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1 Review

# 2 X-ray based *in situ* investigation of silicon growth 3 mechanism dynamics – Application to grain and 4 defect formation

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14 **Abstract:** To control the final grain structure and the density of structural crystalline defects in  
15 silicon (Si) ingots is still a main issue for production of Si for photovoltaic solar cells. It concerns  
16 both innovative and conventional fabrication processes. Due to the dynamic essence of the  
17 phenomena and to the coupling of different scale mechanisms, the *post-mortem* study of the  
18 solidified ingots gives limited results. In the past years, we developed an original system named  
19 GaTSBI for Growth at high Temperature observed by Synchrotron Beam Imaging, to investigate *in*  
20 *situ* the mechanisms involved during the solidification process. X-ray radiography and X-ray Bragg  
21 diffraction imaging (topography) are combined and implemented together with the running of a  
22 high temperature (up to 2073 K) solidification furnace. The experiments are conducted at the  
23 European Synchrotron Radiation Facility (ESRF). Both imaging techniques provide *in situ* and real  
24 time information on the morphology and kinetics of the solid/liquid (S/L) interface, as well as on the  
25 crystal structure deformation and structural defect dynamics including dislocations during growth.  
26 Essential features of twinning, grain nucleation, competition, strain building and dislocations  
27 during silicon solidification are characterized and allow a deeper understanding of the fundamental  
28 mechanisms of silicon crystal growth.

29 **Keywords:** Silicon; growth; grains; defects; twins; strain; dislocations; X-ray radiography; X-ray  
30 topography; Bragg diffraction imaging.

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## 32 1. Introduction

33 Current research on crystalline Si used for photovoltaic solar panels focuses on several key  
34 targets from silicon purification to cell manufacturing including the silicon ingot fabrication process  
35 step. Several alternative methods are proposed to optimize the Si growth process to increase the  
36 production yield while reducing the costs. However, this cannot be done at the expense of the  
37 crystalline quality of the final ingot as the performance of the solar cells is directly related to it. Three  
38 main methods aim at mastering the initial grain nucleation and defect generation from the first stage  
39 of solidification: the dendritic casting method [1, 2], the cast mono solidification (cm-Si) [3-5] and the  
40 high performance multi-crystalline silicon (HP mc-Si) [6]. HP mc-Si and cm-Si techniques are both  
41 used in the industry and allow producing ingots with a lower dislocation density compared to the  
42 conventional mc-Si while allowing the use of low-cost casting solidification methods. In the case of  
43 cm-Si, a pavement of monocrystalline seeds is placed on the bottom of the crucible in order to take

44 up the initial orientation of the seed [3]. However, cm-Si efficiencies are still limited due to the  
45 presence of structural defects such as parasitic grain nucleation on the walls of the crucible [4, 7], twin  
46 formation and more importantly, dislocations. The latter, can be either arranged in cellular patterns,  
47 in the entire cm-Si ingot and are known as background dislocations [8] or generated on the top of the  
48 seeds [9,10], at their junctions [10] on precipitates and propagate vertically along the growth direction  
49 [7,11-16] generating the formation of sub-grain boundaries. HP mc-Si technique is based on a very  
50 different approach aiming at obtaining small-size and uniform grains at the initial stage of  
51 solidification with random angle and coherent grain boundaries [6, 17]. This results in low density of  
52 dislocation clusters thanks to the interaction of blocking mechanisms by which dislocations that  
53 nucleate at the beginning of the crystallization process cannot propagate further along the growth of  
54 the ingot. Recent work by Stokkan et al. [17] highlighted the necessity to control the first nucleation  
55 events to improve the crystalline quality. It is worth noting that in the other main process in the  
56 market (Czokralski, Cz) heading at the fabrication of monocrystalline ingots, the issue of dislocations  
57 and structural defects remains a main concern especially in the process of improving the method  
58 (higher volumes, faster process, reusable crucibles and seeds...) [18, 19].

59 Grain boundaries and dislocations can severely limit the conversion efficiency of solar cells by  
60 reducing the minority carrier lifetime [20-23]. Dislocations remain one of the most important  
61 efficiency limiting defects in Si solar cells [24, 25], because they can act as preferential segregation  
62 sites for impurities, ultimately reducing the carrier lifetime [11, 16, 26]. At a higher scale, sub-grain  
63 boundaries and grain boundaries of high planar mismatch can be more detrimental than high  
64 symmetry grain boundaries such as symmetric coincidence site lattice (CSL) twin boundaries, also  
65 due to decoration by impurities [27]. Various studies show that the crystalline quality of an ingot in  
66 general and the twin relationship between the grain boundary types in particular can have a  
67 significant impact on the photoelectric properties [27-29]. Moreover, although it has been shown that  
68 perfect symmetric  $\Sigma 3$  twins have no major impact on the photovoltaic properties, the repetition of  
69 twinning has important consequences for the final grain structure and distribution of  
70 crystallographic orientations [30, 31]. The importance of twinning in the development of the grain  
71 structure has been highlighted for very different solidification processes including directional mc-Si  
72 solidification [32] and ribbon growth [33]. Another issue is to control and lower the density of strained  
73 regions of the crystal structure that can be at the origin of dislocation emission during growth or  
74 subsequent cooling down and solar cell fabrication processes. Recent molecular dynamics  
75 simulations of silicon growth highlighted the interrelation between, strain field, dislocation  
76 generation relatively to the growth direction and twin nucleation [34]. The control of the structural  
77 defect formation is thus motivated by their direct impact on the PV properties. Such a control is only  
78 possible if a thorough understanding of the crystal growth mechanism is achieved. The  
79 understanding of the structural defect development during growth is limited by the difficulty of  
80 accessing, from the *ex situ* study of the solidified ingots, to the history of defect formation and  
81 interrelation. Moreover, these structural defects cover by essence a large scale range (from  
82 dislocations to grains).

83 To answer these issues and key points, benchmark experiments have been proposed to  
84 investigate the growth from silicon melt *in situ*. Characterisation of the solidification of an  
85 undercooled levitated silicon droplet was performed using an X-ray diffractometer and by recording  
86 the droplet surface image using a high speed video camera [40]. The *in situ* solidification behaviour  
87 of Si droplets on silicon wafers was also characterised using IR thermal imaging [41]. Fujiwara *et al.*  
88 [2,36,39,42-43] use a confocal scanning laser microscope to carry out *in situ* observations of crystal  
89 growth behaviour from silicon melt by providing live images of solid-liquid interface features and of  
90 the growth of grains. With this method, a detailed investigation of the Si microstructure during  
91 growth has been carried out. X-ray Bragg diffraction imaging (topography) is also used to  
92 characterise crystalline defects in particular [26]. More information and explanation on this technique  
93 will be given in the following as this is a method of choice to characterise crystalline defects that we  
94 use in our experiments. It is worth mentioning the pioneer work of Pr. Chikawa [44, 45] who  
95 conducted *in situ* X-ray topography on the solidification of silicon.

96 Starting from the considerations that *in situ* characterisation of silicon growth constitutes an  
97 invaluable tool to understand the crystal growth phenomena and the formation of structural defects,  
98 we implemented *in situ* X-ray imaging during the solidification of silicon. The GaTSBI (Growth at  
99 high Temperature observed by Synchrotron Beam Imaging) tool was developed to fulfil this  
100 objective. This present paper is a review paper of our major results concerning the formation of  
101 grains, twinning and competition [38, 46-53] using advanced *in situ* and complementary *ex situ*  
102 characterisation methods. *In situ* X-ray imaging and methods are described in details. Our results  
103 concerning dislocations and the effect of impurities [54] are not presented in details here.

