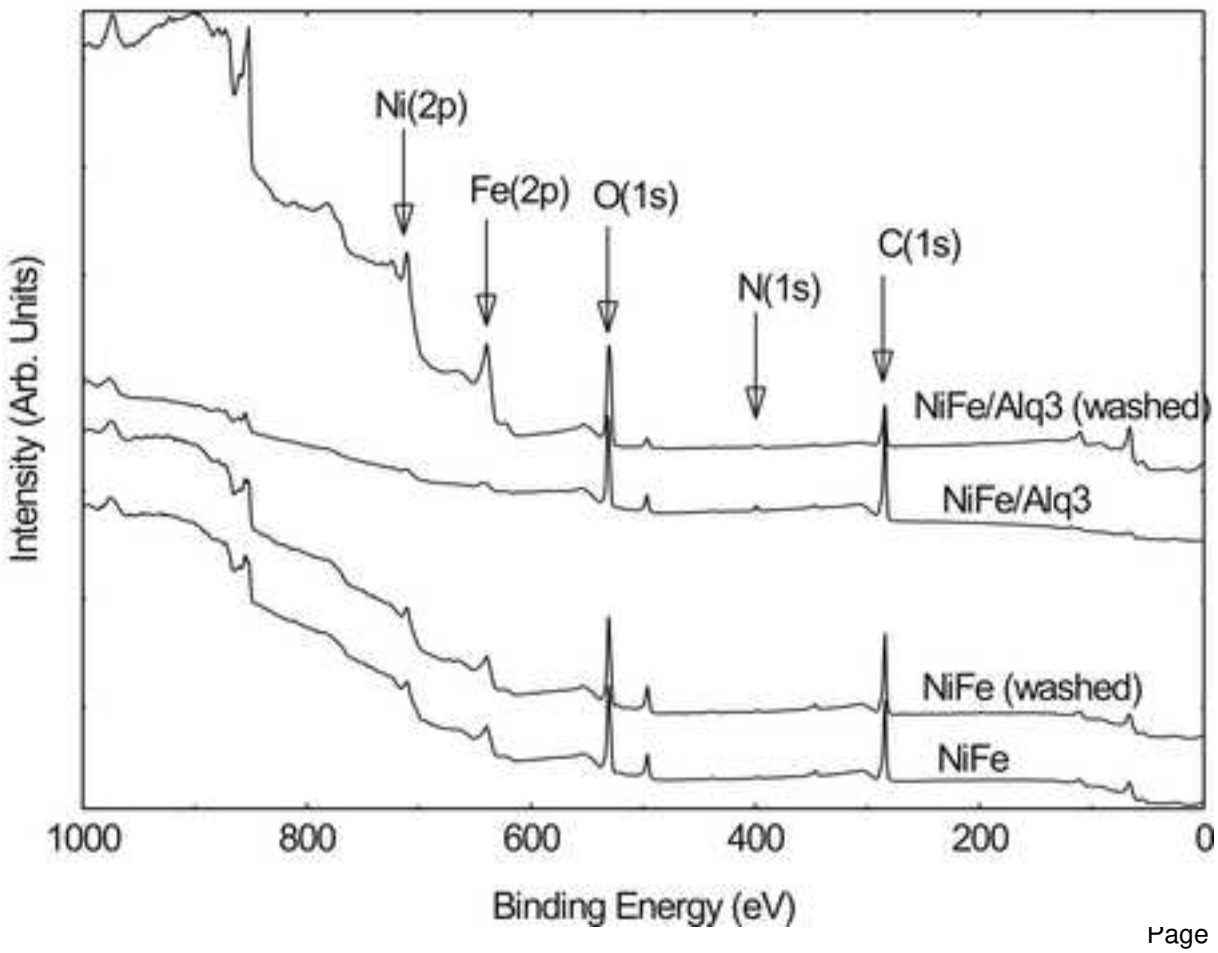

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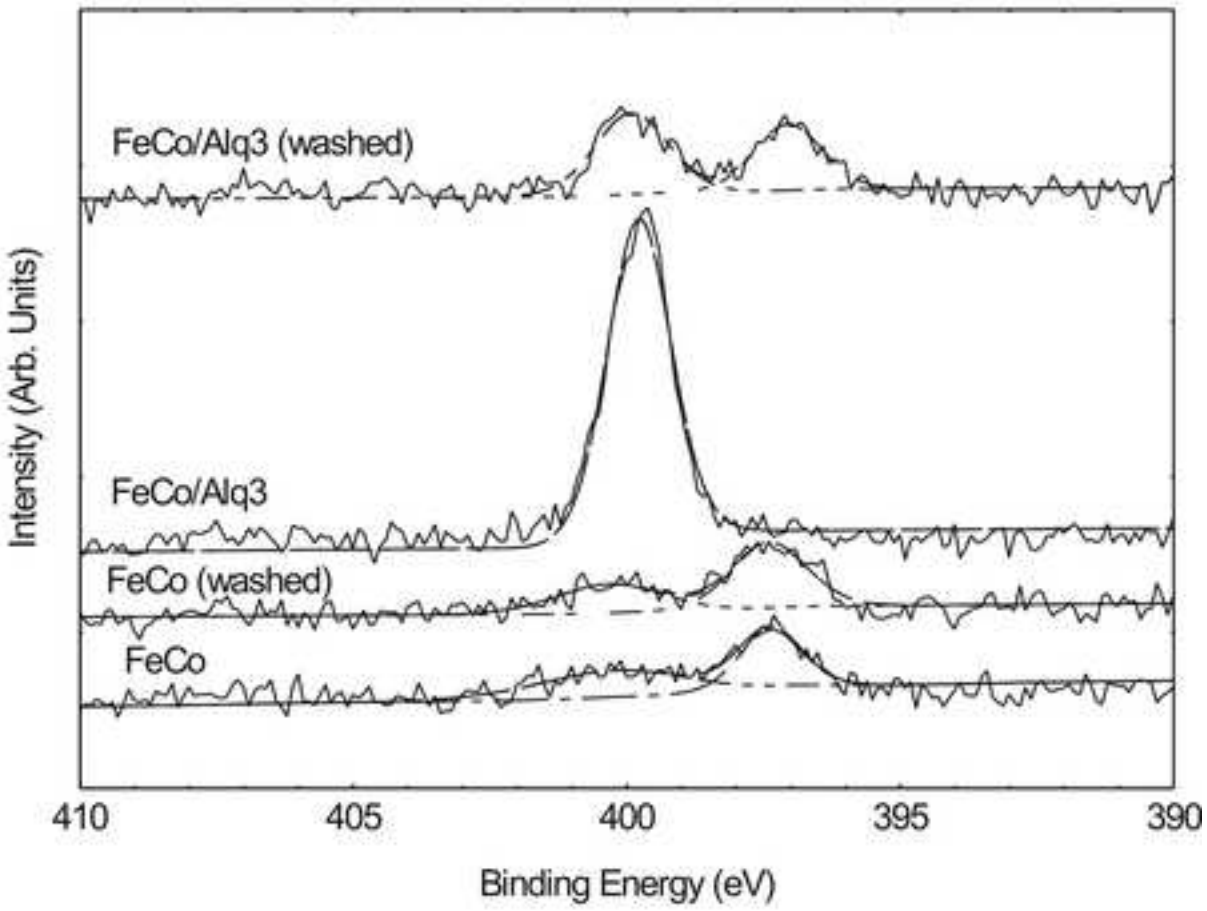

