EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** ***Real-time*** **dissolution of calcite crystals**	**Experiment number**: es1244
Beamline: ID13	**Date of experiment**: from: 25/01/2023 to: 29/01/2023	**Date of report**:
Shifts: 15	**Local contacte(s)**: Aicha Asma Medjahed	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

- Paul Fenter, Chemical Sciences and Engineering Division, Argonne National Laboratory (Lemont, USA).
- Virginie Chamard, Institut Fresnel, University of Aix-Marseille (Marseille, France).
- Marc Allain, Institut Fresnel, University of Aix-Marseille (Marseille, France).
- Tilman Grunewald, Institut Fresnel, University of Aix-Marseille (Marseille, France).
- Fernando Bartolomé, Institute of Nanoscience and Materials of Aragon, INMA, CSIC/University of Zaragoza (Zaragoza, Spain).
- Irene Calvo-Almazán, Institute of Nanoscience and Materials of Aragon, INMA, CSIC/University of Zaragoza (Zaragoza, Spain).

Report:

- **Experiment goal:**

The goal of our experiment was to study in real-time the dissolution of calcite nano-sized crystals grown on a 25 µm thick Kapton substrate and in contact with a liquid solution, by developing a new Bragg coherent diffraction imaging (BCDI) approach where the measurement time is significantly reduced. Thereby, we wanted to monitor the time evolution of the crystal morphology and internal structure at subsequent stages of the dissolution process, by performing rocking curve scans lasting few seconds (less than one minute). These results would be used to test our hypothesis about the existence of specific strains connected to the intense chemical reactivity of corners and edges, which are absent from flat terraces and which link the chemical reactivity to the structural features of the 3D interface of a nanocrystal.

However, due to an important instability of the Kapton surface under the beam, we were forced to re-orient our experimental approach. Finally, we decided to apply the new BCDI methodology to observe the morphology and internal structure of a Si nano-structured crystal evolving upon beam radiation damage.

- **New BCDI methodology:**

This new approach called "speckle-(sp)BCDI", consists in modulating the coherent beam wavefront with a phase plate (see Figure 1, panel h), to produce higly non-uniform illumination: "speckle illumination" to enhance the efficiency of sampling of the diffracted intensity around a Bragg peak in a rocking curve scans (RCS). The illumination of the crystal with speckles produces shifted copies of the Bragg peak along the rocking curve direction. Therefore, the detector at a single rocking angle intercepts simultaneously various components of the diffracted signal arising from different directions, and thereby, increasing the 3D information content in each cut of the reciprocal space. This effect is used to relax the oversampling ratio (OSR) in the rocking curve direction since it enables to reduce the number of diffraction patterns required to retrieve a 3D image of the crystal.

- **Experimental protocol**

The MLL lens setup of ID13, was optimized to produce a focused beam of ~ 70 nm size at 13 keV. Two detectors were available: an Eiger and a Medipix to perfom 2D forward ptychography and 3D BCDI. We mounted the phase plate at ~ 15 cm upstream of the optics and we set the upper stream slits to an opening gap of 75 x 75 µm.

The experiment was divided into two parts: First of all, we performed a complete characterization of the phase plate and the resulting speckle illumination at the focus of the lens by performing a series of 2D forward ptychography measurements on a siemens start pattern.

The second part was devoted to the real-time study of a dynamically evolving system. For this, we used a crystalline Si-(110) pad on which code bar structures had been nano-patterned with typical sizes ranging from 60 up to 200 nm (see Figure 2). On this sample,we first collected a series of spBCDI rocking curve scans with a high OSR of 4 at various positions on the sample. This was done while the sample was static under the beam. Then, we launched a radiation dammage measurement performing a battery of ultra fast rocking curve scans while the sample was degrading under the beam)

- **Results**

Figure 1 shows one of the reconstructions produced from the inversion of the forward ptychography data taken on the siemens star pattern with a speckle illumination. We can observe the great spatial resolution accomplished in the reconstruction of the object (panels *a* and *e* for amplitude and phase respectively). We can also reconstruct the speckle illumination at the focal plane (panels *c* and *g* for amplitude and phase) arising from the modulation of the coherent wavefront by the phase plate. More interestingly, we calculated from the reconstructed probe the complex diffracted wave field at the detector position (panels *c* and *g* for amplitude and phase) There, we can recognize the same structural features which are present in the simulated (panel *d)* and actual phase plate (SEM image in panel h).