## 104 2. Materials and Methods

### 105 2.1 GaTSBI tool

106 GaTSBI is a unique device that allows following in real time the solidification processes during  
107 growth. It is a specially designed instrument composed of a high temperature (up to 2073 K)  
108 directional solidification (DS) furnace employed in conjunction with synchrotron radiation X-ray  
109 imaging techniques (Bragg diffraction imaging - topography and radiography).

#### 110 2.1.1 Directional solidification furnace

111 The DS furnace is based on two heating graphite resistors that are inside a vacuum chamber  
112 under dynamic vacuum ( $\sim 10^{-6}$  mbar). The heater resistances are regulated by the DS furnace external  
113 controller that uses pyrometer temperature measurements pointing on the heaters for adjustments.

114 The typical sequence used in our experiments concerning silicon solidification and in the  
115 experiments analysed in the following falls down in six steps:

- 116 • Step 1 – Preheating: the sample is heated by applying the same temperature to the bottom and  
117 top resistances of the furnace (isotherm conditions) up to 1373 K.
- 118 • Step 2 – Temperature gradient: a vertical temperature gradient is applied from 1373 K by  
119 imposing a controlled temperature difference between both heaters. The same temperature  
120 gradient is maintained until silicon melting is observed by imaging.
- 121 • Step 3 – Partial melting: the sample is partially melted and thus a seed crystal, preserving the  
122 initial orientation of the sample, is kept within the field of view of the X-ray imaging.
- 123 • Step 4 – Solidification: a cooling rate is applied on both heaters until the region of the silicon  
124 sample observed within the field of view is fully solidified. The same cooling rate is applied on  
125 both heaters to maintain a constant temperature gradient during solidification. In some  
126 particular cases, not reported in this manuscript, solidification is conducted by pulling down the  
127 sample. In both cases, the solidification is directional in the upward direction due to the imposed  
128 vertical temperature gradient.
- 129 • In some experiments, a new cycle is started again from step 3.
- 130 • Step 5 – Controlled cooling down: the sample is cooled down until 923 K by applying cooling  
131 rates of -13 K/min and -10.4 K/min to the top and bottom heaters, respectively.
- 132 • Step 6 – Cooling down to room temperature: free cooling down takes place from 923 K as  
133 temperatures below this value cannot be controlled by design of the furnace.

#### 134 2.1.2 Crucible assembly

135 Two thin pyrolytic boron nitride (BN) plates serve as crucible material. One of the BN plates has  
136 a mechanically machined slot with the dimensions of the samples. The typical sample dimensions  
137 are: length 40 mm, width 6 to 8 mm and thickness about 0.3 mm. The front and back sides of the  
138 sample are in contact with the crucible walls. The two BN plates are held together from the outside  
139 by two Molybdenum clips so that it applies a pressure on the main surfaces of the samples. In a  
140 further step, the silicon sample housed in the BN crucible, is introduced inside the DS furnace.

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### 143 2.1.3 Origin of the silicon samples

144 The initial monocrystalline Si samples are cut from double side mechano – chemically polished  
145 intrinsic (resistivity beyond 5000  $\Omega\cdot\text{cm}$ ) float-zone (FZ) wafers 50.8 mm, or from conventional Cz  
146 industrial ingots (typical oxygen concentration:  $0.5 - 1 \times 10^{18}$  at/cm<sup>3</sup>). The FZ samples provided by  
147 SIL'TRONIX Silicon Technologies are produced with 9N material by the float-zone technique and  
148 contain no visible dislocations at the beginning of the experiments. Oxygen and carbon  
149 concentrations are below  $< 10^{15}$  at cm<sup>-3</sup> and metallic impurity contamination is limited to  $10^{11}$  at/cm<sup>-3</sup>.

### 150 2.1.4 X-ray imaging

151 The GaTSBI set-up is not only a DS device but is specifically designed to allow X-rays to cross  
152 the furnace windows and elements up to the sample without deleterious absorption and diffraction  
153 of the incoming X-rays. The beam crosses the entry and exit vacuum chamber windows that are made  
154 out of 0.5 mm thick aluminium. Additional vitreous carbon plates are positioned in the beam path  
155 serving as insulation of the furnace. As a consequence, a high photon flux is needed to ensure good  
156 quality imaging. This is one of the reason although not exclusive why the experiments are conducted  
157 using synchrotron X-ray generated at the European Synchrotron Radiation Facility.

158 During the experiments, the sample inside the DS furnace is constantly illuminated by the X-ray  
159 synchrotron polychromatic beam, which avoids variations of the heat load due to the beam. Indeed,  
160 the polychromatic beam creates heat load which is minimised with filters introduced in the beam  
161 before reaching the DS furnace. A compromise between minimised heat load and sufficient photon  
162 flux needs to be achieved resulting in the utilisation of Al filters between 0.5 mm to 0.7 mm in our  
163 experiments. On the one hand, a sufficient photon flux level is assessed qualitatively by checking that  
164 the solid-liquid interface can be characterised with a counting time not higher than 1 s which is  
165 requested to be able to follow its dynamic evolution during solidification. On the other hand,  
166 variations of the heat load needs to be minimised for two reasons:  
167 . it is sufficient to modify the thermal field inside the sample,  
168 . it modifies the behaviour of the crystals used in the post-monochromator that will be described  
169 in the following.

171 Two imaging techniques, X-ray radiography and X-ray Bragg diffraction imaging (topography),  
172 are used during the steps described in section 2.1 (heating, solidification and cooling down of the  
173 samples). Both imaging techniques are non-destructive.

#### 175 1. X-ray radiography

177 In the X-ray radiography mode, the direct beam passing through the sample is used to record  
178 images of the growing solid-liquid interface. A polychromatic beam is needed for the diffraction  
179 imaging mode, whereas a monochromatic beam is needed in the case of X-ray radiography to increase  
180 the legibility of the images. First, the polychromatic direct X-ray beam goes through the sample and  
181 exits the furnace vacuum chamber. The polychromatic direct beam is then turned monochromatic at  
182 a target energy, empirically determined as explained in the following, using a vertically diffracting  
183 Si (111) double-crystal monochromator. Finally, images are recorded using a camera equipped with  
184 a scintillator to interface X-rays with the camera matrix detector.

185 X-ray attenuation contrast is the dominating imaging modality used in the frame of this work.  
186 Considering the use of synchrotron light sources, an additional modality present is related to the  
187 refraction at interfaces, frequently termed propagation-based X-ray phase contrast [47, 48]. Due to  
188 the rather coarse pixel sizes used and the relatively short distance between sample and detector, the  
189 effect of phase contrast is not pronounced in the images shown in this work and therefore only  
190 mentioned for the sake of completeness. Thus, the contrast in X-ray imaging radiographs shown here  
191 is mainly due to the differential absorption of the different sample regions. The Beer-Lambert law  
192 determines the absorption of a material (Equation 1). Incident monochromatic beam intensity is

193 exponentially attenuated as a function of the thickness and of the nature of the sample and of other  
 194 materials crossed by the incident beam:

$$I_t = I_0 e^{-\mu_i(T,C) \cdot l} \quad (1)$$

195 where  $I_t$  is the transmitted intensity,  $I_0$  is the incident intensity,  $\mu_i$  is the linear absorption coefficient  
 196 (in  $m^{-1}$ ), which depends on the temperature  $T$  and on the composition  $C$  while  $l$  is the thickness. The  
 197 linear absorption coefficient is a function of the density of the material.