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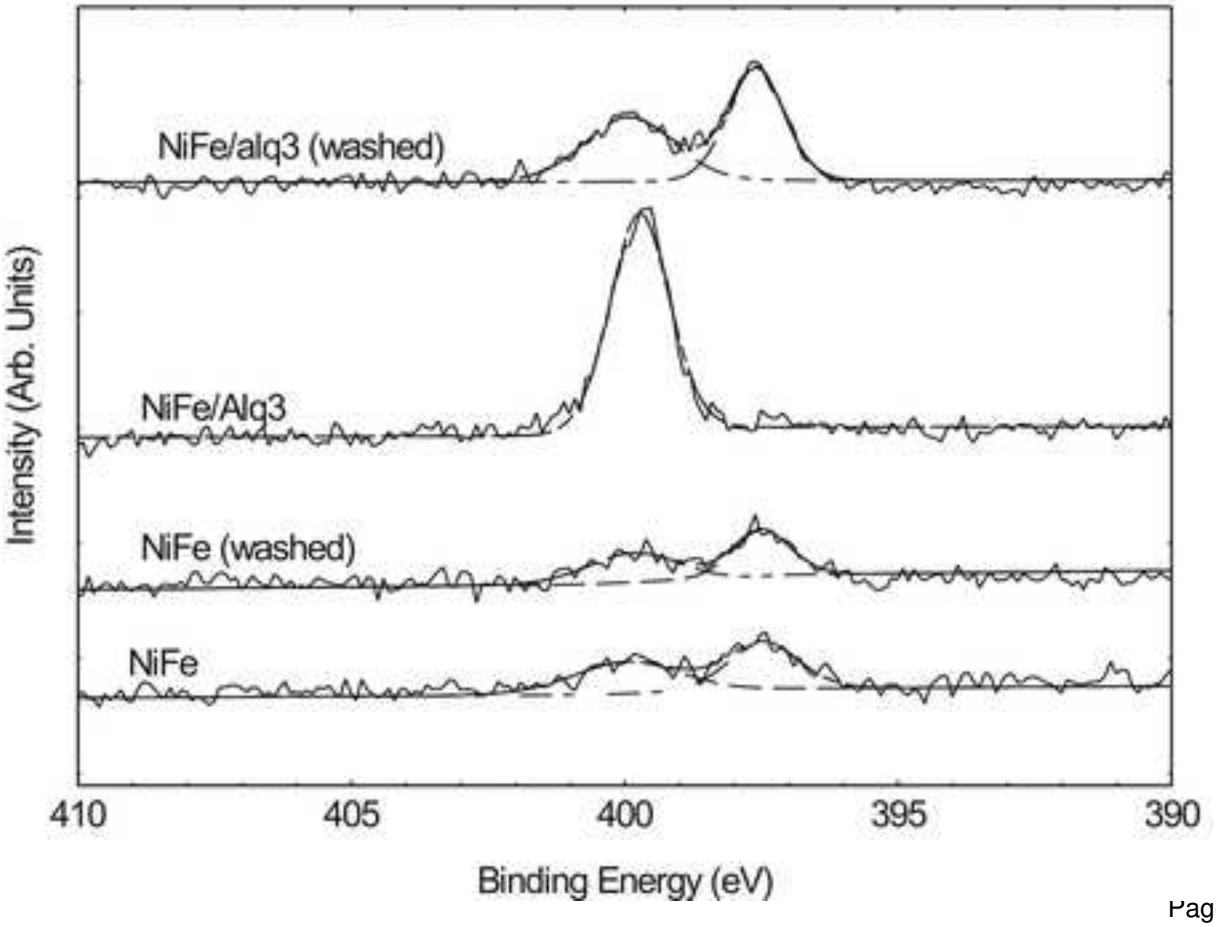
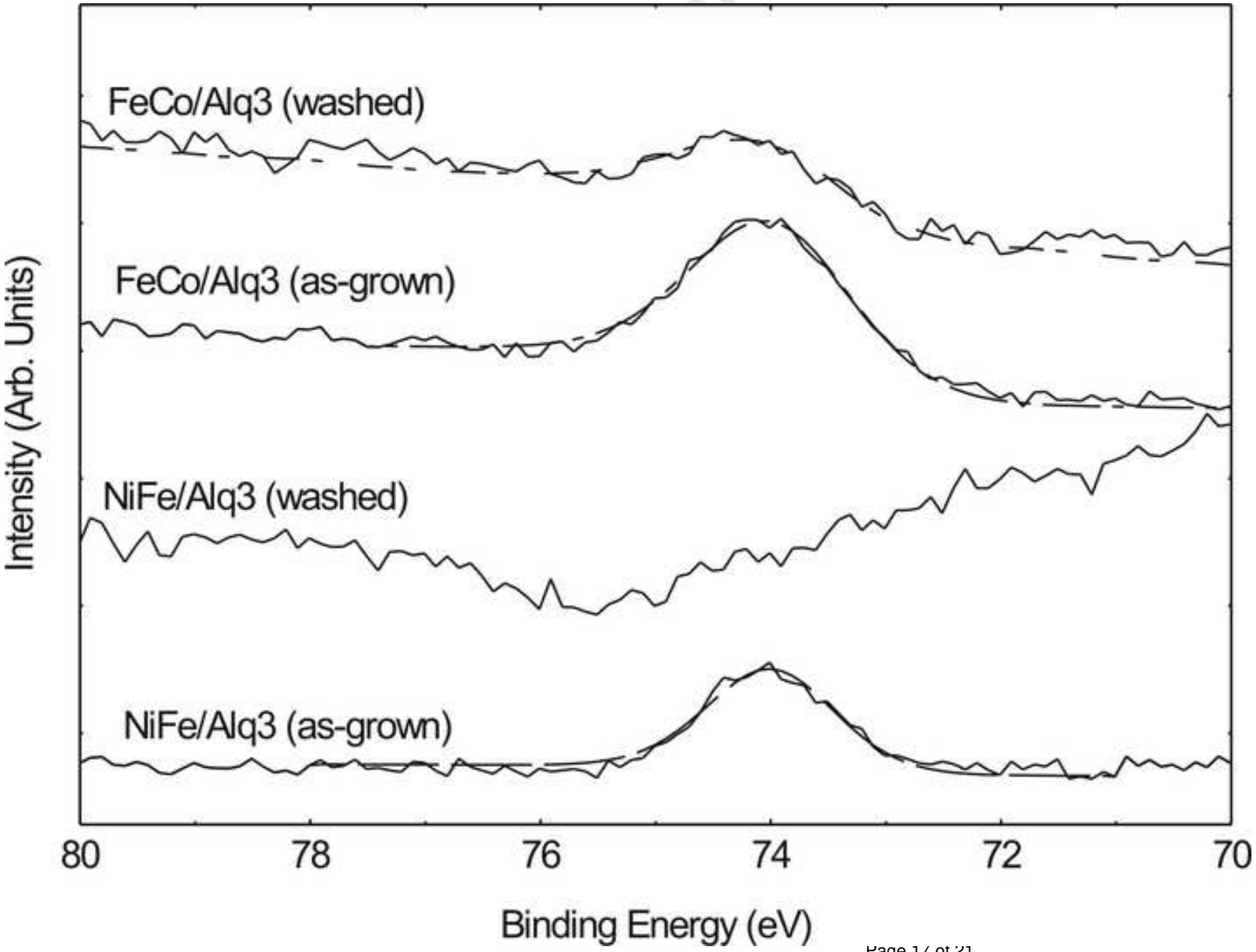


