ESRF	**Experiment title:** SURFACE PHASE DIAGRAM OF Fe_2O_3(0001) VERSUS Fe_3O_4(111) WITH RESPECT TO OXYGEN PARTIAL PRESSURE AND TEMPERATURE.	**Experiment number**: SI-1144
Beamline: ID03	**Date of experiment**: from: 29.062005-8:00 to: 04.07.2005-8:00	**Date of report**: 19.07.2005
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Report:

In the CEA laboratories the elaboration and the characterization of tunnel junctions by atomic oxygen assisted molecular beam epitaxy (OA-MBE) is a major topic [1-3] as well as the elaboration of spin valves on oxide antiferromagnets [4]. Different iron oxide compositions, mainly Fe_2O_3 and Fe_3O_4, are obtained by varying the oxygen partial pressure and temperature during the growth of the layers. Unfortunately, during elaboration the oxide layers often transform partially or totally from one phase to another making the thickness and preparation control extremely difficult. Understanding this phenomenon on the complete structure is an almost impossible task and a more fundamental approach was required.

The present experiment aimed at describing the transformation rate and reversibility with the oxygen partial pressure and temperature of hematite (α-Fe_2O_3) versus magnetite (Fe_3O_4) since the description of the transformation rate and reversibility with the oxygen partial pressure and temperature are almost missing. We used grazing incidence surface X-ray diffraction to tackle these important parameters.

We have investigated a 20 nm thick α-Fe_2O_3 layer elaborated by OA-MBE on a α-Al_2O_3(0001) substrate. The sapphire substrate peaks were used to index the reciprocal space. The initial hematite layer has been thoroughly investigated by in plane radial scans along the major directions, large azimuthal scans to check the layer symmetry, rocking scans through Bragg peaks and some maps at variable L (out of plane index) to investigate the out of plane structure. The layer was found, as expected, of single phase with a 6-fold symmetry and the crystalline quality could be improved through an anneal at 530°C that reduced the in-plane mosaic spread from 2.45° to 0.65° with a domain size of 80 nm.

In order to produce the reduction of hematite the temperature was raised by steps of typically 30°C which required frequent sample re-alignment because of the temperature driven misalignments. The transformation in the surface region starts at temperatures as low as 384°C and is found progressive: further increase of the temperature increases the relative

fraction of magnetite with respect to hematite (see figure 1). The phase change was monitored a constant temperature during several hours and found mainly limited by kinetic effects and thus fully out of thermodynamic equilibrium. The layer formed after anneal at about 500°C was investigated in detail. Magnetite appears in two forms: an epitaxial one that has the same mosaic spread than hematite and a polycrystalline one (that could be evidenced by out of plane mapping of the reciprocal space). Moreover variable incidence scans showed that the magnetite layer is located close to the surface only.

The Fe_3O_4 layer was then oxidized at 420°C under oxygen pressures ranging from 10^{-7} mbar to 1 bar by steps of a decade of mbar. A large fraction of the layer transforms back to α-Fe_2O_3 below 3 mbar oxygen (see figure 2). The remaining fraction of the Fe_3O_4 layer transforms into γ-Fe_2O_3. From this situation another Fe_3O_4 layer could be produced. Unfortunately, attempts to oxidize this layer into α-Fe_2O_3 up to 1 bar O_2 pressure failed because of the occurrence of γ-Fe_2O_3 that appeared very stable. Cycling through successive reducing and oxidizing conditions appeared thus impossible.

In summary the experiment was very fruitful and revealed many important structural parameters of our layers. Moreover the transformation of hematite to magnetite is found progressive and irreversible because of the occurrence of γ-Fe_2O_3 (which should be thermodynamically metastable). It is an important and unforeseeable result. We have shown that the temperature and oxygen pressure ranges accessible on ID03 are very well suited for the present topic. However, many questions about this most interesting phase transformation remain. The problem appears more complex because of the additional occurrence of the γ-Fe_2O_3 phase which could only be evidenced through the proposed method. A continuation proposal will thus be necessary to establish the full phase diagram.

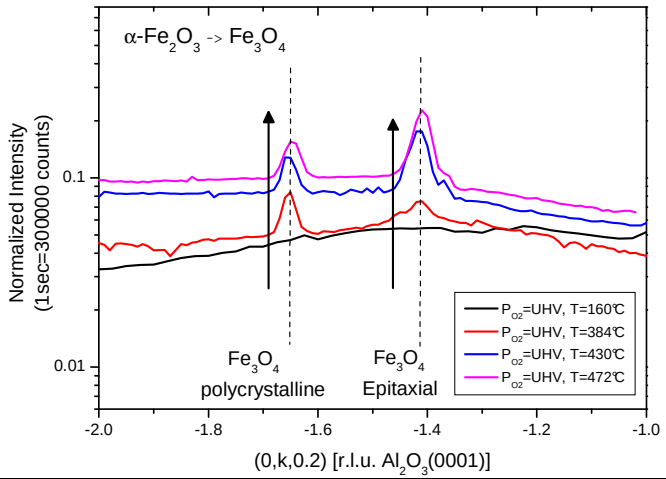

Figure 1:
Reduction of α-Fe_2O_3 to Fe_3O_4 as measured by GIXD showing evidence of epitaxial Fe_3O_4 (at (0,-1.4,0.2)) mixed up with polycrystalline Fe_3O_4 (at (0,-1.6,0.2)).

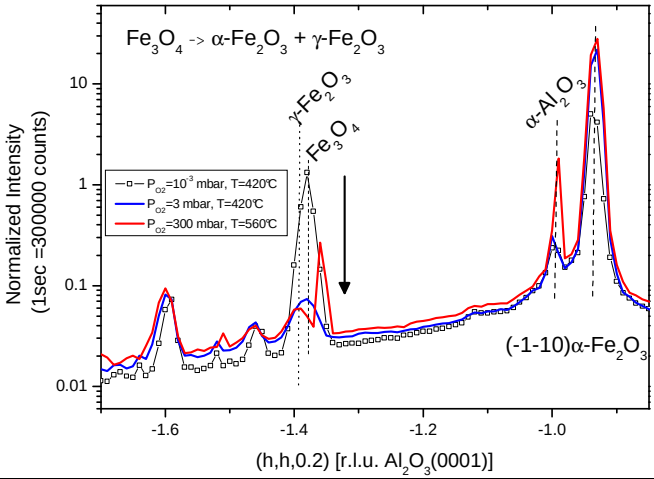

Figure 2:
Backward oxidation of Fe_3O_4 embedded in α-Fe_2O_3.After a first oxidation step yielding α-Fe_2O_3 a fraction of the layer transforms into γ-Fe_2O_3.

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[4] C. Mocuta, A. Barbier, S. Lafaye, P. Bayle-Guillemaud, M.Panabière, Phys. Rev. B **68**, 014416 (2003).