198 As the absorption of other materials crossed by the beam is constant, the only contribution to  
 199 the image contrast comes from the sample. In the case of a pure material such as silicon, a difference  
 200 in transmission, and therefore a contrast in the images, is expected only from the density difference  
 201 between the solid ( $2.33 \text{ g/cm}^3$ ) and the liquid ( $2.56 \text{ g/cm}^3$ ) close to the melting temperature  $T_m$ . This  
 202 density difference is only 9 %. The use of monochromatic light is essential to exploit the weak  
 203 attenuation contrast originating from the density difference between the solid and the liquid silicon  
 204 phases in the radiography images. The choice of the monochromatic energy used for X-ray  
 205 radiography is based on a compromise between an acceptable transmission and a contrast allowing  
 206 to reveal the solid-liquid interface features. During our experiments, it has been empirically  
 207 determined that an energy of 17.5 keV must be used, which corresponds to a transmission of 63 % of  
 208 the liquid phase. However, the contrast between the solid and liquid phase is then only about 4 %.  
 209 Due to the limited density difference and the compromise in energy, the solid-liquid interface is  
 210 hardly distinguishable on the raw images oppositely to the case of alloys for which a higher density  
 211 difference is obtained because of the presence of several phases and of solute [57]. In addition, the  
 212 legibility of the images is considerably affected by the unavoidable non-uniform profile of the X-ray  
 213 beam and the surface inhomogeneity of the silicon crystals in the post-monochromator. As a  
 214 consequence, image processing is absolutely needed.

215 The image processing is based on the principle of pixel by pixel division and is performed using  
 216 the ImageJ software [58]. By dividing two images recorded at different times, the areas that remain  
 217 in the same state (liquid or solid) have the same transmission and corresponding pixel values in the  
 218 images, thus the result of the division is equal to 1. As the liquid transmission is lower than the solid  
 219 transmission, zones that change from liquid to solid appear in lighter grey (the result of the division  
 220 is lower than 1), and zones that change from solid to liquid appear in darker grey (the result of the  
 221 division is higher than 1).

222 Two types of treatment are used:

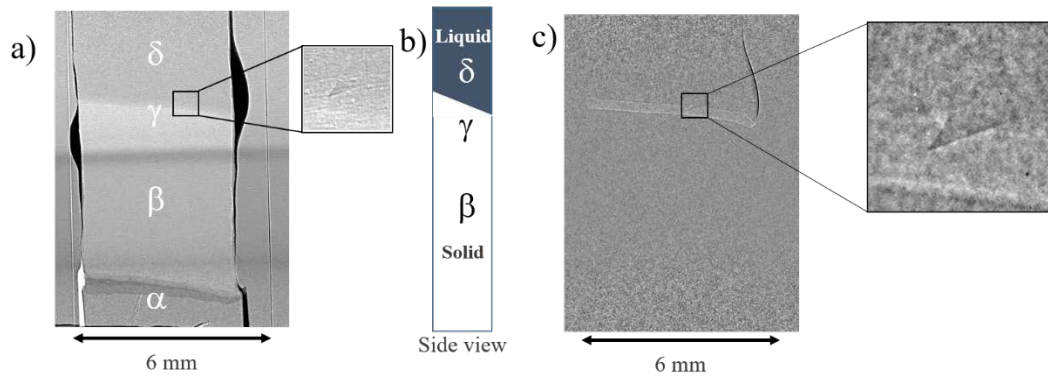
- 223 • Division by the first image taken after cooling starts:

224 For this treatment, all images of the solidification sequence are divided by a single reference  
 225 image recorded just after applying the cooling rate. A typical image is shown in Figure 1.a,  $\alpha$ ,  $\beta$  and  
 226  $\delta$  indicate the region of the regrown interface, the fully solid and liquid regions, respectively. A light  
 227 grey area is observed above the fully solid zone ( $\gamma$  in Figure 1.a). This area corresponds to a zone  
 228 constituted of solid and liquid that exists within the thickness of the sample at the level of the solid-  
 229 liquid interface. This is first due to the fact that the images correspond to a projection of the sample  
 230 volume hit by the beam and second to the orientation of the solid-liquid interface which is not  
 231 necessarily parallel to the incident beam. An illustration of a possible solid-liquid interface side view  
 232 configuration is depicted in the sketch in Figure 1.b. At the level of the solid-liquid interface region,  
 233 the beam crosses at the same time solid and liquid regions which explains the grey level neither  
 234 corresponding to a fully solid volume nor to a fully liquid volume.

235 This treatment allows following the evolution of the solid-liquid interface during growth.  
 236 Dynamic features can be observed and the growth velocity of the solidification front can be measured.

- 237 • Division of two successive images:

238 For this treatment, each image is divided by the previous one or by an image separated from the  
 239 current one by a few images only (Figure 1.c). In this case, the resulting image is less prone to noise  
 240 and artefacts variations in beam intensity with time as for the first treatment. Then, sharper contours  
 241 are obtained, revealing more details of the solid-liquid interface as can be seen in the close-up in  
 242 Figure 1.c which shows more clearly the same grain boundary groove (close-up in Figure 1.a). The  
 243 morphology of the interface and of the grain boundary grooves can thus be studied in details.



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**Figure 1:** X-ray radiography image recorded during solidification (applied temperature gradient: 30 K/cm and cooling rate of -1 K/min applied on both heaters) from a FZ-Si seed, (a) Image resulting from the pixel by pixel division of the current image by the first image after starting the cooling down ( $\alpha$ : seed-regrown interface,  $\beta$ : fully solid region,  $\gamma$ : solid-liquid interface region,  $\delta$ : fully liquid region), (b) Sketch of the side view, (c) Image resulting from the pixel by pixel division of two successive raw images with a time interval of 3 s and close-up at the level of the interface at the same instant and position as in (a).

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The radiography technique allows observing the growth of the interface, measuring the growth velocities, studying grain boundary groove evolution and the appearance of facets and twins. It provides a non-deformed image of the solid-liquid interface and of the sample. The volume projection effect needs to be taken into account for quantitative measurements (e.g. for the measurements of the facet normal growth rate discussed in section 3.1 and described in more details in [48]).

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In the experiments presented in the following, the X-ray radiography images are recorded on detectors based on the association of a scintillator to convert X-rays and of a CCD or CMOS camera detector [60]. An optics giving a good compromise between a large field of view encompassing the whole sample width and a solidification height of about 10 mm and a sufficient spatial resolution is used. More precisely, two detectors have been used. First, a CCD camera developed at the ESRF named FReLoN (Fast Readout Low-Noise) with 2048×2048 image pixel size and an optics with 5.8  $\mu\text{m}$  pixel size and a 11.9 × 11.9 mm<sup>2</sup> field of view was used. In our most recent experiments, a detector (sCMOS lens-coupled to a LuAG scintillator) 2048 × 2048 pixels with a nominal pixel size of 6.5  $\mu\text{m}$ <sup>2</sup> and a 16 bit dynamic range is used.

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Radiography images are generally recorded every 3 s with an exposure time of 1 s which is a sufficient time-resolution to be able to characterise solidification.