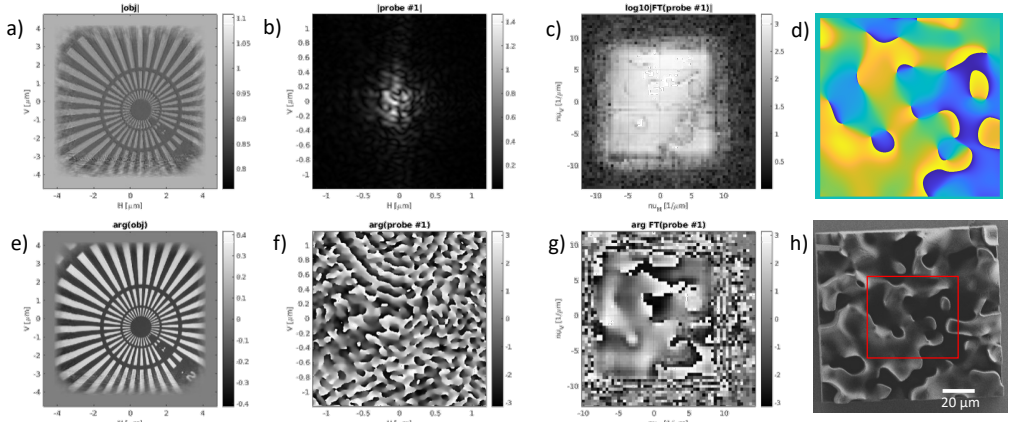

Figure 1: results of the forward ptychography measurements with speckle illumination. The red box in panel h highlights the area of the phase plate which produces the speckles and which is visible in the detector plane shown in pannels c and g.

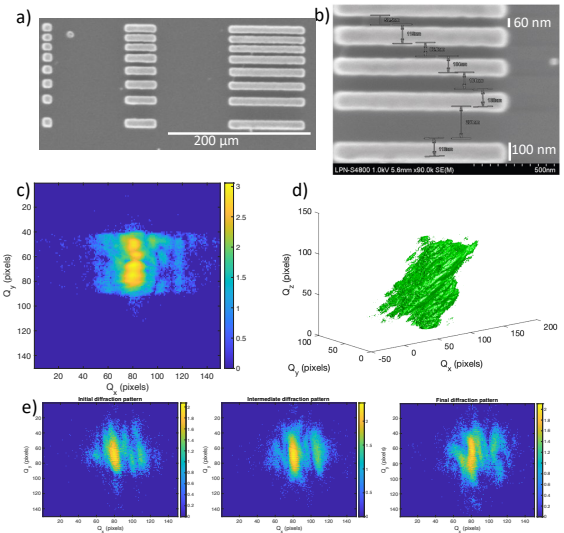

Figure 2: sample and diffraction patterns measured during the "in situ" part of the experiment.

Figure 2 shows the nanostructures patterned in a Si crystalline pad (panel *a* shows a general view while panel *b* displays a detail of the structure, including some typical distances) that we imaged with the speckle illumination in Bragg geometry. Panel *c* displays a diffraction pattern taken from the central part of the rocking curve and panel *d* shows the 3D diffracted intensity distributed around the Si 110 Bragg peak as recorded in the rocking curve. Finally, panel *e* shows in a row the temporal evolution of the intensity diffracted by the small code bar pattern (left column in panel *a*), upon exposure to the beam. The changes in the speckle distribution recorded in the succesive rockign curve scans arise from the change in morphology and internal structure of the nano-structures, due to its interaction with the very intense coherent X-ray beam. Our goal is to invert these series of rocking scan, to retrieve images of the object in 3D at different stages of this process, and thereby, reconstruct a video of the degradation of the nano-structure with time.