Journal of Physics: Conference Series

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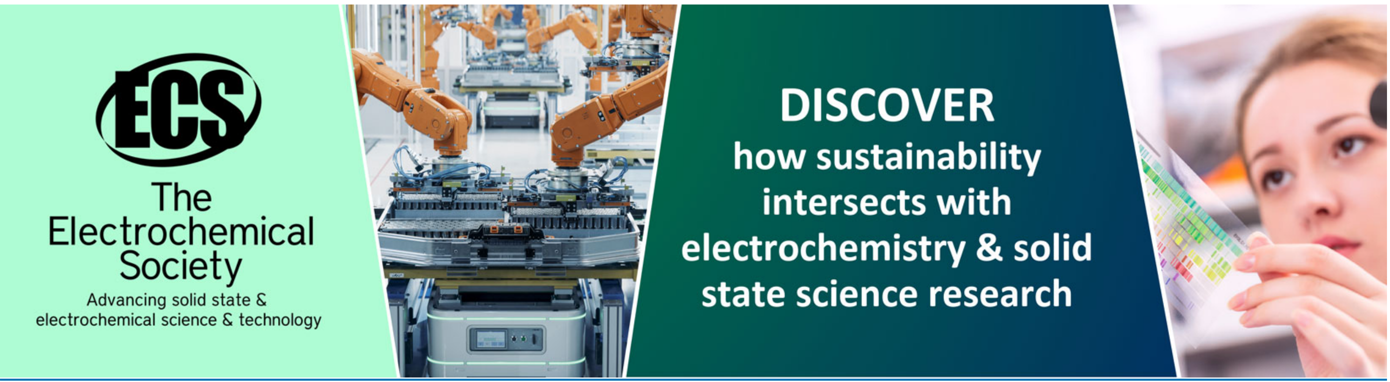
To cite this article: D Gilks *et al* 2014 *J. Phys.: Conf. Ser.* **522** 012036



A STEM study of twin defects in Fe_3O_4(111)/YZO(111)

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Abstract. We observe twin defects on both the (111) and (11-2) planes of thin film Fe_3O_4 using atomically resolved high angle annular dark field (HAADF) STEM imaging. These defects are significant for understanding the previously reported anomalous properties of Fe_3O_4 films as they generate non-bulk bonding configurations leading to non-bulk superexchange interactions in these regions.

1. Introduction

Bulk Fe_3O_4 (Figure 1) is a predicted half metal with a 100% spin polarisation at the Fermi level. [1, 2]. This bulk property makes thin film Fe_3O_4 of interest for future spintronics device applications [3-6]. However, structural defects including anti-phase boundaries (APB) in thin film Fe_3O_4 prevent the fabrication of films with bulk Fe_3O_4 properties. Thin film Fe_3O_4 exhibits negative magnetoresistance and does not magnetically saturate, e.g. bulk Fe_3O_4 shows no magneto-resistance and magnetically saturates at low applied fields. This makes a thorough understanding of defect formation in thin film Fe_3O_4 essential. The presence of APB defects is well documented in the literature [7-9]. In this paper we show that twin defects are also present in epitaxially grown single crystal films and their presence should be taken into account to fully understand the functional properties of Fe_3O_4 thin films. We observe twin defects in Fe_3O_4 films grown on Yttrium stabilized Zirconium Oxide (YZO). Currently twin defects in thin film Fe_3O_4 have

