

TEM study of post-oxidised Fe films

D Gilks¹, J Sizeland¹, L Lari^{1,2}, C Kelley¹, SW Poon¹, S Thompson¹ and VK Lazarov¹

1. Department of Physics, University of York, Heslington, YO10 5DD, York, UK

2. The York JEOL Nanocentre, York Science Park, Heslington, YO10 5BR, York, UK

dg522@york.ac.uk

Keywords: Fe₃O₄, Iron Oxides, TEM, ordering

Bulk Fe₃O₄ is a predicted half-metal, with a gap in the density of states of majority carriers at the Fermi-level. This has led to a lot of research interest in this material as a potential spin injector. [1] However, most attempts to utilise Fe₃O₄ in spintronics devices have not been successful. One of the main obstacles for thin film Fe₃O₄ is to retain the desirable bulk magnetic properties despite the presence of structural defects in thin films. It has been shown that anti-phase domain boundaries [2] have a profound effect on magnetic and magnetotransport properties of thin film Fe₃O₄. For example thin films show negative magnetoresistance [3] and high saturation fields. Therefore understanding and controlling the defects in thin film Fe₃O₄ is crucial for application in spintronics devices. It has recently been reported that Fe₃O₄ films obtained by post-oxidation methods show bulk like properties [4]. These findings were explained as a lack of structural defects in such films. In order to confirm the origin of magnetic properties of post-oxidised films we undertake a (S)TEM study presented here.

Post-oxidised Fe films have been produced by molecular beam epitaxy of Fe on MgO(100). Post-oxidation was achieved by exposure to molecular oxygen at 300°C. Thin film samples have been mechanically polished and Ar⁺ milled to electron transparency to allow (S)TEM imaging using a double C_s corrected JEOL JEM-2200FS.

Figure 1 and 2 show cross-sectional TEM from post-oxidised films. Post-oxidation has produced atomically sharp interfaces between oxidised Fe layers and underlying Fe. The oxidation depth is well stabilized at ~3nm and is independent of the post-oxidation time. Self limiting oxidation has been documented on other systems [5], however the stability of this process and the atomically sharp interface between iron oxide and Fe observed in these films is of interest. This sharp interface suggests the oxidation is not being driven by O transport along defects or by preferable O transport along particular Fe planes since no regional oxidation depth variations are observed. Instead this suggests a pathway for oxygen-Fe reaction at the surface of the film requiring continuous diffusion of Fe at the surface.

The simple process of exposing Fe to O₂ leads to a range of possible iron oxide structures as oxidation levels increase. The TEM data (Figure 2) shows the inverse spinel structure of either Fe₃O₄ or γ-Fe₂O₃. However, diffraction results (Figure 3) indicate Fe₃O₄ film structure by the lack of super-reflections due to Fe vacancies in the γ-Fe₂O₃ phase. Figure 3 shows TEM and SAD from a 2 nm Fe post-oxidised film. The post-oxidation process fully oxidised the Fe ultrathin film. Moreover the epitaxial relationship between MgO and the Fe-oxide film is observed indicating Fe₃O₄ formation (Figure 3b).

The time series shows Fe₃O₄ film quality degrades as a result of extended oxidation time with a reduction in the octahedral (B)-site ordering (as indicated in Figure 2, and STEM result-not shown here). In addition we observe disordering at the tetrahedral Fe sites which underpin high quality Fe₃O₄ structure. This indicates the structural ordering of the Fe₃O₄ layers could be rather disordered.

The ability of iron oxide films to exist in similar structural phases makes the production of high quality Fe₃O₄ films a continuing challenge and has made experimental verification of thin-film half metallicity challenging. The results of these experiments suggest that Fe₃O₄ growth by means of post-oxidation will only be possible for films of ~3nm thickness. The bulk ordering of the Fe₃O₄ films is very sensitive to post-oxidation conditions and can be controlled by the O₂ exposure time.

In conclusion the post-oxidation technique can be utilised to produce various Fe-oxides films, though bulk like ordering remains a challenge in thin films.

References

- [1] A Yanase and K Siratori. J. Phys. Soc. Jpn. **53** (1984) 312-317
- [2] D T Margulies, F T Parker, M L Rudee *et Al.* Phys. Rev. Lett. **79** (1997) 5162-5165
- [3] M Ziese and H J Blythe. J. Phys.: Condens. Matter **12** (2000) 13-28
- [4] P K J Wong, W Zhang, X G Cui *et al.* Phys. Rev. B **81** (2010) 035419
- [5] N Cabrera and N F Mott. Rep. Prog. Phys. **12** (1949) 163

