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XPS and XMCD Study of Fe₃O₄/GaAs Interface

Yongxiong Lu¹, Jill S. Claydon¹, Ehsan Ahmad¹, Yongbing Xu¹, Sarah M. Thompson², Karen Wilson³, and Gerrit van der Laan⁴

¹Spintronics Laboratory, Department of Electronics, The University of York, York, YO10 5DD, U.K.

²Department of Physics, The University of York, York, YO10 5DD, U.K.

³Department of Chemistry, The University of York, York, YO10 5DD, U.K.

⁴Daresbury Laboratory, Warrington, WA4 4AD, U.K.

Ultrathin Fe oxide films of various thicknesses prepared by post-growth oxidation on GaAs(100) surface have been investigated with X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and X-ray magnetic circular dichroism (XMCD). The XPS confirms that the surfaces of the oxide are Fe₃O₄ rather than Fe₂O₃. XAS and XMCD measurements indicate the presence of insulating Fe divalent oxide phases (FeO) beneath the surface Fe₃O₄ layer with the sample thickness above 4 nm. This FeO might act as a barrier for the spin injection into the GaAs.

Index Terms—Half-metallic Fe₃O₄, post-growth oxidation, spintronics, XMCD.

I. INTRODUCTION

HALF-METALLIC Oxide Fe₃O₄ (magnetite) is one of the most promising materials for spintronic applications as it has high Curie temperature and large spin polarization at the Fermi level [1], [2]. For example, magnetite has been used as electrode material in magnetic junctions [3], [4]. To inject spin into semiconductors, such as GaAs, synthesis of Fe₃O₄/GaAs half-metal/semiconductor hybrid structure is essential. However, to inject spin into semiconductors, the electron diffusion method has proved to be less efficient compared with electron tunneling method, where there is a barrier between the spin injection source and the semiconductor [5], [6]. Previously, Fe divalent oxide, namely FeO, has been found to be an insulator with band gaps of 1.3 and 2.2 eV for the Fe 3d/O 2sp-Fe 4s and Fe 3d/O 2sp-Fe 3d transitions, respectively [7], [8]. So an interesting problem arises: can we achieve a spin tunneling hybrid structure with an insulator layer between the half-metallic Fe₃O₄ and the semiconductor GaAs?

We have demonstrated in our previous work that an ultrathin Fe film on GaAs can be oxidized into Fe₃O₄ by post-growth oxidation [9]. In this paper, we present our work on the surface and interface of the Fe oxide/GaAs(100) hybrid structure using X-ray spectroscopy techniques, namely X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). A series of samples with nominal Fe thickness of 2, 3, 4, and 6 nm were prepared by post-growth oxidation. The thickness dependencies of the interface magnetic properties and chemical composition have been investigated.

II. EXPERIMENT

The samples were prepared by post-growth oxidation of ultrathin Fe films on GaAs. After wet etching by H₂SO₄:H₂O₂:H₂O (4:1:1) solution, the GaAs(100) substrates were loaded into a molecular beam epitaxy (MBE) chamber. A thermal annealing

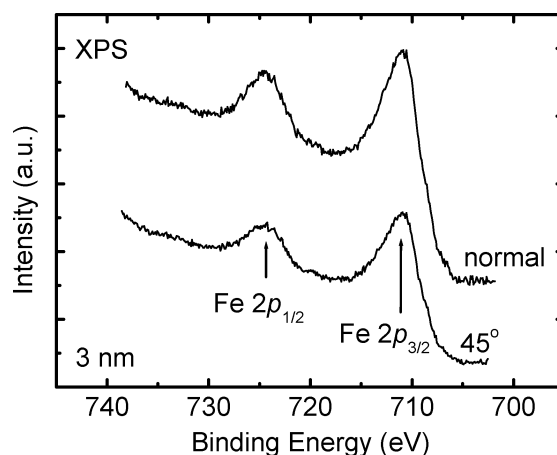


Fig. 1. Fe 2p XPS measurements of the 3-nm sample with the sample surface normal or 45° tilted to the incident X-ray. The geometries are labeled. Both spectra show widened peaks and no shake-up satellite can be identified.

at 800 K about 40 min followed, prior to the Fe growth. The Fe was then evaporated from a crucible, at a distance of 400 mm away from the fixed GaAs substrate. The growth rate was monitored by a quartz microbalance and set to 2 Å/min. After Fe growth, the samples were oxidized in an O₂ environment with a partial pressure of 5×10^{-5} mbar, and at a temperature of 500 K for 5 to 10 min, until a stable reflection high-energy electron diffraction (RHEED) pattern has been achieved.

