

Pulsed laser deposition growth of Fe₃O₄ on III–V semiconductors for spin injection

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(Received 19 January 2003; accepted 10 March 2003; published 5 August 2003)

We report on the growth of thin layers of Fe₃O₄ on GaAs and InAs by pulsed laser deposition. It is found that Fe₃O₄ grows epitaxially on InAs at a temperature of 350 °C. X-ray photoelectron spectroscopy (XPS) studies of the interface show little if any interface reaction resulting in a clean epitaxial interface. In contrast, Fe₃O₄ grows in columnar fashion on GaAs, oriented with respect to the growth direction but with random orientation in the plane of the substrate. In this case XPS analysis showed much more evidence of interface reactions, which may contribute to the random-in-plane growth. © 2003 American Vacuum Society. [DOI: 10.1116/1.1588648]

I. INTRODUCTION

Half metals are magnetically oriented compounds for which the electrons of one spin orientation have metal-like energy bands, whereas electrons of the opposite spin encounter an energy gap about the Fermi energy. To date, the canonical identification of half metals has relied on electronic structure calculations which have produced a handful of such compounds, the Heusler alloy NiMnSb being the first material to be designated a “half metal.”¹ Among the more celebrated examples are CrO₂,² La_{0.7}Sr_{0.3}MnO₃,³ and Fe₃O₄.⁴ Since half metals, by definition, have electrons of only one spin state present at the Fermi energy, they are logical candidates for use as spin injectors.

Experimental verification of half-metallicity, i.e., 100% spin polarization of the conduction electrons, has proven more intractable. The measurement techniques available are spin-polarized photoemission, transport measurements (utilizing point contacts or tunnel junctions between two spin-polarized materials), or Andreev reflection between the candidate half metal and a superconductor. Typical experimental results reported for theoretically identified half metals range from 60% to 100%.^{3,5–7} For example, Fe₃O₄ exhibits a point contact polarization of 84%.⁸ To put this in perspective, the canonical conduction electron spin-polarization result for the common transition-metal ferromagnets Fe, Co, and Ni are around 40%.⁵

For use as a spin injector, the growth of Fe₃O₄ on semiconductor materials will need to be studied. Most studies of Fe₃O₄ thin films involve growth on MgO substrates because the two materials share a similar lattice constant.^{9–14} Fe₃O₄ has also been grown on Si(001) and GaAs(001).¹⁵

In this work we report on the growth of Fe₃O₄ via pulsed laser deposition (PLD) on GaAs(001) and InAs(001) substrates. The nature of the Fe₃O₄ thin film growth is studied via reflection high energy electron diffraction (RHEED) and x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENT

Two substrates were prepared for deposition of Fe₃O₄: epitaxially grown *p*-type InAs on an InAs (001) substrate and *p*-type GaAs on a GaAs (001) substrate. The samples were grown in a Perkin–Elmer model 430 molecular beam epitaxial (MBE) system by traditional III–V MBE techniques. Gallium and indium were evaporated from Knudsen cells and arsenic was sublimated from a cracking effusion cell to create As₂ dimers for growth. In each case 1 μm of epitaxial material was grown. The InAs substrate was kept at approximately 450 °C during growth, whereas the GaAs substrate was kept at approximately 600 °C. The crystallinity and surface reconstructions of the materials during growth were monitored by RHEED.

After growth the samples were transferred in vacuum to a separate chamber for XPS analysis. The samples were examined in a Perkin–Elmer model 5800 XPS system utilizing an hemispherical energy analyzer and a 16 channel electron multiplier detector. All spectra were obtained using a monochromated Al anode x-ray source operating at 14 kV and 350 W and the samples were held such that photoelectrons had a 45° takeoff angle to the detector.