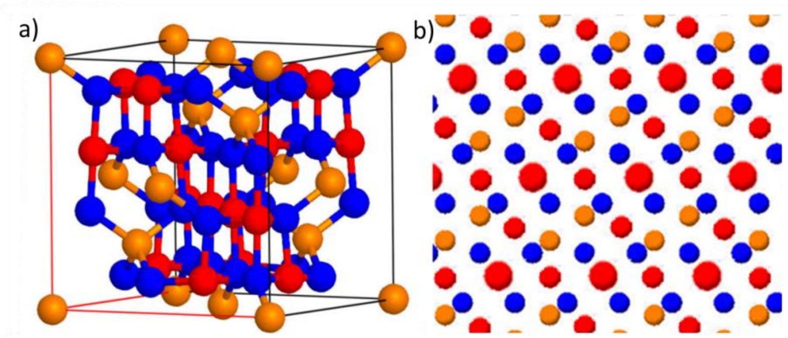

Figure 1. a) The unit cell of Fe_3O_4 consisting of 32 O atoms, 16 Fe in octahedral (B) positions and 8 Fe in tetrahedral positions (A). b) Fe_3O_4 viewed along the [1-10] direction showing all the atomic columns occupied by single atom types.

not received significant research attention, consequently the impact of twin defects on the overall magnetic and transport properties of thin film Fe_3O_4 are not well known at present.

2. Methods

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) data has been collected using a JEOL 2200FS microscope operating at 200kV and equipped with CEOS 3rd order imaging and probe aberration correctors. Diffraction patterns have been acquired using a JEOL 2011. Image simulations have been calculated using parallelised QSTEM image simulation software [10] with 30 thermal diffuse scattering iterations performed for each simulation. Aberration coefficients values used for the simulations were C_s(1.1 μm), C_5 (1.76 mm) and C_c (1.6 mm) respectively, as measured by the CEOS corrector software before HAADF image acquisition. Fe_3O_4 films have been grown using PLD methods with a KrF excimer laser incident on a Fe_3O_4 target, films were grown at 300 ˚C in an oxygen partial pressure of 2×10^{-4} Pa followed by high temperature post-annealing at 1100˚C in a CO/CO_2 atmosphere as discussed elsewhere [11]. TEM samples have been produced by mechanical thinning and low angle argon ion milling to electron transparency following the protocol described in [12].

3. Results and Discussion

The annealed films show atomically sharp film/substrate interfaces and uniform film thickness across the samples as shown in Figure 2. We find two types of twin defects in these films. The first type of twin defect propagates in the film growth direction from the film/substrate interface to the film surface (Figure 3). These defects are not seen to nucleate or discontinue within the film, nor are they seen to deviate from the single (11-2) planes on which they are located. The second type of twin defect is perpendicular to the growth direction on a (111) twin-plane, Figure 4; as the first type of defects they are also atomically sharp.

In the (11-2) twins, we observe defects originating from bunched step edges in the YZO substrates indicating that surface steps could be potential twin nucleation sites. We have also observed that the twins are highly mobile whilst being annealed at 1100˚C, as their density drops considerably as a result of the annealing process. From this it is unclear whether the twin defects nucleate as a result of the substrate step edges, or migration of twin defects during the annealing procedure pins them to the step edges. By studying a series of films with varied annealing times (or temperatures) and the resultant defect density and morphology it should be possible to identify a relationship between initial deposition characteristics in the films and the evolution of these defects during the annealing procedure.

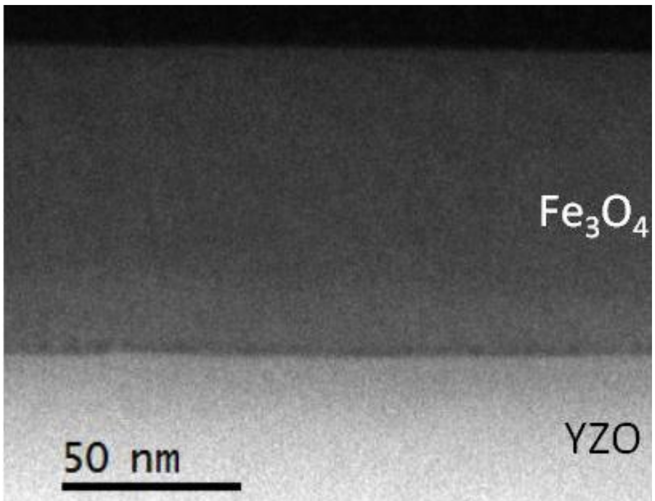

Figure 2. HAADF-STEM image of a Fe_3O_4 film grown on YZO substrate.

