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

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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:** Nanophase formation in Fe-implanted SrTiO3	**Experiment number**: HC 1012
Beamline: BM20B	**Date of experiment**: from: 30 October 2013 to: 03 November 2013	**Date of report**: 25-08-2014
Shifts: 12	**Local contact(s)**: Carsten Baehtz	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* Dr. Lino Miguel da Costa Pereira

Prof. Dr. Kristiaan Temst

Prof. Dr. André Vantomme

* Dr. Enric Menéndez Dalmau (experimentalist, not applicant)

Goal:

The experiment consisted of determining if and which secondary phases where formed in Fe-implanted $SrTiO_3$ for the implantation and annealing conditions that had been previously observed to result in ferromagnetic behavior (as well as for the annealing conditions that rendered the ferromagnetic samples non-ferromagnetic).

Samples:

sample ID	implanted element	ion fluence (at. /cm^2)	nominal concentration (%)	preceeding annealing step	annealing temperature ºC	annealing environment (mbar)	ramping protocol identifier
S1	-	-	-	-	-	-	-
S2	Fe	5E15	8	-	900	vacuum (~1E-6)	"fast"
S3	Fe	5E15	8	-	900	vacuum (~1E-6)	"slow"
S4	Fe	1E16	16	-	900	vacuum (~1E-6)	"fast"
S5	Fe	1E16	16	-	900	vacuum (~1E-6)	"slow"
S6	Fe	1E16	16	-	900	vacuum (~1E-10)	"fast"
S7	Fe	1.5E16	24	-	900	vacuum (~1E-6)	"fast"
S8	Fe	1.5E16	24	-	900	vacuum (~1E-6)	"slow"
S9	Fe	5E15	8	S2	1000	air	"fast"
S10	Fe	1E16	16	S4	1000	air	"fast"
S11	Fe	1E16	16	S5	1000	air	"fast"
S12	Fe	1E16	16	S6	1000	air	"fast"
S13	Fe	1.5E16	24	S7	1000	air	"fast"
S14	Fe	1.5E16	24	S8	1000	air	"fast"
S15	Co	1E16	16	-	900	vacuum (~1E-6)	"fast"

The samples (listed in the table above) consisted of commercial $SrTiO_3$ single-crystalline substrates, implanted with Fe (the implanted layer corresponds to the top ~50 nm) to three different nominal Fe concentrations *x* (8%, 16%, and 24%) corresponding to implanted fluences (areal densities) of 5×10^{15}, 1×10^{16} and 1.5×10^{16} at./cm^2, respectively. These concentrations were selected based on SQUID and Mossbauer spectroscopy measurements showing that: samples with x = 8% and x = 16% are ferromagnetic (after 700-900ºC annealing in vacuum ~1×10^{-6} mbar) but no magnetic secondary phases could be identified; samples with x = 24% show a distinct ferromagnetic behavior and metallic α-Fe could be identified by Mossbauer spectroscopy. The observed ferromagnetic behavior was found to depend on the temperature ramping rate, which we isolated in two separate regimes ("fast" and "slow" are identifiers for two distinct multistep annealing procedures). In all cases, no ferromagnetism was observed after annealing in air at 1000ºC. For comparison, some aditional samples were prepared: S6 (16% Fe) was annealed in ultra-high vacuum (~1×10^{-10} mbar); S15 was implanted with 16% Co.

Results:

sample ID	phases identified by GIXRD	phases identified by symmetric 2θ/ω scans
S1	-	-
S2	-	-
S3	F1	F5, F7
S4	-	F2
S5	F1	F5, F7
S6	-	-
S7	-	F2, F3
S8	F1	F2, F3, F4, F6
S9	-	-
S10	-	F5
S11	F1	F5, F7
S12	-	-
S13	-	F5
S14	F1	F4, F5, F6
S15	-	F8

phase ID	coumpound	crystal structure	orientation relation with substrate
F1	$SrTiO_3$	perovskite	policrystalline
F2	Fe	fcc (γ)	epitaxial
F3	Fe	bcc (α)	preferential
F4	Fe_3O_4	spinel	preferential
F5	Fe_2O_3	α/γ?	preferential
F6	FeO	cubic	preferential
F7	$SrFeO_2$	P4/mmm	preferential
F8	Co	fcc	epitaxial

In general, the observed ferromagnetism could be correlated with the presence of Fe-rich ferromagnetic or ferrimagnetic secondary phases (cf. tables above). The change in magnetic behavior upon air annealing could be correlated with the oxidation of metallic phases or the change in O-stoichiometry of already oxide phases. "Slow" annealing procedures were found to result in policrystalline regrowth of the $SrTiO_3$ implanted layer (amorphized upon implantation), contrary to "fast" annealing procedures which lead to a perfectly epitaxial recrystallization. This was found to affect very strongly the phase segregation behavior, as the grain boundaries in "slow" annealed samples appear to act as nucleation centers for additional oxide phases (e.g. $SrFeO_2$). We are currently preparting a manuscript on the identfication of these different phases, combining this SR-XRD data with complementary structural and magnetic characterization (Rutherford backscattering and channeling spectroscopy, SQUID magnetometry and Mossbauer spectrosocopy). We are also preparing proposals for SR-XRD experiments at BM20B and EXAFS experiments at BM26A (DUBBLE CRG) to further study two specidifc phases (γ-Fe and $SrFeO_2$) which are anomalous both structuraly and magnetically, and ideal model systems in which to investigate magneto-structural coupling.