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:** Conduction and local breakdown mechanisms in conductive channels at interfaces	**Experiment number**: HC-4965
Beamline: ID-01	**Date of experiment**: from: 22/02/2023 to: 28/02/2023	**Date of report**: 21/03/2023
Shifts: 18	**Local contact(s)**: T. Schülli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
Cristian MOCUTA (*, remote), Synchrotron SOLEIL
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Report:
The aim of this project was to investigate the conduction and breakdown mechanisms occurring in local conduction channels of nanocircuits created by a polarized near field tip at otherwise insulating multiferroic spinel MFe_2O_4 (MFO, M = Co, Ni, Mn and Fe) ferrites / epitaxial $BaTiO_3$(001) (BTO) interfaces. Using local probe X-ray diffraction, we aimed to determine:
(i) the changes on the crystalline structure (phase, lattice parameters) following modifications induced by Piezo Force Microscopy (PFM) writing (resistivity changes) and junctions poling, since crystalline phase change is a pre-requisite for resistance changes in our systems;
(ii) the location of the breakdown and in particular the role of defects like edges between regions of different compositions during breakdown, and
(iii) interface effects on the PFM written zone crossing interfaces between 2 different materials.

We considered 2 types of epitaxial heterostructures, namely Fe_2O_3 / $BaTiO_3$ and $NiFe_2O_4$ / $BaTiO_3$, both grown on Nb (1%) doped $SrTiO_3$(001) single crystalline substrates. These interfaces correspond to 2 extreme situations: (1) $NiFe_2O_4$ being very difficult to reduce (3-8% resistance change) and (2) Fe_2O_3 that transforms partially into Fe_3O_4 which is a conductive semi-metal (75-99% resistance change). All layers were grown by Atomic Oxygen assisted Molecular Beam Epitaxy at CEA/Saclay and were single crystalline and well-ordered (Fig. 1a). Photolithography (Fig. 1b, 1c) was used to produce gold leads with different sizes of rectangular openings (1-5 µm). Chemical interface reduction between the leads was realized by positively polarized PFM tip (Fig. 1c).

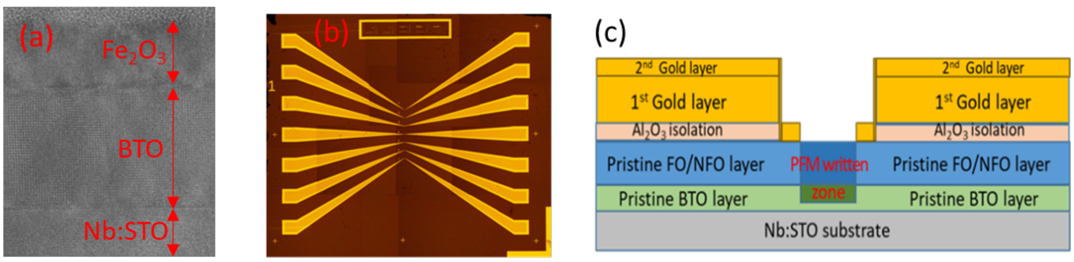

Fig.1 (a) Typical HRTEM image of Fe2O3/BTO/Nb:STO epitaxial heterostructures. (b) typical sample after lithography containing 7 junctions. (c) illustration of a typical stack realized by lithography to create PFM written junctions.

For the *in-situ* current injection implementation on ID-01 beamline, we built a dedicated montage setup that allowed current injection in the sub-µm scale junction, as well as a facile and efficient switch of samples (5-15 mins). All beamline staff, especially the local contact and beamline engineer, helped us adapt and realize the dedicated sample montage setup.

For the diffraction measurement, a 10 keV monochromatic X-ray beam was focused using a Fresnel Zone Plate (FZP) to about 130 nm × 80 nm (H × V). The spot was ensuring the lateral resolution of the measurement. Using the k-map approach, XY maps consisting of ~ 100×70 points in X and Y direction were measured for different angular positioning of the detector and incident angles (40 – 60 combinations), thus resulting in the possibility to reconstruct, at each lateral position, a 3D-Reciprocal Space Map (RSM). These measurements were then performed for the pristine state, several values of the injected current, and up to the complete breakdown of the junction. This allows for a quantitative characterization (extract meaningful parameters as diffraction peak area, peak position, full width at half maximum FWHM, film thickness, etc.) of the changes and quantify the modifications upon the different injected current in the junctions, up to complete breakdown.