Several scenarios are possible to create twin defects in Fe_3O_4 grown on YZO. The underlying stacking sequence of the YZO substrate should 'direct' the stacking of the Fe_3O_4 film and give a preferred stacking sequence in the deposited film, however, in these films it seems that the stacking sequence through the interface is often not maintained. This suggests that stacking faults at the Fe_3O_4/YZO interface are either of low formation energy or different surface termination of YZO can provide growth templates for different atomic films-substrate interfaces which ultimately result in twin-related stacking sequence that propagate as the films is grown.

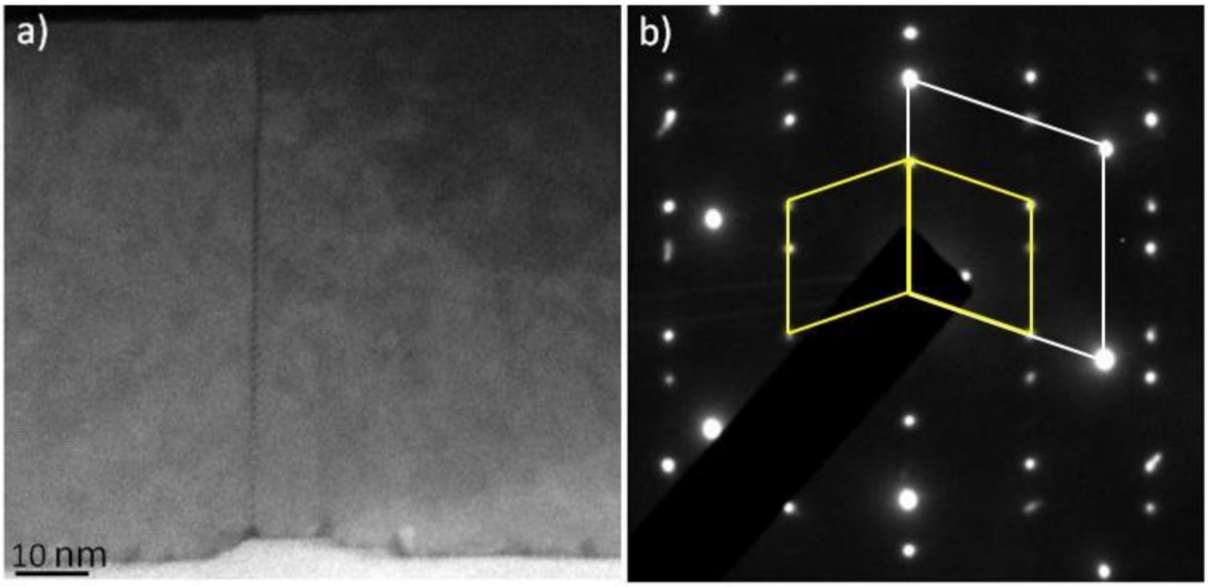

Figure 3. HAADF-STEM and diffraction patterns of a twin defect in Fe_3O_4 imaged in the [1-10] zone axis. a) Shows a twin running vertically from a stepped region of the film/substrate interface to the film surface. b) Shows the overlaid diffraction patterns of the YZO substrate (white/largest rhombus) and two Fe_3O_4 diffraction patterns (two yellow/smaller rhombuses) the twinned structure can be identified through the mirror symmetry of the Fe_3O_4 diffraction spots from left to right in the pattern.

The twin structures we observe running perpendicular to the growth direction demonstrate that Fe_3O_4 can form twins even when the underlying stacking sequence of well ordered Fe_3O_4 is already present in the film. This indicates the formation energy of twins defects on the (111) plane of Fe_3O_4 is low. In the twin defects we have observed the octahedrally co-ordinated Fe_B plane appears to form the twin with structural symmetry about this plane.