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## 2. X-ray Bragg diffraction imaging – Topography

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X-ray Bragg diffraction imaging (X-ray topography) is the complementary and essential non-destructive technique used to characterize the grown crystal quality during the same experiment. When the polychromatic beam illuminates the silicon sample installed inside the solidification furnace, diffraction occurs according to Bragg's law, generating a Laue diffraction pattern in addition to the direct beam exploited for X-ray radiography. The Laue diffraction pattern is constituted of several diffraction spots related to specific lattice planes. The use of a polychromatic beam allows collecting multiple spots in a single exposure that corresponds to different crystallographic planes  $\{hkl\}$  of the same grain.

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The transmission mode is used i.e. the incident beam is transmitted through the sample and the diffracted beams expose a detector that is placed after the sample. Transmission mode is the only possible one in our experiments as the sample is installed inside the vacuum chamber containing the furnace. The use of a polychromatic beam allows the collection of several spots originating from multiple grains in a single exposure as well as several spots corresponding to the different crystallographic planes of a single grain.



286 Each spot provides an image of the crystal generated by the beam diffracted by the {hkl} plane  
 287 family of a grain, called topograph [61]. These Bragg spots are then characterized by the hkl Miller  
 288 indices of the diffracting plane and by the projection of the diffraction vector  $\vec{g}$  (reciprocal lattice  
 289 vector), indicating the orientation of the spot with respect to the position of the direct beam. This  
 290 technique can obviously give information on the crystallographic orientations of the grains  
 291 considering the relative position of the diffraction spots, but its major output concerns the internal  
 292 structure of the individual spots as they contain information on misorientations, strain fields and by  
 293 extension on the presence of structural defects in general. Indeed, this is a powerful technique that  
 294 can be used for the visualization of defects (dislocations, twins, domain walls, inclusions, impurity  
 295 distribution) present in the crystal volume as it records their long range distortion fields and / or the  
 296 strain fields associated with a macroscopic crystal deformation. However, one drawback of the  
 297 technique is the complex analysis of the obtained images which are distorted images of the crystals.  
 298 The origin of the contrast observed in the images is briefly explained here, the reader is directed to  
 299 several references for more details [9, 59, 61-63].

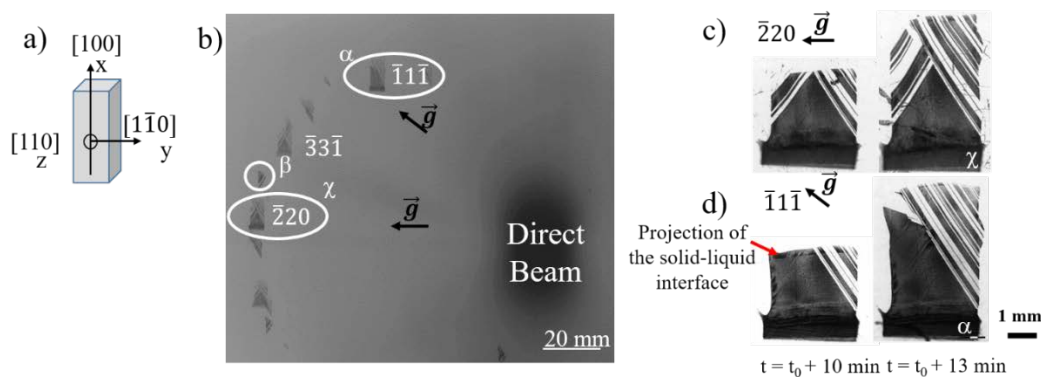
300 Due to the small beam divergence of the incoming synchrotron X-ray beam and to its large size,  
 301 the whole width of our samples can be illuminated providing images exhibiting a minimum  
 302 geometrical deformation effect. In our case, the diffracting volume corresponds to the width of the  
 303 sample  $\times$  the height of the field of view (generally 10 mm)  $\times$  the thickness of the sample. It is worth  
 304 noting that contrarily to more classical diffraction configurations, a limited number of diffraction  
 305 spots can be collected during our experiments. This is due to both the distance between the sample  
 306 and the diffraction pattern detector and the detector size. Indeed, although distance minimisation is  
 307 always possible to some extent, some hard limits are imposed by the DS furnace vacuum chamber  
 308 needed to run solidification experiments. It explains why only a few diffraction spots are recorded  
 309 on the films when they are used to record the diffraction pattern.

310 A few mechanisms are responsible for the contrast and intensity on the X-ray topographs we  
 311 recorded. They are structure factor contrast, orientation contrast, and the so-called "direct image"  
 312 mechanism. All of them derive from diffraction theory and Bragg's law as explained for example in  
 313 [64] and are evidenced in Figures 2 and 3.

### 314 Orientation contrast

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 316 A particularly clear illustration of the orientation contrast is given in the presence of twins  
 317 observed in our experiments (Figures 2 and 3) [46, 51].

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321 **Figure 2:** X-ray diffraction images (topographs) recorded during solidification (applied temperature  
 322 gradient: 30 K/cm and cooling rate of -1 K/min applied on both heaters at  $t_0$ ) from a FZ seed, (a)  
 323 Crystallographic orientation of the seed, (b) Laue pattern recorded at the end of solidification showing  
 324 the diffraction spots in the field of view. Images of the (c)  $\bar{1}\bar{1}\bar{1}$  and (d)  $\bar{2}\bar{2}\bar{0}$  topographs recorded at  
 325 two instants during solidification.

326 Indeed, in the case of twinning during growth, the diffraction images are very different  
 327 depending on the diffraction spots as can be seen in Figure 2. A typical hatched aspect is observed  
 328 for the diffraction spots corresponding to {hkl} family planes as can be seen in Figure 2.b (e.g.  $\alpha$ ,  $\beta$   
 329 and  $\chi$ ). The diffraction spot  $\chi$  ( $\bar{2}20$ ) shows a diffraction spot corresponding to {hkl} family planes  
 330 which are not common with twinned grains that developed on both right and left hand sides of the  
 331 sample (Figure 2.c). The complementary image corresponding to the twinned grains on the left  
 332 (Figure 2.b  $\beta$ ) is found at another position of the diffraction pattern, whereas the diffraction spot  $\alpha$   
 333 ( $\bar{1}\bar{1}\bar{1}$ ) includes the diffraction patterns of the common family planes of the central main grain and of  
 334 the twinned grains on the left (Figure 2.d). This is a particularly important element to be kept in mind  
 335 when analysing the topographs. Indeed, the observation of a single diffraction spot can be  
 336 misleading. This is one of the reasons why several diffraction spots must be analysed to be able to  
 337 conclude.