Samples then were transferred in vacuum to a third chamber equipped with an apparatus for performing PLD. Fe₃O₄ was deposited by impinging light from a frequency tripled (355 nm) Nd:yttrium–aluminum–garnet laser onto a formed iron oxide target in vacuum. Pulses of 5 ns duration and energy of approximately 100 mJ/pulse at a repetition rate of 10 Hz were used for the deposition. The source to substrate distance was kept at about 11 cm. The stoichiometry of the target was Fe₂O₃ instead of Fe₃O₄, and no background oxygen flux was used during the deposition. For films deposited under these conditions, the oxygen to iron ratio was 1.3 as determined by the ratio of the XPS spectral weight of the O 1*s* and Fe 3*p* peaks normalized by their atomic sensitivity factors.

It was found that above about 400 °C the InAs samples would undergo a change in reconstruction to an indium stabilized surface if no arsenic flux was present. Since the chamber in which the Fe₃O₄ was grown had no arsenic

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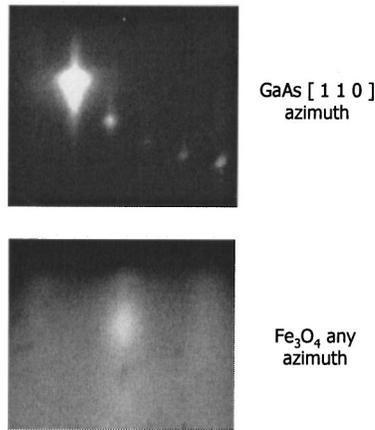


FIG. 1. RHEED images of Fe_3O_4 growth on GaAs (001): (Top) Epitaxial GaAs along a $\langle 110 \rangle$ azimuth which shows a fourfold reconstruction. (Bottom) Fe_3O_4 along any azimuth, i.e., the image did not change with substrate rotation.

source, the substrate temperature was kept at 350°C to ensure a repeatable, arsenic stabilized surface. While the GaAs samples could have been heated more while maintaining their surface reconstruction, the same Fe_3O_4 growth temperature was used so that the interface reactions and the nature of the Fe_3O_4 growth could be compared under the same conditions.

The thicknesses of the Fe_3O_4 films were measured *ex situ* by x-ray reflectivity and ellipsometry. These measurements suggested a growth rate of 0.3 \AA/s for the growth conditions described above.

III. RESULTS

A. Gallium arsenide

Growth of Fe_3O_4 on GaAs resulted in a dim but streaky RHEED pattern that did not change as the substrate was rotated (see Fig. 1). As the laser ablation began, the arsenic-stabilized $c(4 \times 4)$ reconstruction of the GaAs quickly gave way to a dim amorphous background. After several minutes of growth, faint, wide streaks began to appear. Kennedy and Stampe¹⁵ reported that Fe_3O_4 grows on silicon and GaAs in columnar fashion with the growth direction being parallel to the $\langle 111 \rangle$ direction of the cubic Fe_3O_4 structure and the in-plane orientation being completely random. This is consistent with our observation of a stationary RHEED pattern.

Figure 2 shows XPS spectra of the epitaxially grown GaAs surface, an Fe_3O_4 surface after several hundred angstroms of growth and the surface after about 50 \AA of Fe_3O_4 growth. Figure 3 shows details of the Ga $3d$ and As $3d$ regions before and after 50 \AA of Fe_3O_4 growth. It can be seen that after Fe_3O_4 growth, features have appeared on either side of the bulk GaAs peak. There is a strong peak at lower binding energy consistent with the formation of Ga-Fe bonds¹⁶ and a higher binding energy peak that is probably due to the O $2s$ peak of the Fe_3O_4 spectrum [Fig. 2(c) shows where this peak is located relative to the rest of the spectrum]. There is also added spectral weight on the high bind-