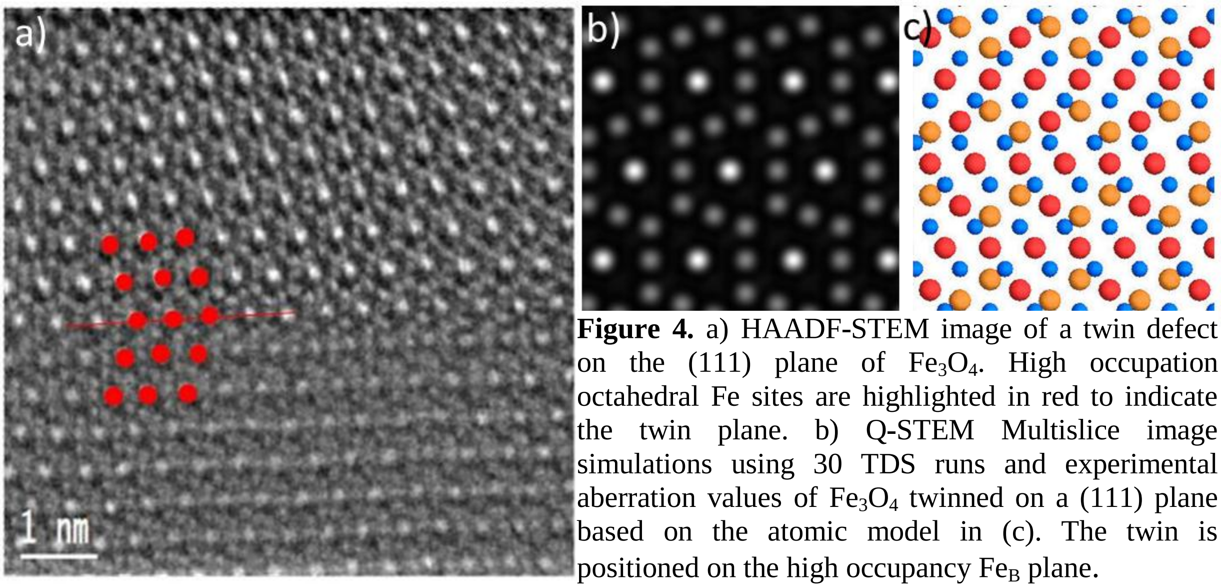

Figure 4. a) HAADF-STEM image of a twin defect on the (111) plane of Fe_3O_4. High occupation octahedral Fe sites are highlighted in red to indicate the twin plane. b) Q-STEM Multislice image simulations using 30 TDS runs and experimental aberration values of Fe_3O_4 twinned on a (111) plane based on the atomic model in (c). The twin is positioned on the high occupancy Fe_B plane.

Unlike in the (11-2) plane defect, this (111) twin does not lead to a heavily relaxed interfacial structure, rather the Fe_3O_4 structure simply continues but with an inversion of the stacking sequence across the twin boundary. From the Figure 4 it can be observed that the octahedral Fe-O-Fe bond angles are significantly increased compared to 90˚ bonds in bulk Fe_3O_4. This is of importance as the bond angles define the superexchange interactions between Fe-O-Fe
sites. As bond angles between Fe sites increase the superexchange interaction become strongly anti-ferromagnetic.

4. Conclusions

We show direct evidence of two distinct styles of twin boundaries in thin film Fe_3O_4. While the origin of the vertical (11-2) twin defects could be influenced by several mechanisms, the formation of perpendicular (111) twins is most likely driving by their low formation energy. The effect of twin structural defects on the magnetic and magneto-transport properties of magnetite thin films is still to be explored. These properties will be studied using atomistic magnetic modelling and *ab. Initio* structural refinement and electronic structure calculations. This will allow a comparison between simulated magnetisation properties and structure with experimental in-plane magnetisation and transport measurements.

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