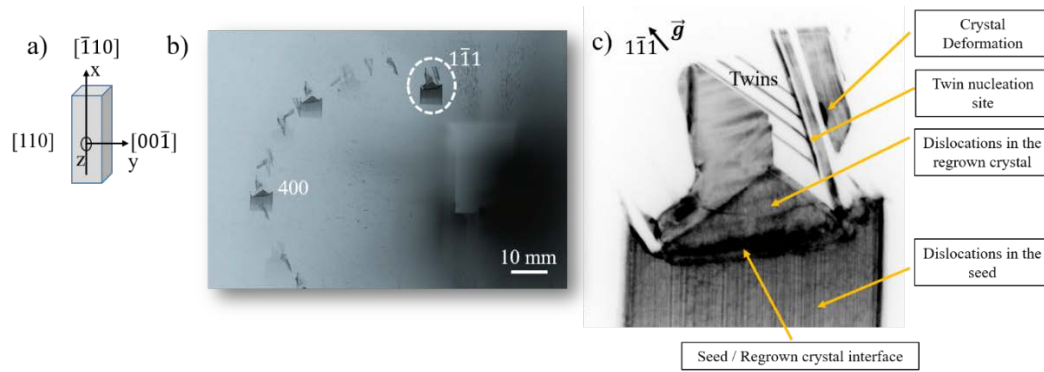
338 Orientation contrast can be also produced, for instance when the sample displays sub-grain  
 339 boundaries. For a monochromatic beam, the region corresponding to a {hkl} plane family is imaged  
 340 at a position given by the Bragg's law. Regions of different crystallographic orientations are not seen  
 341 simultaneously on the diffraction image and appear as non-illuminated (white) zones. When a  
 342 polychromatic beam is used, the misoriented regions are all in diffraction position simultaneously,  
 343 but for different wavelengths. The images diffracted by neighbouring sub-grains can exhibit a  
 344 contrast associated with geometrical local superimpositions or separations of the diffracted beams on  
 345 the topographs, according to the dimensions of the misoriented zone and to the value of the  
 346 misorientation.

347 Crystalline defects such as precipitates, dislocations and impurities, act on the diffraction  
 348 process through their associated effective misorientation angle variation  $\delta\theta_m(\vec{r})$ , which can be  
 349 approximated by Equation 2 [59, 63]:

$$\delta\theta_m(\vec{r}) = \frac{\delta d}{d}(\vec{r})\tan\theta_B \pm \delta\theta(\vec{r}) \quad (2)$$

350 where  $\theta_B$  is the Bragg angle,  $\frac{\delta d}{d}(\vec{r})$  is the local relative change of the lattice parameter and  
 351  $\delta\theta(\vec{r})$ , the local change in crystallographic orientation. The double sign has to be chosen to take into  
 352 account the effect of the deformation on the Bragg angle (decrease or increase of its value). This  
 353 effective misorientation corresponds to the strain field generated by the defect, which is at the origin  
 354 of Bragg diffraction of components of the incident beam that do not participate to the diffraction for  
 355 the perfect crystal matrix [38, 62]. This is the "direct image" mechanism that leads, in the X-ray low  
 356 absorption case we are concerned with, to supplementary diffracted intensity associated to distorted  
 357 regions. Andrew Lang developed this technique and revealed dislocations in silicon in his pioneer  
 358 work [61]. The diffraction imaging technique was also used by Oriwol *et al.* [26] to study dislocations  
 359 and the formation of sub-grain boundaries *ex situ* in Si ingots. Indeed, diffraction imaging applied to  
 360 silicon crystals have proven to give unique insights into the evolution of dislocations [65, 66] and  
 361 cracks [67]. As can be understood from the above, one of the main advantages of diffraction imaging  
 362 is that it can reveal low scale structural defects like dislocations on wide field images encompassing  
 363 complete crystals as shown for example for diamonds by Burns *et al.* [62] and for Si [38, 53, 68].  
 364

365 An illustration is given in our work on Figure 3.c. In this topograph corresponding to the  
 366  $\bar{1}\bar{1}\bar{1}$  diffraction spot and recorded during the solidification from a silicon FZ seed (orientation Figure  
 367 3.a), black contrasts revealing deformation of the crystal structure are present at several places.  
 368 Moreover, the deformation due to single dislocations can be clearly revealed in the seed and above  
 369 the seed-regrown interface.



**Figure 3:** X-ray diffraction imaging (topography) during solidification (applied temperature gradient: 30 K/cm and cooling rate of -1 K/min applied on both heaters) from a FZ seed, (a) crystallographic orientation of the seed, (b) Laue pattern showing the diffraction spots recorded at the end of solidification in the field of view, (c) topograph of the  $1\bar{1}1$  diffraction spot during solidification.

Importantly, if the strain field created around a defect is related to particular crystallographic orientations, it is not visible in all diffraction spot images (topographs). Indeed, if the displacement vector is perpendicular to the diffraction vector, the defect is not visible on the topograph. This is the case of dislocations whose image is extinct for the diffraction spots corresponding to diffraction vectors perpendicular to the Burgers vectors as also seen in TEM investigations [69, 70]. On the one hand, this means that the absence of a dislocation strain field on a single diffraction spot does not mean that no dislocations are present. Depending on the dislocation character, at least two diffraction spots with different diffraction vectors perpendicular to each other must be analysed before being able to conclude on the presence or not of dislocations. On the other hand, extinction is a powerful method to retrieve the Burgers vector direction as explained in details for example in [71].

### 2.1.5 Dynamic evolution

Another main originality of the experimental configuration we use is that several Laue patterns or topographs are recorded during a solidification experiment [38, 46, 72]. Then, it is possible to obtain sequences showing the evolution with time of the Laue pattern and of the topographs during the development of the grains. Such sequences allow a better understanding of the competition between the grains and of the occurrence of the twinning phenomenon. At the same time, the dynamics of the formation and evolution of defects as dislocations is followed during growth. The study of the growth of individual grains is then possible, along with the development of strain fields produced in the crystal structure by the structural defects. The combination of both imaging techniques and of the DS furnace provides complementary dynamic information about crystal growth and competition and about the crystal structure deformation.

Up to 2018, both *in situ* and real time X-ray imaging techniques: X-ray radiography and Bragg diffraction imaging (topography) were used alternately during growth. In this configuration, the different diffraction spots are collected on photographic films positioned after the furnace regularly during the experiment thanks to a specially designed device. X-ray diffracted beams are successively recorded on X – ray sensitive films (AGFA Structurix D3-SC, 17.6×12.5 cm<sup>2</sup>) positioned at a distance about 300 mm from the sample. The exposure time used to record the diffraction patterns is usually of 0.5 s. In this configuration, radiographs and topographs are thus recorded alternately.

In 2018, we implemented together with the ESRF ID19 team a solution to record simultaneously radiographs and diffraction images (topographs). In this configuration, a scientific CMOS camera lens-coupled to a LuAG scintillator (commercial Ce-doped Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, Crytur company – Czech Republic) is used to record the images of one of the diffraction spots (topograph). The camera has 2048 × 2048 pixels with a nominal pixel size of 6.5 μm<sup>2</sup> and a dynamic range of 16 bit. It is coupled with a ×1.5 optic to decrease the pixel size to 4.3 μm<sup>2</sup>. In this new configuration, images recorded from both modes are fully synchronised. The image acquisition rate is of 2 frames per second in experiments reported in [53] which is sufficient to follow the solidification front of the samples. The

411 choice of the diffraction vector of the recorded spots and the alignment of the camera with respect to  
412 the sample face is an important aspect because it influences the appearance and the information that  
413 can be revealed from the recorded topographs. Ideally a spot with a high intensity induced by the  
414 crystal plane structure factor should be chosen to better reveal defects. A detailed description of the  
415 equipment and imaging methods and configurations (alternate or simultaneous recording) can also  
416 be found in our previous publications [50, 51, 53].