Figure


FeCo/Alq3 (washed)
FeCo/Alq3 (as-grown)
NiFe/Alq3 (washed)
NiFe/Alq3 (as-grown)
Intensity (Arb. Units)
80
78
76
74
72
70
Binding Energy (eV)

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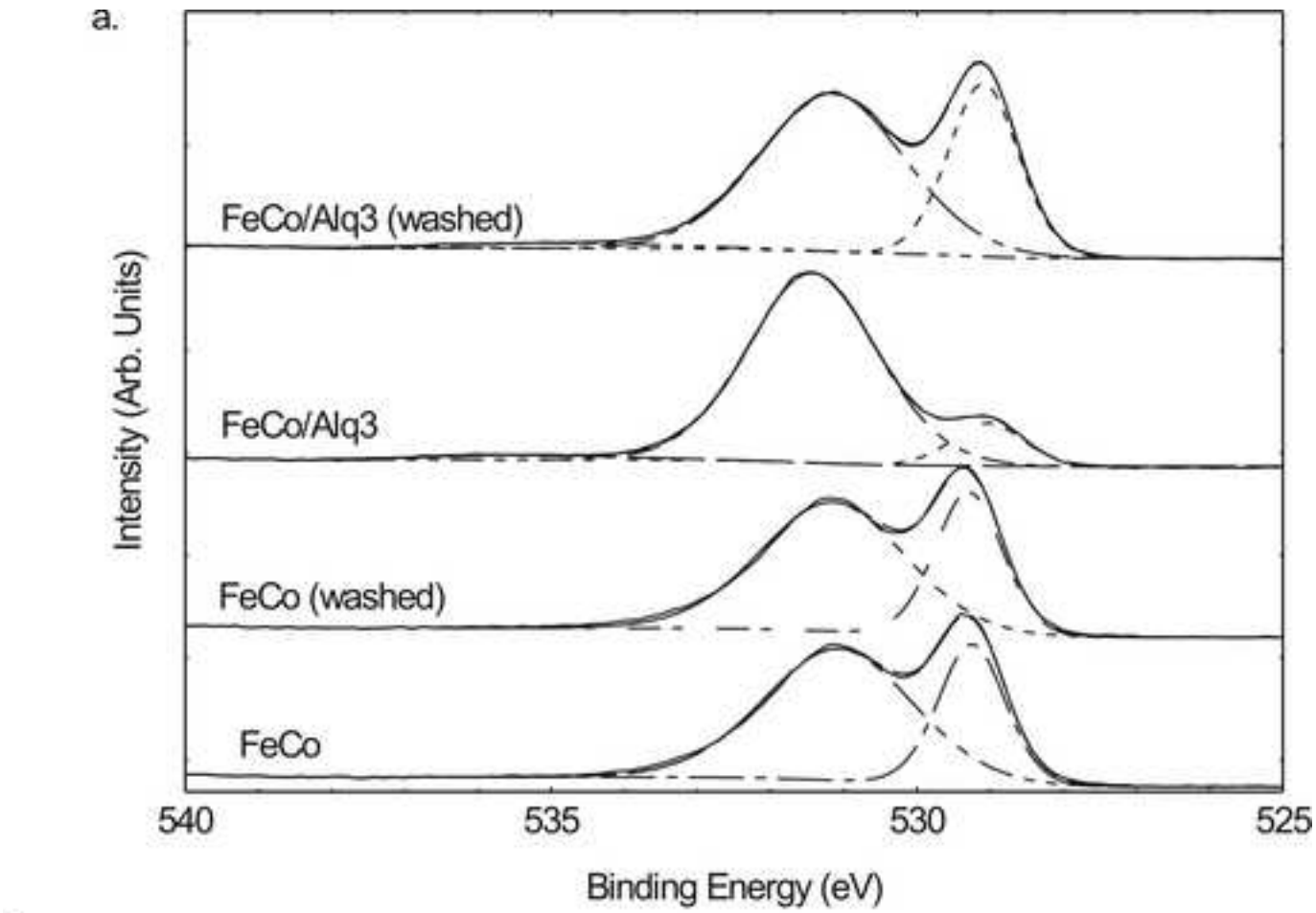

