ESRF	**Experiment title: In situ and real time observation of multicrystalline silicon for photovoltaic applications**	**Experiment number**: MA-1377
Beamline: BM05	**Date of experiment**: from: 09/11/2011 to: 13/11/2011	**Date of report**: 16/03/2012
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Scientific Objectives:

The general scientific objectives of our experiments are to provide benchmark data concerning the solidification of multi-crystalline Si (mc-Si) for photovoltaic (PV) applications. These original experiments consist in synchrotron X-ray imaging characterisation of the mc-Si during its solidification.

These experiments and proposal are part of a larger project entitled Si-X (Characterisation and understanding of the crystallisation of photovoltaic **Si**licon: **X**-ray synchrotron imaging) which is funded by the HABISOL (Habitat Intelligent et Solaire Photovoltaïque) program of the French National funding agency (ANR). ESRF is a full partner of this project.

One objective of the MA-1377 campaign was to test a crucible set using glassy carbon. Indeed, boron nitride crucibles used in the previous experiments can induce boron diffusion that modifies the electrical properties of the material.

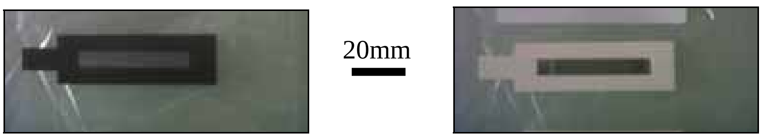
However, the main scientific objective was to study formation of the grains with different control levels of impurities in silicon.

Experimental method:

The MA-1377 experiments were carried out on the beam line BM05 using the experimental device for X-ray radiography and topography of the solidification of mc-Si described in the report for MA-1274 experiments.

The samples studied were: Czochralski (Cz) and Solar Grade (SoG). To better understand the influence of some particular impurities which cannot be done when using metallurgical grades silicon full of numerous impurities, we studied the solidification of two types of Solar Grade silicon: SoG-Si PSX25 (high concentrations of Carbon and Oxygen), SoG-Si PSX67 (high concentration of Carbon).

The surface of the samples has been reduced to *38 x 5.6 mm*^{2} in a crucible housing of *40 x6 mm*^{2} of surface and *300µm* of depth. Concerning the glassy carbon crucibles, the housing depth was less *than 300µm*, therfeore the thickness of the samples for these crucibles were less than *300µm*. Figure 1.a and 1.b show respectively a glassy carbon and a pyrolitic boron nitride crucible with the silicon sample inserted inside.



(a) **(b)**

Fig. 1:Silicon samples in crucible housing made of : a) glassy carbon; b) pyrolitic boron nitride.

Results:

During the experiments using the glassy carbon, we observed a considerable loss of the material after the first melting of the sample (see figure 2). The aspect of the remaining material suggests that there may have been a reaction between the silicon and the glassy carbon. A Si-C reaction was expected on a few µm thickness but such a results was totally unexpected so that further analysis are in progress. This sample is being analysed using post-mortem techniques to understand the phenomena that took place and to evaluate the adequation of glassy carbon crucibles in our experiments.

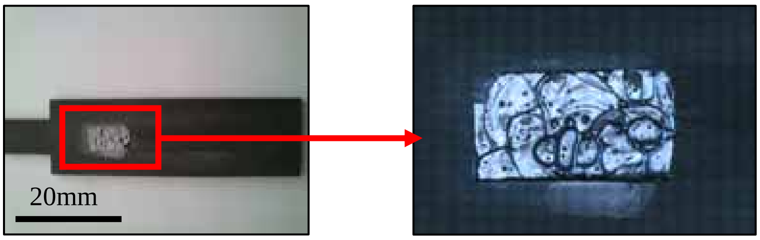


Fig. 2: Cz-Si sample in a glassy carbon crucible after first melting/solidification

Using boron nitride crucibles, we were able to obtain systematic results on the grains formation in mc-Si, in particular on the origin of small grains in these materials. These small grains can be important defects from the PV properties point of view.

We were also able to evidence the formation of repetitive twins. For example, with a sample cut inside a Czochralski ingot, we observed the formation of twins inside the growing silicon. As an example, figure 3 shows the image of one grain recorded on topographs taken at different instants during the solidification of a Cz Si at a temperature gradient of 16K/cm and for a cooling rate of 0.2K/min. Twins are evidenced in topographs by the hachured aspect of the grain image (Figure 3) due to the misorientation of some crystallographic planes compared to the crystallographic orientation of the main grain.

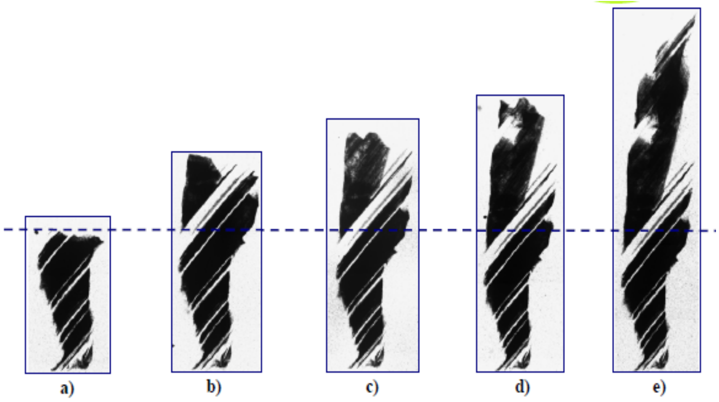


Fig. 3: Subsequent images of a grain on topographs obtained for CZ Si solidification at a temperature gradient of 16K/cm and with a cooling rate of 0.2K/min. a) t_0, b) t_0+12min, c) t_0+18min, d) t_0+25min, e) t_0+49min.

Current and future work

During these experiments, we obtained rich information on the growth microstructure of multicrystalline silicon for differing grades and controlled impurity levels. We improved our understanding of the impact of the growth parameters and of the impurities on several feature like and, among others, the occurrence of small grains and the formation of twins.

Our present work consists in analysing the data collected from the experimental campaigns MA-1138, MA-1274 and MA-1377. We are now in the process of getting quantitative information from the experiments performed (growth rate, groove depth) as a funtion of the material grade and of the growth parameters. Important phenomena as the groove formation are systematically studied making use of the advantages of both radiography and topography techniques. Some targetted experiments are also foreseen to deepen our understanding.

In the meantime, these results are resulting in scientific publications and conference presentations. These experiments of in situ and real time observation by X-ray imaging combining both radiography and topography of the solidification of mc-Si provided and will provide unique benchmark data.