The XPS measurements were done with Mg K α radiation. The XMCD measurements were carried out in the station 1.1 of the Synchrotron Radiation Source at Daresbury Laboratory (U.K.). The resulting current output from the sample was measured in total electron yield mode as a function of the X-ray photon energy. The dichroism was obtained as the difference spectrum, $I^+ - I^-$, achieved by reversing the direction of the applied magnetic field at fixed polarization.

III. RESULTS AND DISCUSSION

Plotted in Fig. 1 are the XPS measurements of the 3-nm sample, at normal and 45° incident angles with respect to the surface. In Fe₂O₃, the Fe atoms are completely oxidized

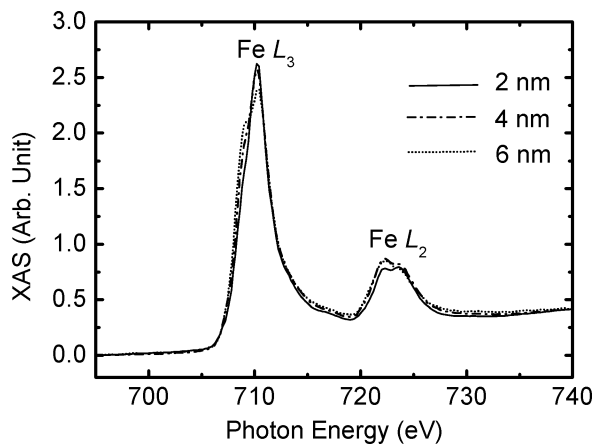


Fig. 2. XAS measurements with thickness dependency. The start and end points of the 4- and 6-nm spectra have been normalized to the 2-nm spectrum for better comparison.

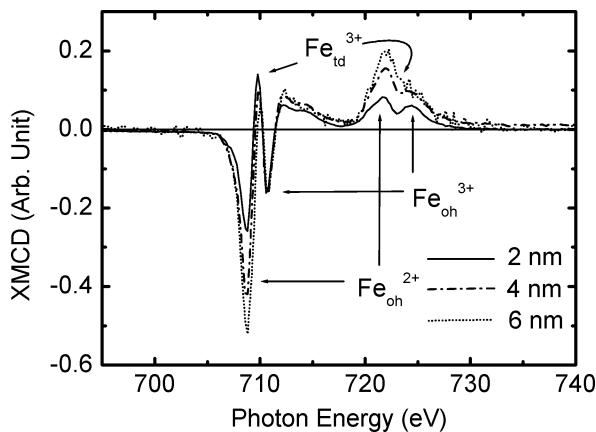


Fig. 3. XMCD spectra illustrating thickness dependency of the dichroism on the photon energy. The intensities are normalized to the Fe_{oh}³⁺ peaks and the photon energies are shifted to the same position. The peaks from different chemical compositions are deduced from relative photon energies.

into trivalent Fe cations, generating narrower peaks in the XPS compared to Fe₃O₄, which consists of both divalent and trivalent Fe cations. Fe₂O₃ also features its XPS spectra with shake-up satellite peaks between the main peaks [10]. From the widened and shake-up satellite-free spectra in Fig. 1, it is clear that the sample composition is Fe₃O₄ rather than Fe₂O₃, which cannot be differentiated by the RHEED patterns during growth. It is worth noting that there is little difference between the two measurement geometries, normal or tilted 45° to the surface of the sample, suggesting a uniform composition for the 3-nm sample since the two measurement geometries have different penetration depths in the sample.

Fig. 2 illustrates the thickness dependencies of the XAS measurements. For the 2-nm thick sample, both Fe L₂ and Fe L₃ edges show clearly different chemical states which comes from the Fe₃O₄ in the sample. While at the lower energy edge for the 6-nm film, a strong peak distorts the Fe L₃ edge absorption. This may be due to the presence of more Fe²⁺ cations, rather than ferromagnetic atomic Fe atoms in the 6-nm film, as discussed below.