## 417 2.2 *Ex situ* complementary investigations

418 After the last melting – solidification cycle, the samples are cooled down to room temperature  
419 and removed from the GaTSBI furnace. *Ex situ* electron backscatter diffraction (EBSD) measurements  
420 are performed after mirror polishing down to 1  $\mu\text{m}$  diamond paste using a FEG-SEM JEOL JSM 7001F  
421 equipped with a HKL Nordlys camera with either a 7  $\mu\text{m}$  or a 0.7  $\mu\text{m}$  step size depending on the  
422 studied area. In order to depict the three – dimensional orientation of the crystals in the sample,  
423 inverse pole figure (IPF) orientation maps are generated with respect to the three space directions:  
424 normal to the sample surface (z), transverse direction (y) and in the growth direction (x). Moreover,  
425 the coincidence site lattice map (CSL) is reconstructed to evidence the grain boundaries with a special  
426 character. In this paper,  $\Sigma 3$   $\langle 111 \rangle$  (red colour in the maps),  $\Sigma 9$   $\langle 110 \rangle$  (blue) and  $\Sigma 27a$   $\langle 110 \rangle$  (yellow)  
427 twin boundaries labelling refer to rotations around  $\langle h k l \rangle$  axis that satisfy the misorientation ranges  
428 given by the Brandon criterion,  $(60 \pm 8.66)^\circ$ ,  $(38.94 \pm 5)^\circ$  and  $(31.58 \pm 2.89)^\circ$ , respectively. Additionally,  
429 the grain orientation spread (GOS) map is extracted as well from the EBSD results. The GOS map is  
430 constructed by calculating the difference between the orientation of each pixel in the grain and of the  
431 grain average orientation to evidence the more distorted areas within a grain structure. A colour code  
432 is used to depict the grains without deformation (perfect Si crystal appears in blue) and having an  
433 average crystal structure deformation (red colour for the highest deformation).

## 434 3. Results and discussion

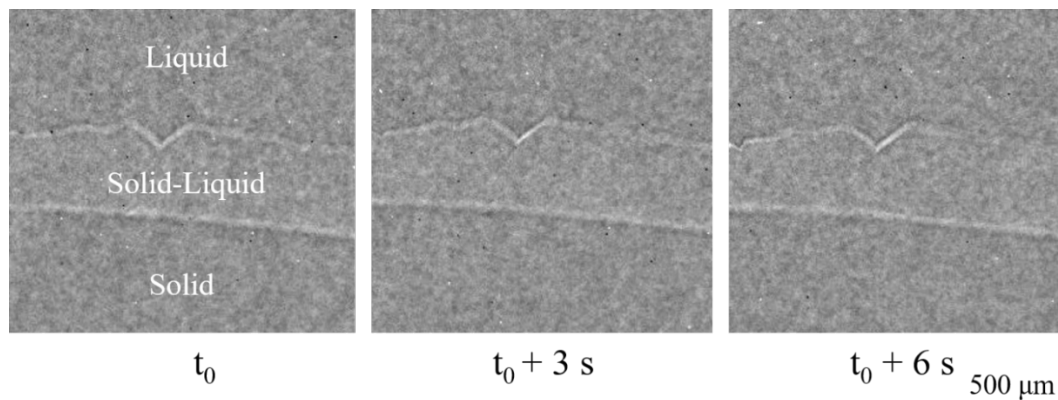
### 435 3.1. $\{111\}$ facet growth and undercooling

436 Theoretical models of the  $\{111\}$  facet growth laws exist [73, 74] and are related to the  
437 undercooling at the level of the  $\{111\}$  facets. However, the orders of magnitude of the undercooling  
438 values for the corresponding laws are very different, so that experimental validation is needed.  
439 Moreover, directional solidification is widely used for the fabrication of multi-crystalline ingots so  
440 that the knowledge of  $\{111\}$  facet dynamics needs to be known during DS. Moreover, it constitutes a  
441 critical building block to develop predictive and quantitative models [75-77]. Moreover, the presence  
442 of  $\{111\}$  facets at the solid-liquid interface leads to the occurrence of twinning ultimately competing  
443 with the central grain growing from the seed as will be discussed in the following. It is thus essential  
444 to understand their formation mechanism and the undercooling at their level which gives conditions  
445 for twin nucleation. Our main objective has thus been to determine the contribution of the  
446 undercooling of the  $\{111\}$  facets at the solid-liquid interface during Si directional solidification.  $\{111\}$   
447 facet growth laws are derived and then compared with theoretical growth models reported in the  
448 literature.

449 At the level of the solid-liquid interface,  $\{111\}$  facets appear at the sample edges and in grain  
450 boundary grooves. Grain boundary grooves are formed due to the encounter between a grain  
451 boundary and the solid-liquid interface [78]. From the theory [79], grain boundary grooves can be  
452 either faceted/faceted, faceted/rough or rough/rough depending on the crystallographic  
453 orientation of the adjacent grains. Experimentally, we are able to characterize faceted/rough and  
454 faceted/faceted grain boundary grooves [48, 80] with a large prevalence for the faceted/faceted  
455 configuration. However, conclusions concerning the predominance of one or the other grain  
456 boundary groove type cannot be drawn from these observations as rough/rough grain boundary  
457 grooves are expected to correspond to lower undercoolings compared to faceted/faceted ones and  
458 thus to smaller depth that can then fall below the spatial resolution used in these experiments.

459 Whatever conditions, facets observed in our experiments are always {111} facets as foreseen in  
 460 silicon [81]. It was checked by determining the crystallographic orientation of the grains and their  
 461 relative {111} facet orientation. In order to determine {111} facet growth laws, the grain boundary  
 462 grooves observed at the solid-liquid interface (e.g. in Figures 1 & 4) have been geometrically  
 463 characterized by their angle and depth in the case of an ideal faceted/faceted groove [82]. The  
 464 geometrical parameters of the grain boundary grooves can be measured directly on the radiography  
 465 images collected during solidification (Figures 1 & 4). The kinetic parameters, growth velocity of the  
 466 interface and normal growth velocity of the groove facets are also measured thanks to the time-  
 467 resolved observation of the solid-liquid interface evolution.

468 When comparing the growth rate of the global solid-liquid interface to the {111} facet growth  
 469 rates, it appears first that the growth rates of the {111} facets both inside the grooves and at the edges  
 470 are smaller than the one of the global solid-liquid interface. This is expected because of the slower  
 471 kinetics of the {111} planes compared to the other crystallographic orientations so that they are  
 472 lagging behind other growing orientations and generally behind the global solid-liquid interface [47].  
 473 A major consequence is that the undercooling is higher in the groove and at the level of the edge  
 474 facets compared to the one at the level of the global solid-liquid interface. This favors nucleation  
 475 events inside grooves and at the edge facets that are indeed often observed in real time during our  
 476 experiments.  
 477



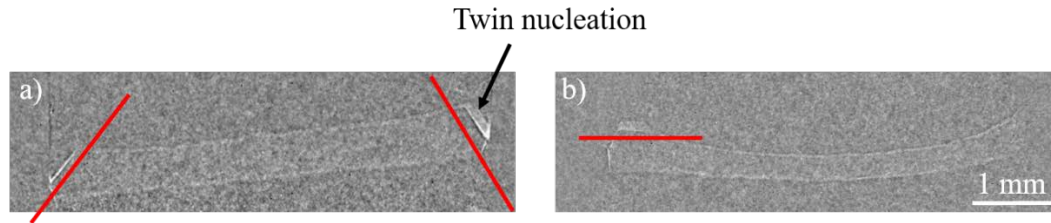
478

479 **Figure 4:** X-ray radiography images recorded during solidification, applied temperature gradient: 30  
 480 K/cm and cooling rate = -1 K/min applied on both heaters. Typical faceted / faceted grain boundary  
 481 groove revealed by division by successive images.