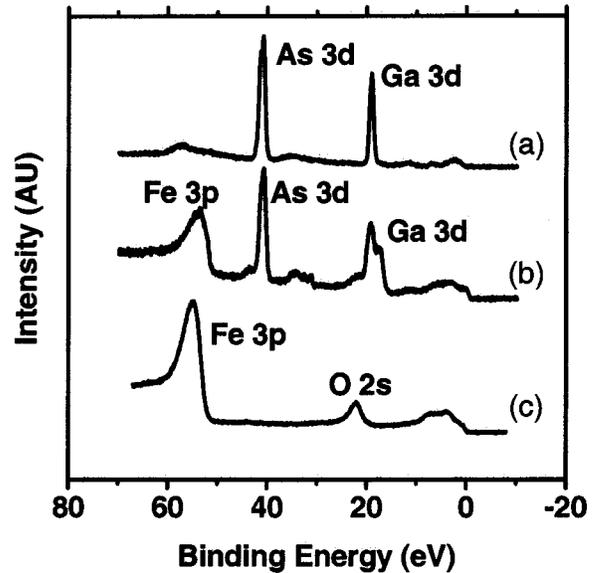


FIG. 2. XPS spectra of: (a) the epitaxial GaAs surface, (b) $\sim 50 \text{ \AA}$ Fe_3O_4 on GaAs, and (c) several hundred angstroms of Fe_3O_4 .

ing energy shoulder of the substrate peak most likely due to formation of gallium oxides. Compared to the Ga $3d$ spectrum, the As $3d$ spectrum shows only a slight change after growth of Fe_3O_4 . However the peak at higher binding energy is consistent with the formation of either As_2O_3 or As_2O_5 .¹⁷ The broadening of the substrate As $3d$ peak is too slight to draw any conclusions about other types of arsenic bonding.

While it is difficult to quantify what species have been created, it is clear that reactions have taken place at the interface involving all four constituent elements: gallium, arsenic, iron, and oxygen. This is probably what causes the

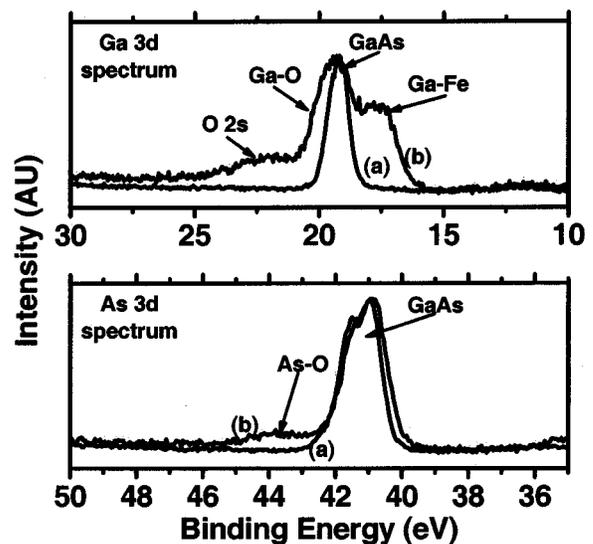


FIG. 3. Detailed XPS spectra of the Ga $3d$ and As $3d$ regions shown in Figs. 2(a) and 2(b). The data labeled (a) are from the epitaxial GaAs sample and the data labeled (b) are from the sample with 50 \AA of Fe_3O_4 . For data labeled (b), the abscissa has been shifted to account for band bending.

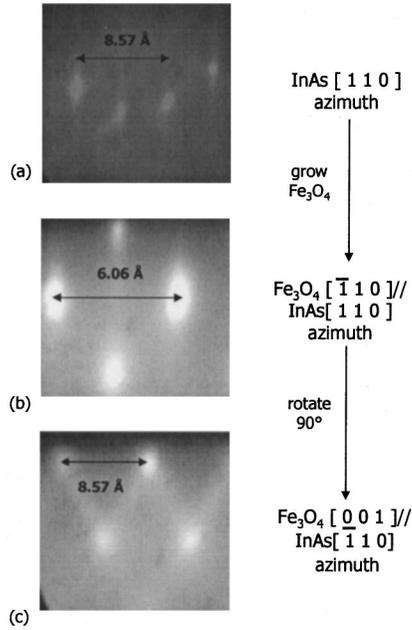


FIG. 4. RHEED images of Fe_3O_4 growth on InAs (001).

