EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

## Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

### Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

## Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| ESRF | **Experiment title:** A SPECTROSCOPIC AND SURFACE DIFRACTION STUDY OF MAGNETITE/ HEMATITE EPITAXIAL BILAYERS | **Experiment number**: 25-02-981 |
|---|---|---|
| **Beamline**: | **Date of experiment**: from: April 21st 2021 to: April 26th 2021 | **Date of report**: February 26th 2022 |
| **Shifts:** | **Local contact(s)**: Jesus López Sánchez, Juan Rubio Zuazo | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

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**Report:**


**Abstract:**

Low energy ion bombardment (LEIB) can be used on single-crystalline oxide thin films to produce epitaxial layers of the corresponding suboxide. There have been successful examples using LEIB to obtain titanium oxide ($TiO(001)/TiO_2(110)$) and iron oxide ($Fe_3O_4(111)/\alpha\text{-}Fe_2O_3(0001)/Au(111)$) epitaxial heterostructures. Based on these previous works, in beamtime 25-02-981 we have carried out an X-ray spectroscopic and X-ray diffraction investigation of the magnetite/hematite bilayer, which is an ideal system to study magnetic exchange effects at the interface. The beamtime has focused on the chemical state and structure of the system, using Surface X-ray Diffraction (SXRD), X-ray Reflectometry (XRR), X-ray Photoemission Spectroscopy (XPS) and Hard X-ray Photoelectron Spectroscopy (HAXPES). The aim of this work has been also to obtain microscopic information on the as-grown system and on the evolution of the system during a high temperature annealing of the bilayers.


**Experimental details and Results:**

Due to COVID-19, this beamtime was not presential, and we had to adapt to the special circumstances. The initial plan was to take to the beamline a single crystal with a pristine epitaxial hematite thin film grown on it, and to monitor the chemical and structural evolution as it was modified in-situ by an ion beam. This plan required the presence of several external researchers, since the experiment was not stardard (it required the installation and continuous control of an ion gun). Due to its complexity and the lack of external researchers in the beamline (motivated by COVID-19) we decided to send the samples already modified from our laboratory in Madrid.

All the samples were grown in the PLUO (in-house lab) of beamline BM-25 SpLine by Pulsed Laser Deposition (PLD). Under the proper conditions, epitaxial $\alpha\text{-}Fe_2O_3(0001)/SrTiO_3(111)$ films were grown, as monitored by RHEED and LEED.

The samples were then sent to Madrid for the ion-beam modification, which was done with Ar at 1 keV. Previous to the ion-bombardment, the samples were annealed in oxygen to clean the surface and see the LEED pattern

before and after the ion bomardment. Two samples showed, after low and medium ion doses, the diffuse LEED pattern of hematite. 2 samples showed, after high and very high ion doses, the diffuse LEED pattern of magnetite. Al the samples were then sent back to SpLine for further anaysis during the beamtime.
So, there have been 4 samples under study:
#1 α-$Fe_2O_3$(0001)/$SrTiO_3$(111), ion bombarded (low dose) (hematite in the surface, according to LEED)
#2 α-$Fe_2O_3$(0001)/$SrTiO_3$(111), ion bombarded (medium dose) (hematite in the surface, according to LEED)
#3 α-$Fe_2O_3$(0001)/$SrTiO_3$(111), ion bombarded (high dose) (magnetite in the surface, according to LEED)
#4 α-$Fe_2O_3$(0001)/$SrTiO_3$(111), ion bombarded (very high dose) (magnetite in the surface, according to LEED)

The X-ray Reflectivity (XRR) curves show the typical oscillations of a thin film with well defined interfaces and with a thickness around 25 nm.
The scans in reciprocal space shows the multiple reflections of the different parts of the system (Figure 1).

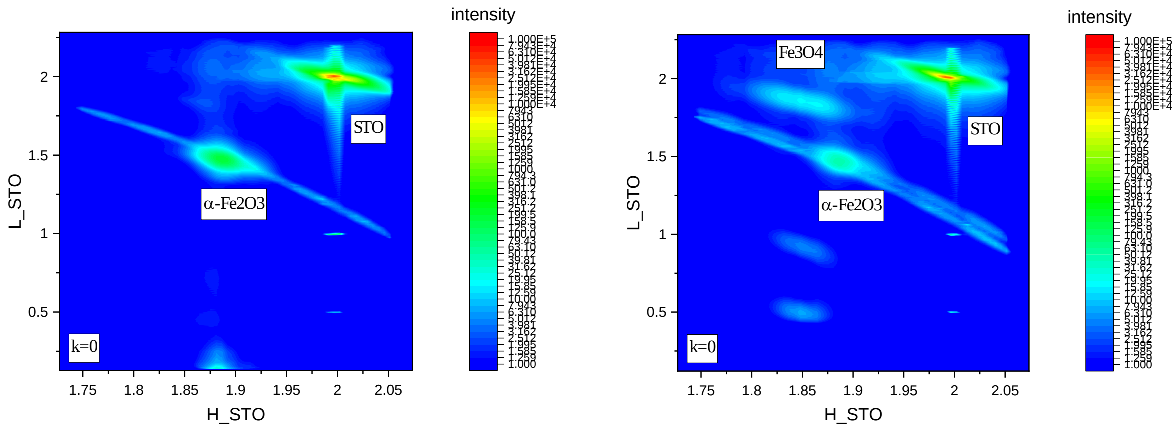


Figure 1: Examples of HL scans showing the reflections of samples #2 (left) and #3 (right). Sample #3 (right) has received a high ion dose and it is formed by a magnetite/hematite bilayer, as shown by the presence of the (2,2) spot of the substrate (STO(111)), a rather elongated and diffuse spot of magnetite (just below the "Fe3O4" mark) and a less elongated reflection of hematite (just above the "Fe2O3" mark). On the contrary, sample #2 (left) has received a medium ion dose which has not been enough to clearly form magnetite. Just a tiny reflection is barely visible above the intense hematite reflection (around L=1.8).