In Fig. 3 the XMCD dependencies are depicted, with their peak intensities normalized to the Fe_{oh}³⁺ (octahedral) peaks and

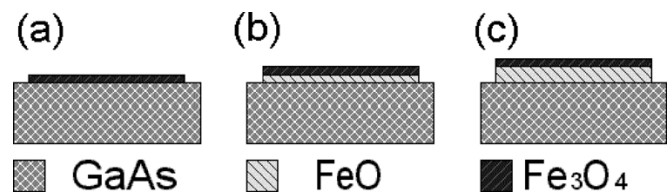


Fig. 4. Sketches of the proposed layered oxide films. (a) Surface layer with total thickness under 3 nm is Fe₃O₄. (b) FeO appears when the thickness achieved 4 nm. (c) FeO thickness increases upon the increasing total thickness, while the surface Fe₃O₄ thickness keeps constant.

the positions of the Fe_{oh}³⁺ peaks are shift to the same energy. The chemical states of the peaks are deduced from the relative photon energy. Interestingly the Fe_{oh}²⁺ (octahedral) peaks have an increasing strength, while the Fe_{td}³⁺ peaks show a reduced strength upon increasing thickness. This decrease in the strength of the Fe_{td}³⁺ (tetrahedral) peak can be explained by the increase of the Fe_{oh}²⁺ strength, which has an inverted strength compared with that of the Fe_{td}³⁺ in the XMCD. Hence, a constant Fe_{td}³⁺:Fe_{oh}³⁺ ratio is found on the surface of the oxide film upon increasing total thickness, taking the counteraction effect into account. Then we come to the conclusion that the surface area of the oxide is still Fe₃O₄, as also suggested by XPS measurements.

The increasing intensity of the Fe_{oh}²⁺ peaks is intriguing. In the oxidation of Fe film, below the top Fe₃O₄, atomic Fe was previously found. That is, a Fe₃O₄/Fe structure might be achieved by low-temperature oxidation [11]. The Fe-O phase diagram also indicates this structure [12]. Since the atomic Fe and divalent Fe cations have different chemical environments, their energy positions on the XMCD spectrum can not be identical. However, in Fig. 3, in which the spectra are calibrated using the Fe_{oh}³⁺ position, all the Fe²⁺ peaks remain at the same energy position despite the increasing intensity with increasing thickness. From both Figs. 2 and 3, it can be concluded that there are more partially oxidized Fe cations (divalent Fe cations) in the sample than the Fe₃O₄ when the thickness achieves 4 nm, and no atomic Fe was identified.

There are two possibilities for the extra Fe divalent cations. First, the sample is not uniform, and the chemical stoichiometry varies upon the depth from the surface to the oxide/GaAs interface. The second possibility is that there is a FeO layer below the surface Fe₃O₄ layer, whereas the surface Fe₃O₄ thicknesses keep constant. When the total thickness increases, once oxidized, the FeO thickness increases. Since the surface is Fe₃O₄, which has a defined quota of the Fe²⁺ cations, the extra partially oxidized Fe²⁺ cations are believed to present under the Fe₃O₄ layer. That is, more Fe²⁺ cations are generated near the oxide/GaAs interface when the total thickness increases, as indicated by Fig. 2. This possibility is supported by the oxidation mechanism [12]. Namely, a layered structure might be present in the oxide, as illustrated in Fig. 4. However, we would like to note that interfacial oxygen defects might form at the interface. These defects would be detrimental to the half-metallicity of Fe₃O₄ and efficient spin injection into GaAs. Further investigation such as high resolution transmission electron microscopy (HR-TEM) is needed.

IV. CONCLUSION

In summary, for the sample thickness below 3 nm, a uniform Fe_3O_4 has been formed on the GaAs(100), constituting a Fe_3O_4 oxide/semiconductor hybrid structure. For the thickness above 4 nm, there is an insulating FeO layer beneath the Fe_3O_4 near the interface and this insulating FeO layer might be a useful tunneling barrier for high efficiency spin injection into GaAs.

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