RHEED to show an amorphous background as the growth is initiated. However it seems that at the growth temperature it is favorable for the Fe_3O_4 to crystallize rather than remain amorphous so the growth proceeds in a polycrystalline phase. The reason for the preferential orientation is less clear. Perhaps $\langle 111 \rangle$ oriented crystallites are the most likely because the $\langle 111 \rangle$ direction has the highest areal atomic density in the Fe_3O_4 spinel crystal structure, thus having the highest probability of satisfying the completely random distribution of dangling bonds coming from the amorphous surface. However there is no preference for orientation in the plane of the substrate. The RHEED pattern shows streaks instead of rings as in randomly oriented polycrystalline material because only the periodicity of the $\{111\}$ surface will be visible. However since the crystallites are oriented randomly in the

plane of the substrate and are most likely small compared to the RHEED spot size there is complete azimuthal symmetry so the RHEED pattern does not change with substrate rotation.

B. Indium arsenide

In stark contrast to the GaAs case, Fe_3O_4 was found to grow epitaxially on InAs(001). The lattice constant of Fe_3O_4 ($\sim 8.4 \text{ \AA}$) is close to the spacing of InAs along a $\langle 110 \rangle$ direction ($\sqrt{2} \times 6.05 \text{ \AA} = 8.56 \text{ \AA}$), mismatched by about 2%. Hence there is some possibility of growth of Fe_3O_4 (001) on InAs (001), rotated by 45° . However RHEED patterns of the Fe_3O_4 films indicated that this was not the case. Figures 4(a) and 4(b) show RHEED images with the electron beam parallel to the $[110]$ azimuth of the InAs substrate before and after Fe_3O_4 growth. Figure 4(c) is an image of the Fe_3O_4 surface with the substrate rotated by 90° relative to Figs. 4(a) and 4(b) such that the electron beam is parallel to what was the $[\bar{1}10]$ azimuth of the InAs. The ratio of the streak spacing for the two different azimuths is exactly $\sqrt{2}$. One possible explanation for a difference in streak spacing of $\sqrt{2}$ for azimuths that are 90° apart is that the Fe_3O_4 is growing with a $\langle 110 \rangle$ direction parallel to the growth direction. As mentioned above, there is a match in the spacing of Fe_3O_4 along a $\langle 001 \rangle$ with InAs along a $\langle 110 \rangle$. Indeed it is observed that the streak spacings in Figs. 4(a) and 4(c) are nearly identical. Thus the Fe_3O_4 is growing with Fe_3O_4 (110)//InAs(001) and Fe_3O_4 $[\bar{1}10]$ //InAs[110]. Still, there is no lattice match in one of the two directions, which makes this crystallographic orientation highly unexpected. Perhaps this situation is similar to that of CeO_2 on silicon (001) where the orientation of the CeO_2 is dictated by oxygen sublattice interacting with the dangling bonds at the silicon surface.¹⁸ Figure 5 shows possible alignments of the oxygen sublattice of an unstrained layer of Fe_3O_4 on InAs for the three main faces of the spinel structure. The least distortion will be required to have the oxygens in the Fe_3O_4 $\{110\}$ face match up with the dangling bonds from the InAs.