482 The dynamics of a faceted / faceted groove during solidification can be seen for example in  
 483 Figure 4. Both facets grow at the same growth rate as can be concluded from the constant angle and  
 484 orientation of the groove. This conclusion is also sustained by the X-ray radiography images contrast  
 485 (Figure 4.c). The white areas on the facets evidence the new grown solid between two successive  
 486 images because of the image processing performed as explained in the experimental section. These  
 487 white regions have the same thickness on both facets which indicates that both facets grow at the  
 488 same rate. This is observed in all studied cases for faceted/faceted grain boundary grooves.

489 The maximum thermal undercooling inside a grain boundary groove can be calculated knowing  
 490 the local temperature gradient and the maximum grain boundary groove depth. Details of the  
 491 calculations can be found in [48]. The measured maximum undercooling has been thus calculated  
 492 inside grain boundary grooves for several experiments with seeds oriented along  $\langle 100 \rangle$ ,  $\langle 111 \rangle$  and  
 493  $\langle 110 \rangle$  directions. In all cases, the maximum undercooling inside the grain boundary groove is found  
 494 to be always lower than 1 K ranging from  $1 \times 10^{-1}$  to  $4 \times 10^{-1}$  K and adds to the solid-liquid interface  
 495 undercooling [47]. Eventually, the mean facet velocity evolution as a function of the additional  
 496 undercooling inside the grain boundary grooves can be obtained.

497 Moreover, {111} facets are also observed at the level of the solid-liquid interface at the sample  
 498 edges as can be seen in Figures 1.c and 5. The same procedure is applied to the {111} facets at the  
 499 edges of the samples except that there is only one facet to consider in this case.



**Figure 5:** X-ray radiography images of the solid-liquid interface during growth with {111} facets at both edges of the sample for the experiments: (a) same experiment as in Figures 2 and 6.a, (b) same experiment as in Figure 6.c. Red lines indicate the traces of {111} planes.

At the level of the edge facets, the measured maximum undercooling is again always lower than 1 K. However, higher values (ranging from  $2 \times 10^{-1}$  to  $8 \times 10^{-1}$  K) compared to the undercooling inside grain boundary grooves are measured at the edges. This result is significant because the same evolution is obtained for several samples and for both grooves at the edges independently from possible sample particularities. The higher undercooling measured at the level of the edge {111} facets has a significant impact on the grain structure obtained at the end of solidification as it increases the nucleation probability during growth at the level of the edge facets. This is clearly confirmed by the grain structure obtained in the samples at the end of the experiments for which twin nucleation is frequent at the far edges of the facets (Figure 6). This major contribution of twins nucleating on edge {111} facets to grain competition and final grain structure was previously reported [7, 38] and was observed repeatedly in our experiments.

The undercooling inside the grain boundary grooves and at the level of edge facets is always lower than 1 K relatively to the global solid-liquid interface which is far smaller than the undercooling values predicted by the bi-dimensional laws (several K) for the growth rates measured during these experiments. As a consequence, bi-dimensional nucleation growth mechanism [73] can be excluded. The experimental results concerning {111} facets kinetics in our experiments can only be compared favourably to the theoretical law corresponding to a growth mechanism eased by the presence of dislocations proposed by Voronkov [74]. This is in agreement with the fact that dislocations are expected to be easily generated during silicon growth and found emerging at the level of facets as shown for example in [38, 83] and as can be seen in Figure 3.

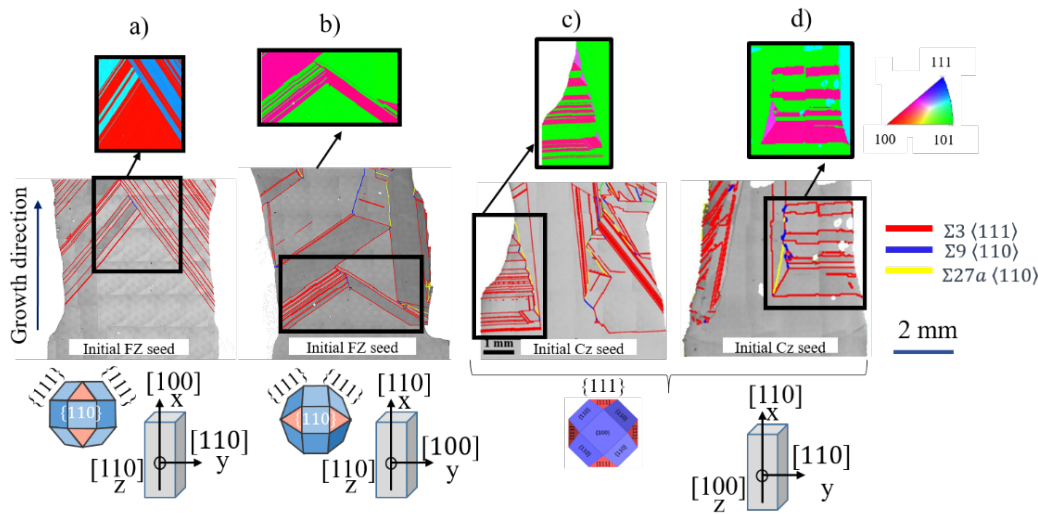
### 3.2 Twinning during solidification:

As discussed in the introduction, the crystalline quality of the ingot and the grain boundary types, in particular the twin boundary characteristics, can have a significant impact on the photoelectric properties [22, 27]. It has been shown that perfect symmetric  $\Sigma 3$  twins have no major impact on the photovoltaic performance. However, the repetition of twinning has important consequences for the final grain structure and distribution of crystallographic orientations [31]. Indeed, the importance of twinning in the development of the grain structure has been highlighted for different solidification processes ranging from directional solidification [84] to ribbon growth [33, 85-86]. In the past few years, we studied rather extensively twin formation, growth and its consequences on the final grain structure and defect formation in general [38, 46, 48, 49, 51, 53, 87].

#### 3.2.1 Twin nucleation

Four typical final grain structures of samples solidified from a seed in the GaTSBI DS furnace are shown in Figure 6. The coincidence site lattice maps (middle line in Figure 6) are shown in order to reveal the grain boundary character and in particular the twin boundaries. These samples are solidified from float-zone (FZ) monocrystalline seeds (Figures 6.a and b) and from Czochralski (Cz) seeds (Figures 6.c and d) after partial melting of the seed. The samples are solidified from seeds with different crystallographic orientations in the growth direction (Figure 6 bottom line). In all cases, side twins develop at the edges from {111} facets and compete with the main central grain issued from the seed, as it was also observed by Trempa et al. [7] in a systematic study. The fact that the behavior of

543 FZ and Cz seeds is comparable suggests that the presence of oxygen (typically:  $0.5 - 1 \times 10^{18}$  at/cm<sup>3</sup> in  
 544 Cz ingots compared to  $< 10^{15}$  at/cm<sup>3</sup> in FZ ingots) is not a predominant factor for the twin nucleation.



545  
 546 **Figure 6:** EBSD measurements revealing the grain structure and twin boundaries after growth and  
 547 cooling down in samples grown from monocrystalline seeds. Applied temperature gradient: 30 K/cm  
 548 and cooling rate applied on both heaters (a) -1 K/min (same experiment as in Figures 2, 8.a-b and 9),  
 549 (b) -1 K/min, (c) -0.2 K/min (same experiment as in Figures 7.b, 8.c-e), (d) applied temperature  
 550 gradient: 20 K/cm and cooling rate: -0.2 K/min (same experiment as in Figure 7.a). Top: Inverse Pole  
 551 Figure (IPF) map along the growth direction. Middle: CSL (Coincidence Site Lattice) map. Bottom:  
 552 Seed orientation and {111} planes.