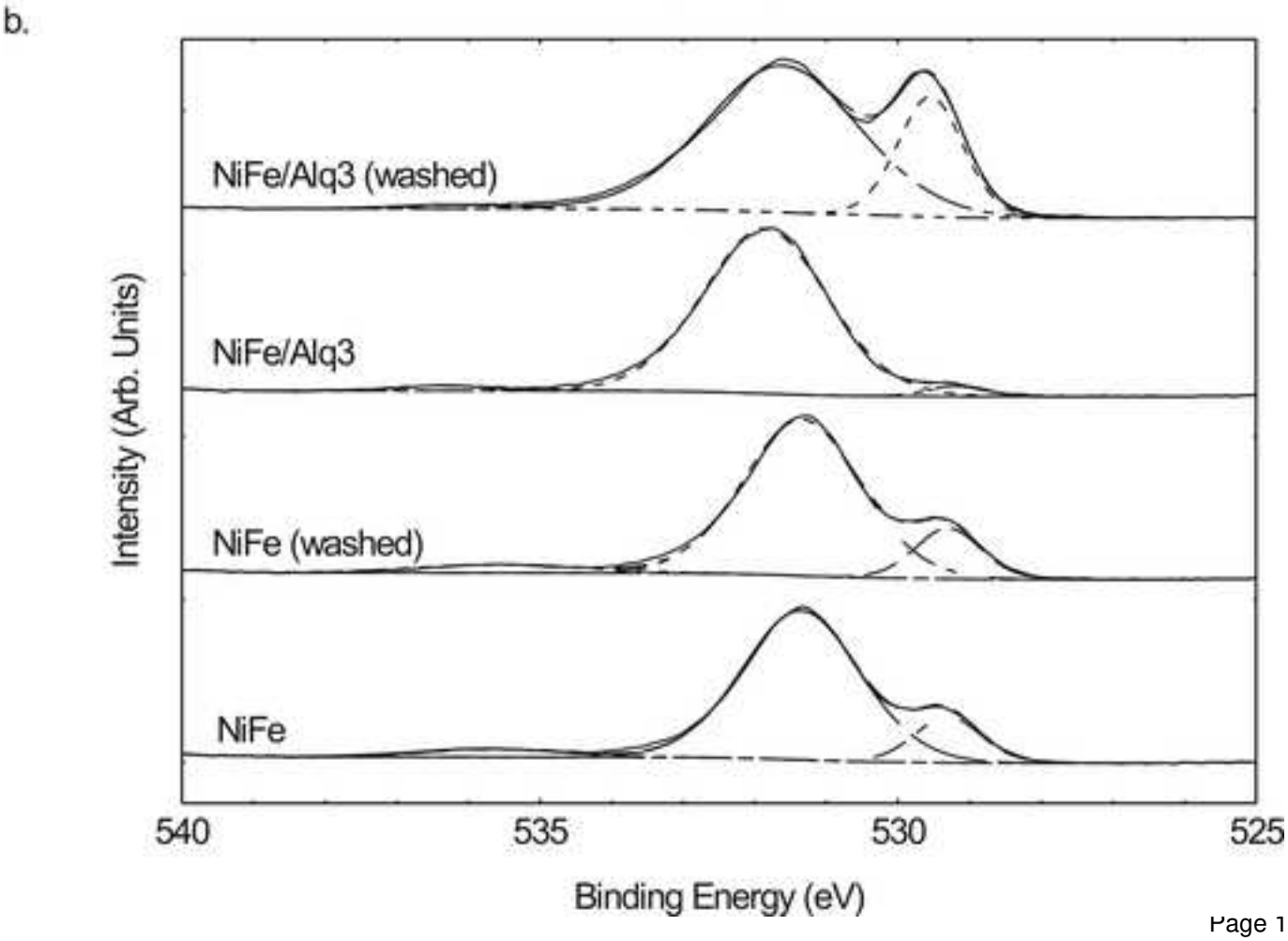

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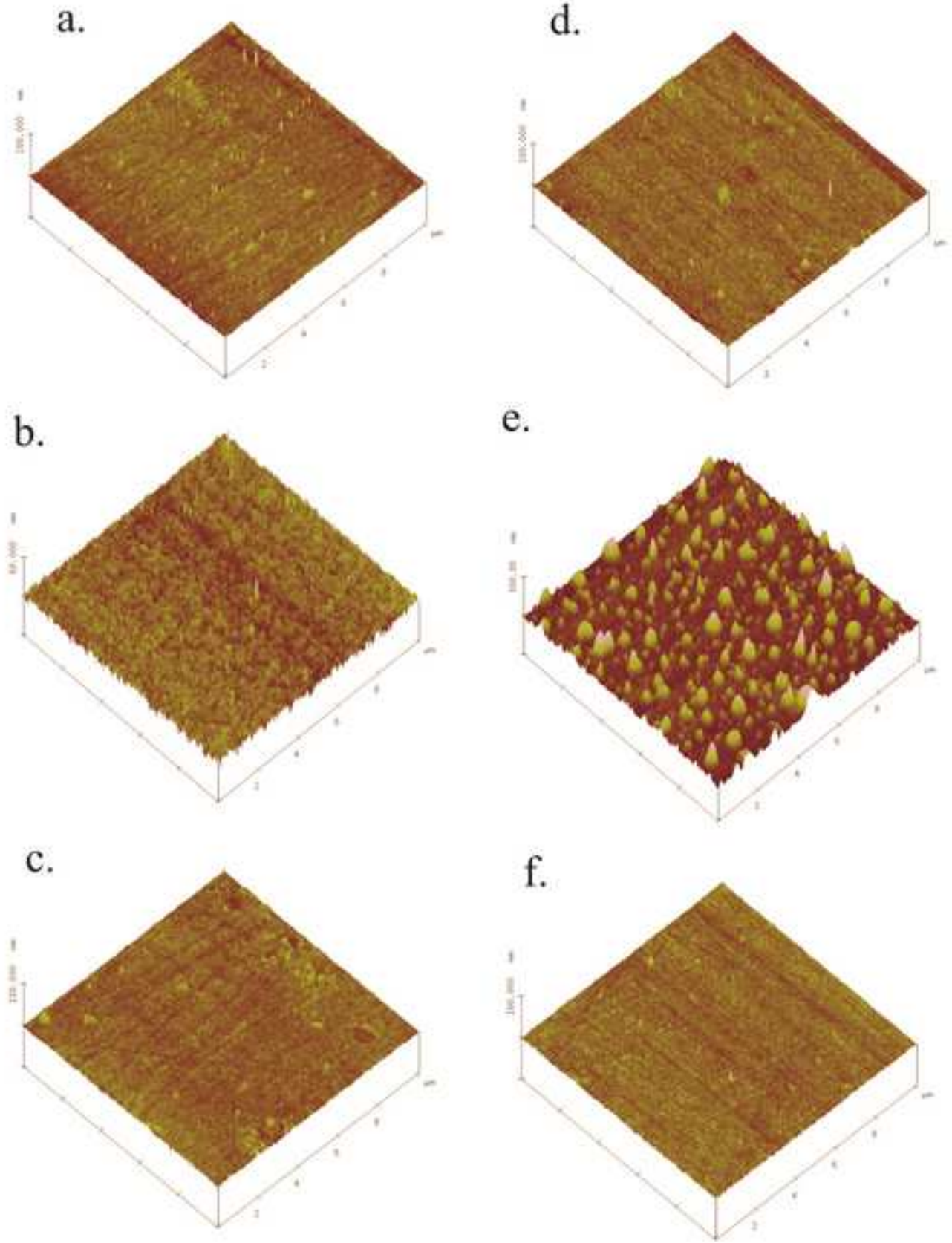