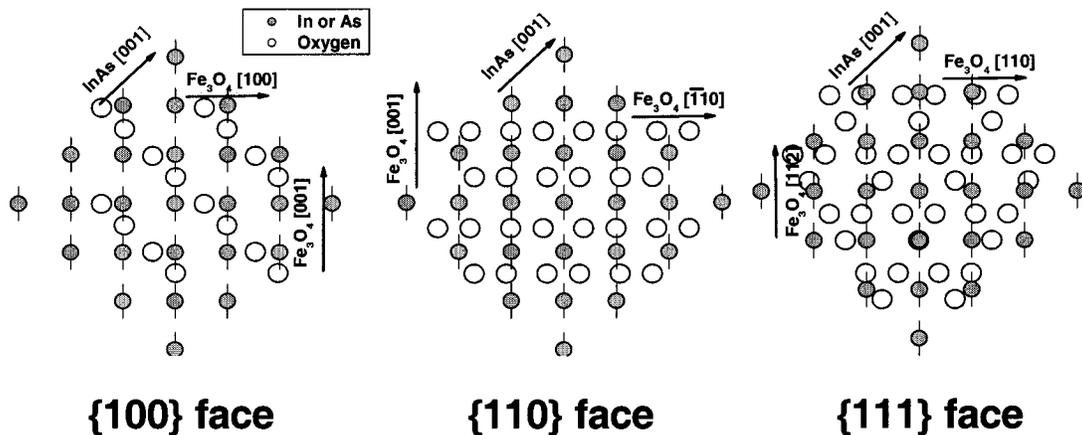


FIG. 5. Schematic representation of unstrained Fe_3O_4 $\{001\}$, $\{110\}$, and $\{111\}$ on InAs (001). The closed circles represent the top face of the zinc blende substrate, the open circles represent oxygens in the Fe_3O_4 lattice and the small lines represent dangling bonds from the substrate atoms.

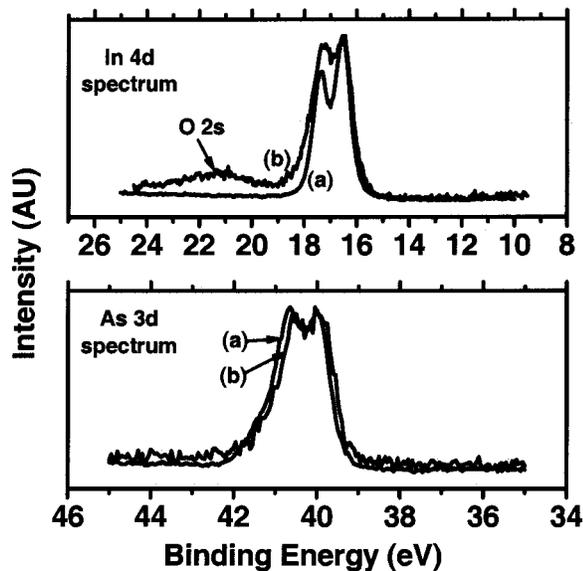


FIG. 6. Detailed XPS spectra of the $\text{In}4d$ and $\text{As}3d$ regions of the InAs sample. The data labeled (a) are from the epitaxial InAs sample and the data labeled (b) are from the sample with 50 \AA of Fe_3O_4 . For data labeled (b), the abscissa has been shifted to account for band bending.

Figure 6 shows detailed XPS spectra of the bare InAs surface and an Fe_3O_4 surface after about 50 \AA of Fe_3O_4 growth. As compared to the GaAs case, there is much less difference in the spectra before and after Fe_3O_4 deposition. In the $\text{In}4d$ spectrum one again can discern the small contribution from the $\text{O}2s$ peak at around 22 eV which comes from oxygen in the Fe_3O_4 . There is evidence of added spectral weight on the high binding energy side of the substrate $\text{In}4d$ peak but none on the low binding energy side. So perhaps there is a small amount of indium–oxygen bonding taking place. The $\text{As}3d$ peaks show almost no noticeable change. It is clear that there is far less formation of interfacial layers between the InAs and the Fe_3O_4 than there is between the GaAs and the Fe_3O_4 .

This lack of a significant interfacial layer, in addition to the fact that GaAs does not have the same lattice match with Fe_3O_4 as discussed above for InAs , probably contributes to the difference in crystallinity of the Fe_3O_4 layers between the GaAs and InAs cases.

IV. CONCLUSION

The nature of the growth of Fe_3O_4 on GaAs and InAs has been studied. On GaAs , Fe_3O_4 growth is polycrystalline but

oriented. All the crystallites orient themselves such that $\{111\}$ planes are parallel to the substrate. The interface between the two is probably amorphous due to interface reactions with the Fe_3O_4 involving both gallium and arsenic. On InAs , Fe_3O_4 growth is single crystalline with a $\langle 110 \rangle$ direction parallel to the growth direction and the Fe_3O_4 $[\bar{1}10]$ direction parallel to the InAs $[110]$. The interface between the two materials shows considerably less reactivity than in the GaAs case.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Defense Advanced Research Projects Agency under a grant monitored by Stuart Wolf and the Office of Naval Research under a grant monitored by Larry R. Cooper.

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