Totally 4 junctions have been investigated. We started with an already broken-down NFO/BTO junction, following an *operando* EXAFS analysis at SOLEIL-LUCIA beamline (Fig. 2a, 2b). We could thus complete the chemistry change (from EXAFS) with crystal structure information. Upon extraction and preliminary processing of data, we identify a clear contrast between two electrodes as well as hot points along the edges of the electrode in the map illustrating the position of BTO diffraction peak (Fig. 2c), signifying a perpendicularly compressed (in-plane expanded) lattice in the top electrode. In the colormap showing the integrated area of the BTO peak, very clear contrast in the PFM written conduction channel is evidenced (Fig. 2d), which indicates the change of crystalline quality of the BTO triggered by PFM writing or breakdown injection.

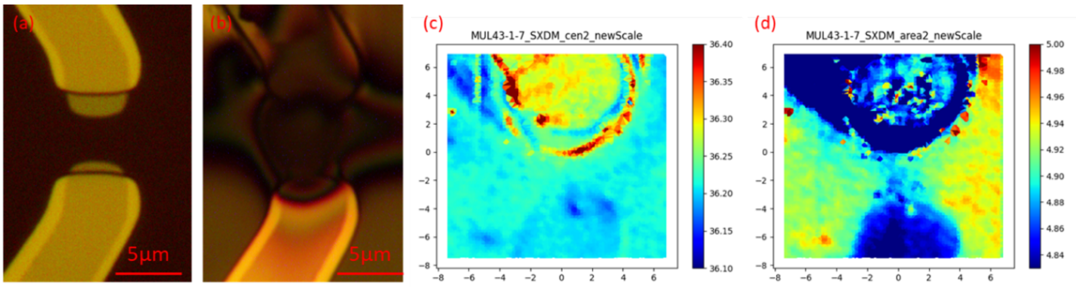

Fig.2 Optical microscope image of NFO/BTO junction in pristine state (a) and in breakdown state (b); colormaps illustrating the center (c) and area (d) of 400 BTO diffraction peak extracted by gaussian fit of 00L curves.

We then carried out more challenging *in-situ* current injection experiments on 3 pristine junctions. Two of them are made of Fe_2O_3/BTO interfaces and poling was realized in different directions, the last one is a NFO/BTO interface with the poling in positive direction only. K-map with reduced angular positions at ferrite and BTO peaks were used to evaluate the junction condition and hence optimize the current steps. All the 3 junctions were thus successfully characterized in pristine, working (increasing current – up to a dozen of situations) and breakdown states, showing both common but also some unique behaviors during the evolution. Here, we illustrate the diffraction data of Fe_2O_3/BTO junction with positive poling (Fig. 3a). In the pristine condition, we can see weak reduced crystalline quality (Fig. 3b) and compressed lattice parameter c (not illustrated) inside the PFM-written channel. The evolution of the junction under current flow manifests not only as the degradation of the crystalline quality in the part where current flows in the lead and the channel but also as the appearance of islands of low crystalline quality near the junction (Fig. 3b, 3c, 3d).

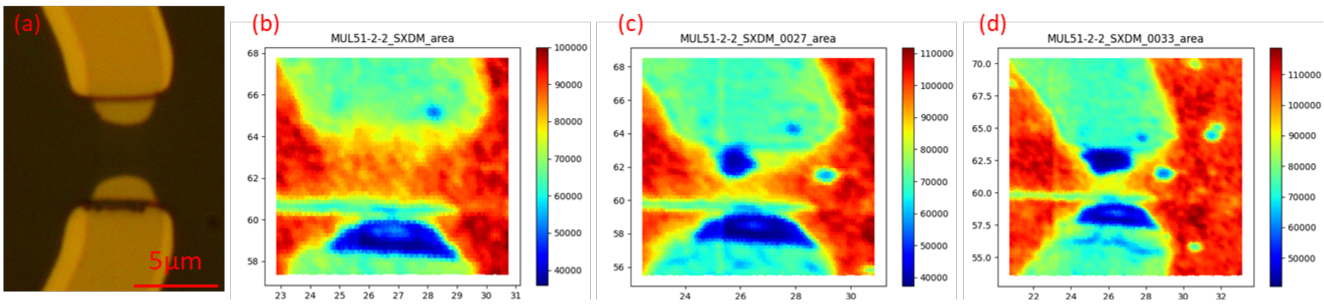

Fig.3 (a)Optical microscope image of the FO/BTO junction in pristine state; colormaps of junction undergoes (b) no current (c) 50µA (d) 260µA (breaking) illustrating the area of 400 BTO diffraction peak.

These data are still under evaluation. The procedures of sample lateral drift correction during the k-maps (40-60 angular positions) are expected to yield better visualization of the changes and enable their better quantification, namely of the lattice parameter variation with increasing current.

Overall, the experiment was very successful, and we could acquire the expected evolution of the crystalline structure of ferrite/BTO junctions realized by PFM polarization. The interpretation of crystal structure data acquired on ID-01 beamline will hopefully help us unveil the mechanism on current injection and breakdown in the conduction channel created by PFM in ferrite/BTO epitaxial systems.