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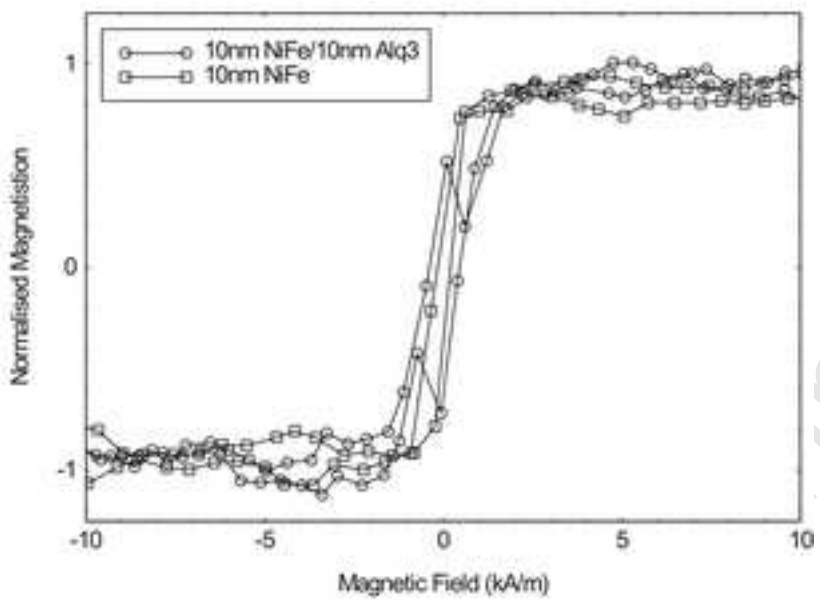

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