ESRF	**Experiment title:** Defect and grain structure characterisation during the growth of silicon for photovoltaic applications using *in situ* and real-time X-ray radiography and diffraction imaging	**Experiment number**: MA-4859
Beamline: ID19	**Date of experiment**: from: 08/06/21 to: 11/06/21	**Date of report**: 28/10/21
Shifts: 9	**Local contact(s)**: Marta Majkut	*Received at ESRF:*

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Report:

Scientific Objectives:

The scientific objectives of the proposed experiments were to decrypt fundamental mechanisms of the solidification of crystalline silicon (Si) for photovoltaic (PV) applications. The original experiments at the basis of this work consist of synchrotron X-ray imaging (radiography and diffraction imaging/topography) applied to the *in situ* monitoring of Si during seed heating, partial melting, solidification and cooling down. The main issues of the defect formation, ranging from dislocations to grains, and of their complex interaction and dependence is thus studied up to high temperatures (melting temperature of silicon: 1414°C). The key fundamental results obtained can contribute to answer to the challenge of defect control to obtain higher PV efficiency for all most advanced fabrication processes of crystalline Si PV cells.

Experimental method:

The experiments were carried out at the European Synchrotron Radiation Facility (ESRF) at beam line ID19. The beamline is ideally suited for this experiment because of the large field of view and of the excellent and uniform flux of photons. The IM2NP device named GaTSBI (Growth at high Temperature observed by Synchrotron Beam Imaging) was used for the experiments. This high temperature furnace allows Si heating in solid phase / melting / solidification and is compatible with X-ray synchrotron imaging methods: radiography and topography. In the radiography mode, the sample is illuminated by the white synchrotron X-ray beam. Radiography enables characterising *in situ* and in real-time the morphology and dynamic evolution of the solid/liquid interface during solidification, and measuring growth kinetics. The beam is monochromatised after the sample in order to keep a constant heat load on the sample; the radiograph image is recorded by a camera. In the simultaneous diffraction imaging mode, topographs are collected and allow to reveal grain orientation, twinning, crystal network deformation and dislocation related strain fields as shown in our previous work [1-3]. In June 2018, a major step forward was achieved [4]. Two individual indirect detector systems were implemented to record simultaneously the topographs and the radiographs. This allowed for an increased image acquisition rate to record the topographs with complete synchronization with the radiograph recording compared with our previous studies that used X-ray sensitive films. Only one diffraction spot could be recorded in this mode whereas the information related to defects is different on each diffraction spot, due to their crystallographic orientation. Another major step forward highly wanted was thus to record time-resolved images of the radiographs simultaneously to at least two diffraction spots with independent but time-synchronised detectors. This objective was attained during the June 2021 experiments with the support of the ID19 ESRF team. A second camera fully synchronised with the others pointed on a second selected diffraction spot during the experiments.

Scientific thematic studied during the campaign:

Monocrystalline Si seeds with several crystallographic orientations were selected and diffraction spots of interest to reveal strain field and defects were sorted out according to our previous work and during the experimental campaign.

Three main related topics were addressed during the MA4859 experiments:

1. Dislocation formation and propagation: For this thematic, a pure mono-crystalline seed was used. The development of dislocations during heating of the seed is first studied in isothermal conditions to characterise the dynamics of dislocations. Then, a temperature gradient iss established to partially melt the sample. At last, solidification is

initiated from the remaining solid seed to study the propagation of the dislocations at the seed-regrowth interface, during solidification at the solid-liquid interface and the interaction of dislocations with other structural defects.

2. <u>Sub-grain propagation and evolution during solidification:</u> For this thematic, a sample initially containing subgrains was used as a seed for solidification. It is worth noting that subgrains are major defects for the photovoltaic industry. These investigations are part of a collaboration with INES (National Institute of Solar Energy). The interaction of subgrain boundaries with the solid-liquid interface is studied as well as their evolution during solidification.
3. <u>Effect of silicon nitride crucible coating on solidification:</u> For this thematic, silicon nitride coating was deposited on the boron nitride crucibles generally used in our experiments. This coating is the most widely used in the industry for the fabrication of multi-crystalline silicon ingots. The objective was to study nucleation and solidification in the presence of this industrial coating. This is part of the project FUSING (Fundamentals of Silicon Nucleation and Growth – PhC N° 45310UH) in collaboration between IM2NP and the group of Pr Marisa Di Sabatino at NTNU in Norway.