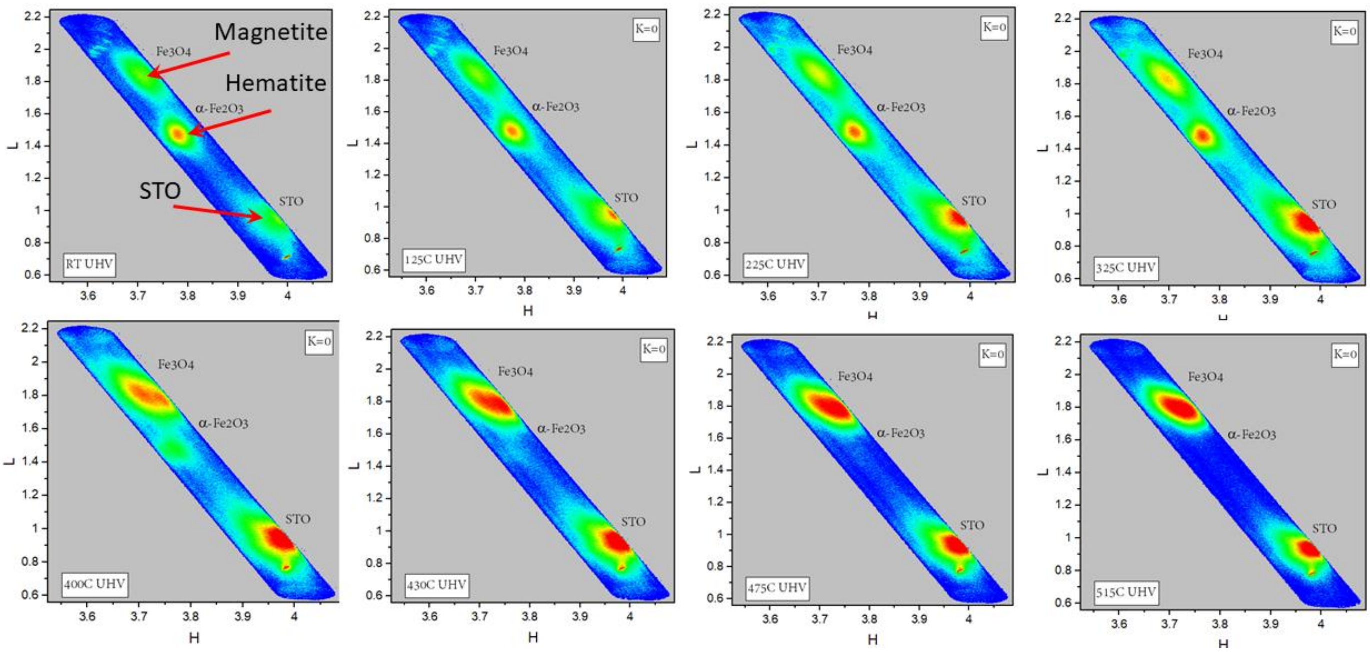


Figure 2: Examples of HL scans showing, in sample #3, the evolution in UHV of the reflections of the substrate (STO), of hematite and of magnetite during a high temperature annealing. The temperatures, from left to right and from top to bottom, are RT, 125 ºC, 225 ºC, 325 ºC, 400 ºC, 430 ºC, 475 ºC and 515 ºC. Around 430 ºC, hematite has dissapeared, driven by its chemical reduction. The continuous loss of oxygen transforms the initial bilayer into a single well-ordered magnetite thin film.

The annealings of the bilayers, both in UHV (see Figure 2) and in a background oxygen pressure of $5x10^{-6}$ mbar, showed the irreversible reduction of the hematite into magnetite, yielding a single magnetite thin film. This result is rather interesnting, and somehow, unexpected.

Also, XPS and HAXPES photoemission spectra of the different samples show the different components of the iron oxides ($Fe^{3+}$, $Fe^{2+}$, magnetite and/or hematite) depending on the specific sample, excitation energy (depth sensitivity) or annealing procedures.

**Conclusions and future work:**

Despite the special circumstances, the results of this beamtime have been very positive. We have identified reflections, degree of epitaxial order, crystalline order, domain size, thicknesses... of the different samples. Furthermore, we have identified that a high temperature annealing, in UHV or HV with a slight presence of oxygen gas, does not avoid the chemical reduction of the hematite and its transformation into magnetite. We have now more control on the system, which will allow us to further continue its investigation (mainly related to its magnetic properties).