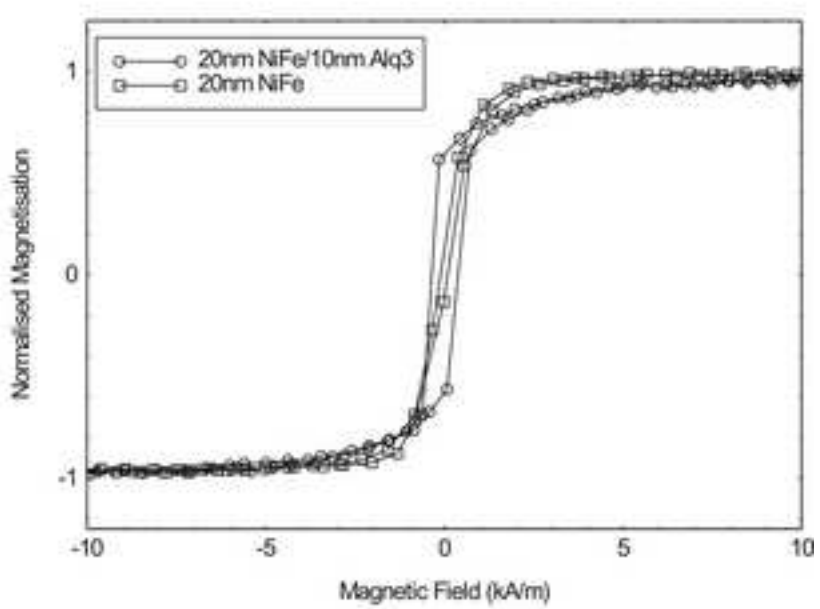

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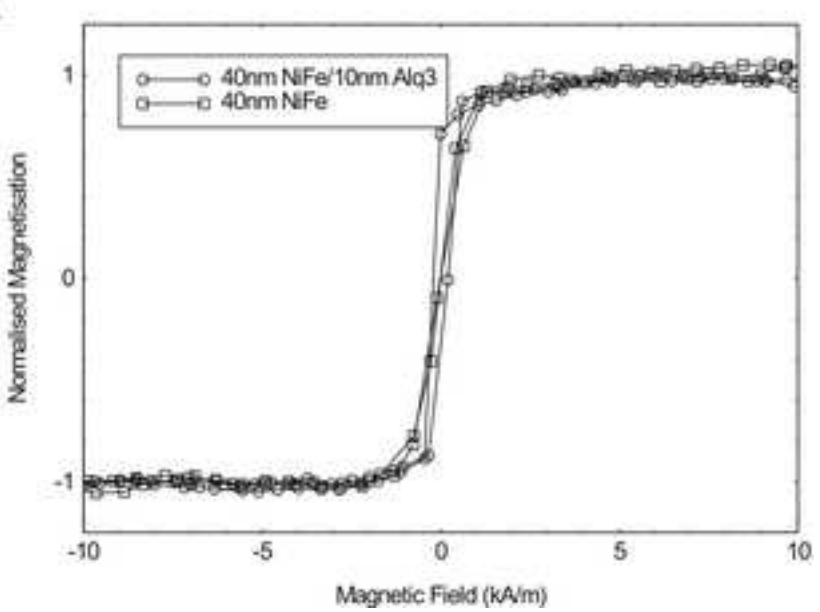