<u>Preliminary results:</u>

During this campaign, these challenging, cutting-edge *in situ* experiments were successfully conducted at temperatures ranging from room temperature to the melting temperature of Si (1414 °C). From a more technical point of view, the challenge to record simultaneously radiographs and two diffraction spots have been met. An example of images recorded during the campaign is shown in Figure 1. Figure 1 shows the simultaneous images recorded in the radiography mode and for two topographs during heating. The strain field related to dislocations is highlighted in light grey on the topographs (Figure 1.c, d, e, f). They are mostly vertically oriented because of the crystallographic orientation of the sample. Dislocation loops can be seen for example in Figure 1.c and their dynamics followed. Due to their complexity and to the need for complementary *ex situ* analysis, the results are still under thorough investigation but there is no doubt that they will contribute to unveil mechanisms during heating and solidification processes and will provide quantitative information on crystallographic defects, twinning, strains and dislocations.

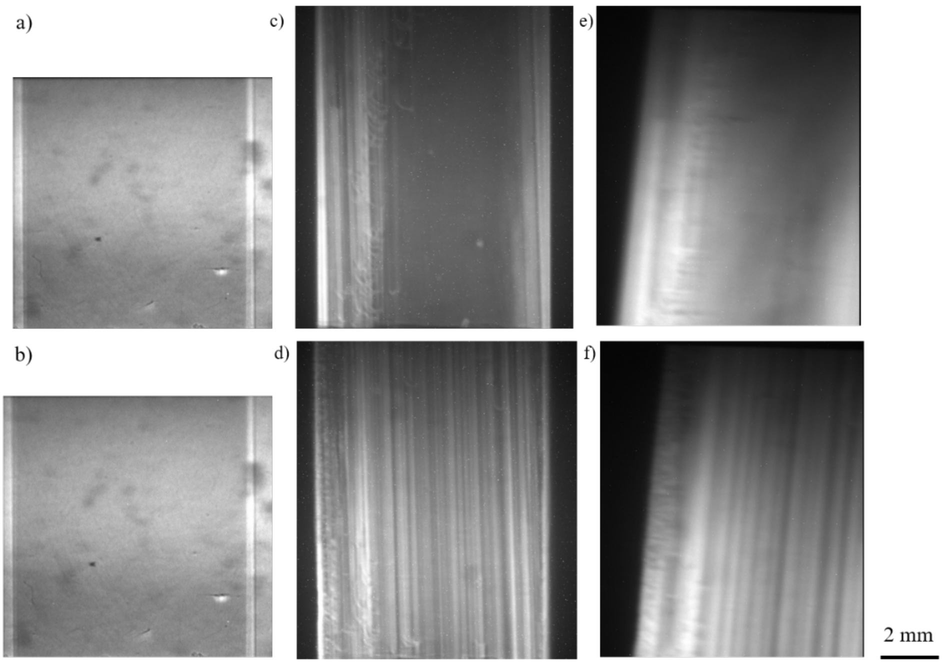

Figure 1: X-ray imaging during heating of a pure mocno-crystalline silicon sample. X-ray radiography (direct beam): a) and b). X-ray topography (Bragg diffraction imaging): spot 115: c) and d); spot 206: e) and f). Top row: upper heater temperature T_U = 1280 °C, bottom heater temperature T_B = 1150 °C and bottom row: T_U = 1316 °C, T_B = 1186 °C.

<u>Future work</u>

The GaTSBI set-up coupled with the ID19 imaging environment together with the experience of both ID19 and IM2NP teams are unique tools to answer to the major issues of crystalline defect formation during growth of materials at high temperature in general. Following the success from the experimental point of view, we would like to take advantage of this unique association between the GaTSBI solidification furnace and advanced X-ray imaging to deepen our understanding of the mechanisms at stake during silicon process steps. As mentionned above, the results obtained during the June 2021 experiments are still under analysis and we expect key results concerning the understanding of defect formation during the heating and solidification of silicon. The scientific thematics presented here are of current interest in industry and in research laboratories and require further investigations. They have been clearly identified by the team and will be further studied in the future.

<u>References</u>

1. H. Ouaddah *et al.* Crystals 10 (2020) 555; **2.** T. Riberi – Béridot *et al.*, *Acta Materialia* 177 (2019) 141-150; **3.** M. Becker *et al.* Solar Energy Materials & Solar Cells 218 (2020) 110817; 4**.** M. Becker *et al.*, *J. of Applied Crystallography* 52 (2019) 1312-1320.