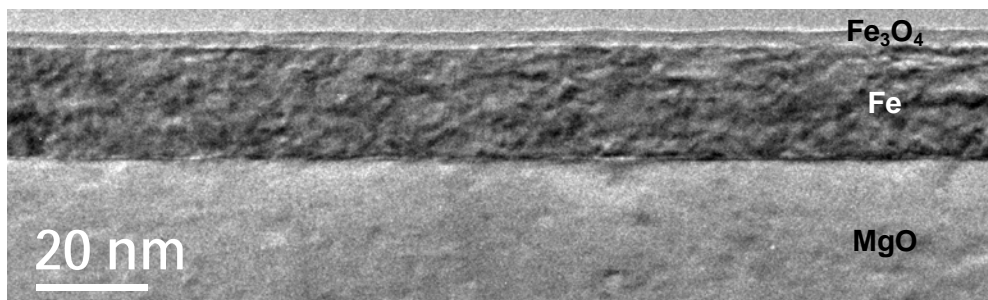


Figure 1. Self limiting oxidation; demonstrating a sharp interface between oxidised/non-oxidised regions in 45 minute post-oxidised Fe film.

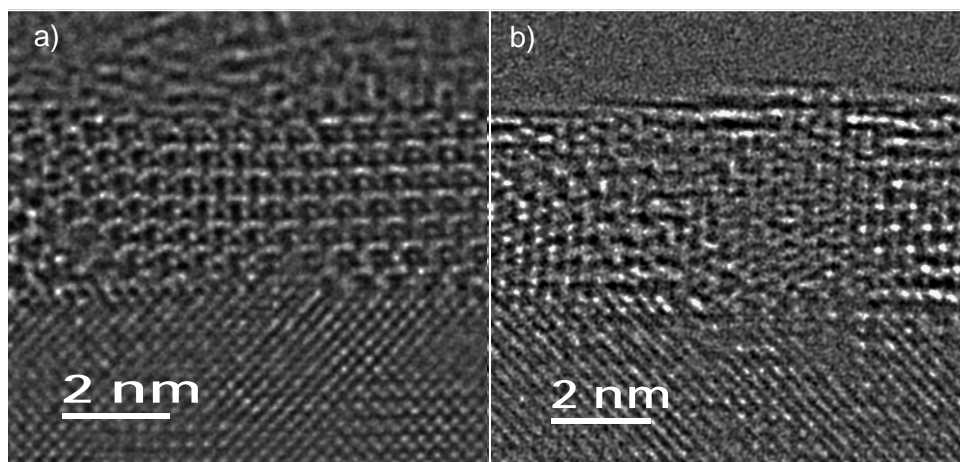


Figure 2. HRTEM of a) 9 minute post-oxidised Fe film and b) 45 minute post-oxidised Fe film show comparable oxidation depth of ~3 nm. Lower oxidation conditions (a) produce better ordered films.

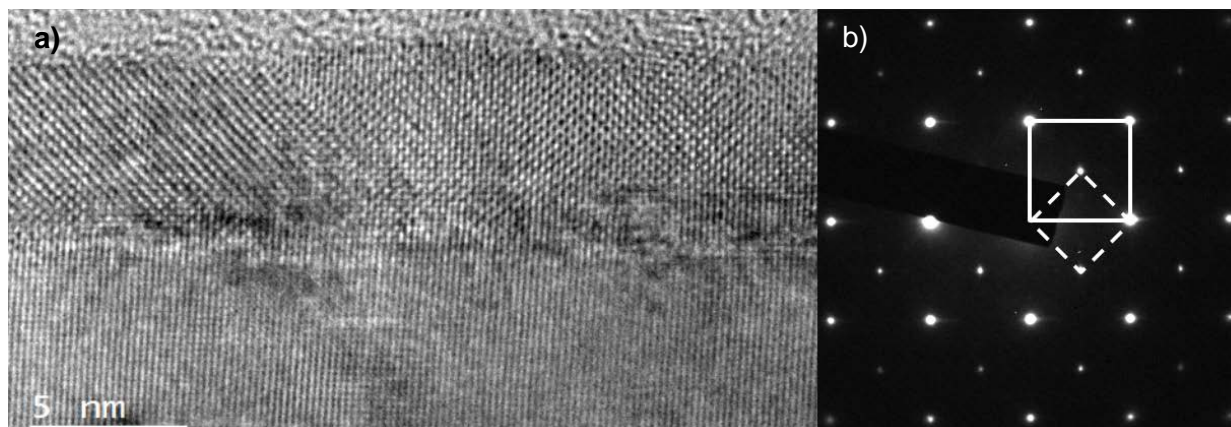


Figure 3. a) Fully post-oxidized ultra-thin film of Fe_3O_4 . b) SAD from $\text{Fe}_3\text{O}_4/\text{MgO}(100)$ shows the films substrate epitaxy and identifies Fe_3O_4