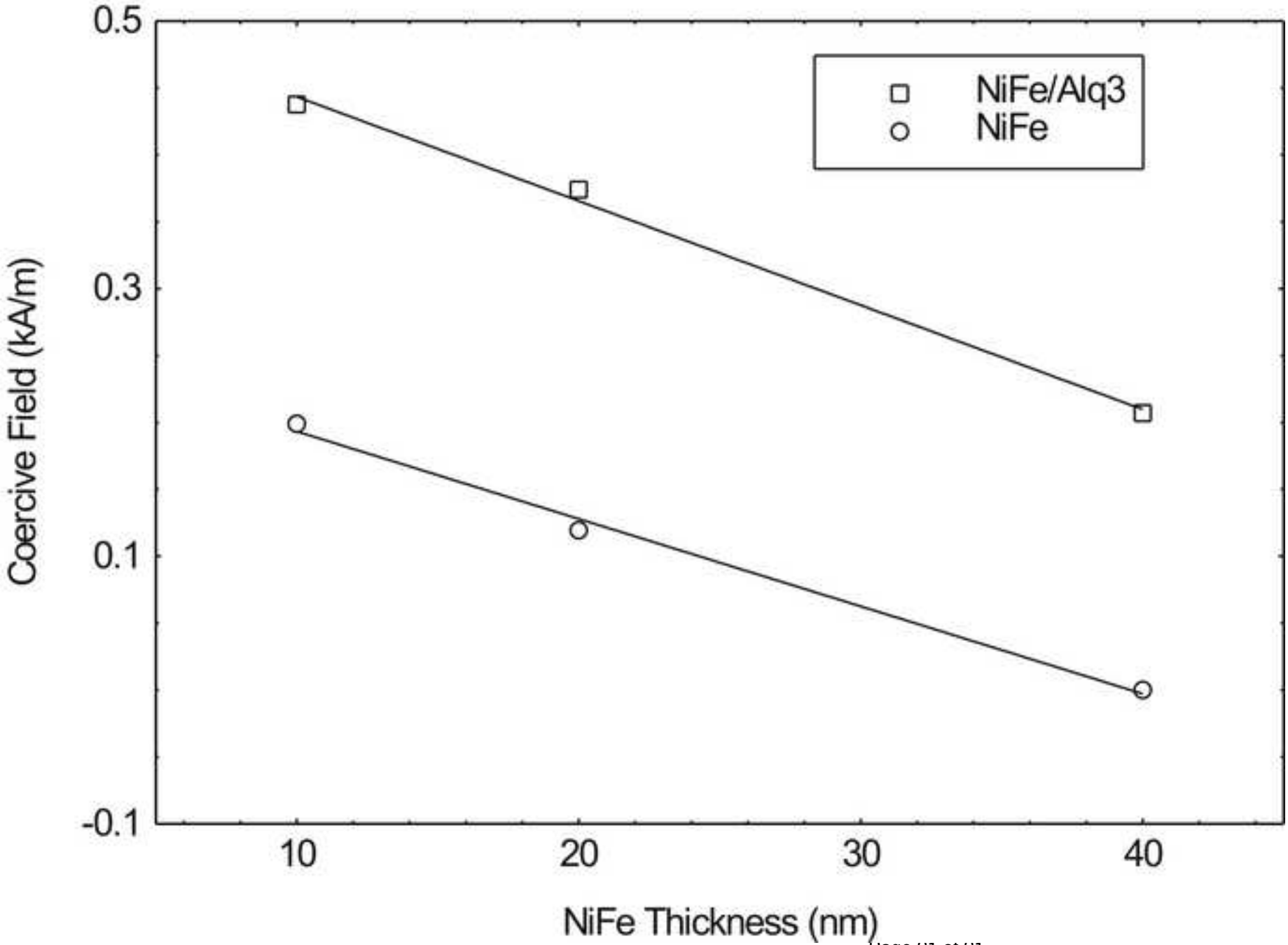


Figure


0.5
0.3
0.1
-0.1
Coercive Field (kA/m)
10
20
30
40
NiFe Thickness (nm)
NiFe/Alq3
NiFe