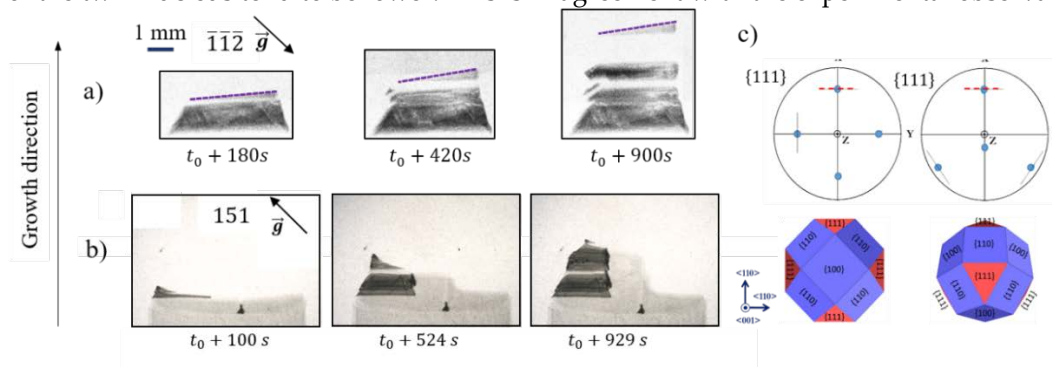
553 Figures 5.a and 5.b correspond to a snapshot at one instant during solidification showing the  
 554 solid-liquid interface of samples in Figures 6.a and 6.c, respectively. The *in situ* X-ray radiography  
 555 images (Figure 5) reveals that the solid-liquid interface is smooth during growth under these  
 556 conditions for both Cz (Figure 5.a) and FZ (Figure 5.b) seeds. No destabilization of the interface can  
 557 be observed in all cases when Cz or FZ seeds are used. Interface destabilization has only been  
 558 observed in the presence of Cu impurities as reported in [54].

559 Despite the global smooth interface, {111} facets can be clearly seen on the X-ray radiography  
 560 images at the edges of the sample (Figure 5). It was verified that they correspond to the projection of  
 561 {111} facets by determining the corresponding pole figures using the measurements performed by  
 562 EBSD. The {111} facet orientation is highlighted by the red lines on Figure 5. Twin nucleation takes  
 563 place regularly on these {111} facets as can be seen for example on Figures 5.a (right) and 5.b (left). A  
 564 video of radiograph images showing the dynamic evolution of the solid-liquid interface during the  
 565 experiment corresponding to Figures 2, 5.a and 6.a is provided as supplementary material. It  
 566 evidences, twin nucleation at the {111} edge facets and the formation of grain boundary grooves at  
 567 the solid-liquid interface due to the subsequent grain competition.

568 Diffraction spot images collected at different times during the solidification of the two samples  
 569 (corresponding to the experiments and grain structure in Figures 6.c and d) are shown in Figure 7.  
 570 The diffraction spots in Figure 7.a display the twinning zone at the right side of the sample in Figure  
 571 6.d, whereas the diffraction spots in Figure 7.b display the twinning zone at the left side of the sample  
 572 in Figure 6.c. The purple dotted line is added in Figure 7.a to indicate the corresponding solid-liquid  
 573 interface shape as observed in the radiographs. It is worth reminding that diffraction imaging shows  
 574 only the crystalline solid areas. The observation of the upper part of the diffraction spots shows that  
 575 the twin nucleation occurs at the edges of the samples at the solid-liquid-vacuum-crucible phase line  
 576 as also seen in the radiographs (Figure 5 and supplementary material). A sudden increase of the solid  
 577 height at the solid-liquid interface is observed at the instant of each new twin nucleation on the time-  
 578 resolved radiography images. From these height differences a value of the nucleation undercooling  
 579 has been estimated and it ranges from 0.1 K to 0.5 K for the experiment corresponding to Figures 5.b,

580 6.c and 7.b, which is also consistent with the results reported in section 3.1. These measurements  
 581 confirm that the undercooling measured in grain boundary grooves and at the edges are sufficient  
 582 for twin nucleation on the {111} facets.

583 A 3D model was proposed by Jhang *et al.* [88] to determine the nucleation probability at the level  
 584 of {111} facets. This model was specifically applied to several of our experimental cases. The twin  
 585 grain nucleation probability was found to be higher when there is a contact between the {111} facet  
 586 and crucible walls. This is generally the case in our thin sample configuration. Additionally, the  
 587 authors showed that the attachment energy and the contact area with crucible walls are the key  
 588 factors for the heterogeneous nucleation of twins. Low attachment energy and lower contact area  
 589 concur to the highest twinning probability on the {111} facets. When applied to our experimental case,  
 590 it is found that twin grain nucleation probability is higher at the sample edge {111} facets compared  
 591 to the ones situated in grain boundary grooves, where the attachment energy and the bottom contact  
 592 area of the twin nucleus tend to be lower. This is in agreement with the experimental observations.



593  
 594 **Figure 7:** Image sequence of diffraction spot images – topographs corresponding to twinning zones  
 595 (a) twinning zone corresponding to the right side of sample Figure 5.d. The purple dotted line  
 596 correspond to the solid-liquid interface, (b) twinning zone corresponding to the left side of sample  
 597 Figures 5.c and 6.b, (c) stereographic projections of the {111} planes of the seed (left) and the first  
 598 twin (right) with both horizontal projections for the experiment in (b) and the corresponding 3D  
 599 representation of the plane arrangements (below).

600 Moreover, the twin growth rate at the nucleation instant (about  $15 \mu\text{m/s}$ ) exceeds the one of the  
 601 global solid-liquid interface ( $2 \mu\text{m/s}$ ). The consequence is that the twin grains that nucleate on the  
 602 edges grow vertically very fast and in advance compared to the global solid-liquid interface inducing  
 603 the triangular images recorded during solidification on the topographs. Such a triangular shape of  
 604 the twins growing at the solid-liquid interface has been repeatedly observed in our experiments  
 605 during solidification. When the crystal arrives at the liquidus isotherm position, stabilization of the  
 606 growth rate is observed until the global solid-liquid interface arrives at the liquidus. As a subsequent  
 607 step, a growth rate plateau is measured, after which the next twin nucleation can take place [38]. The  
 608 nucleation of the twin and growth upwards along the directional solidification direction goes along  
 609 with the propagation of the twin grains towards the center as revealed by the topographs (Figure 7).

610 A main result of our work is that only  $\Sigma 3$  type twinned grains nucleate during growth. This  
 611 conclusion can only be drawn because we are able to monitor the growth *in situ* with X-ray imaging.

### 612 3.2.2 Successive Twinning

613 The successive twinning zones are immediately identifiable on ingots after solidification. It is  
 614 evidenced on both the grain structure EBSD maps (Figure 6, upper line) and diffraction images for  
 615 example on Figures 2, 3 and 7. The successive twinning zone is observable by the alternation of two  
 616 crystallographic orientations (Figure 6) on the EBSD maps and by the striped/hatched aspect of the  
 617 topographs (Figures 2, 3 and 7). Only two crystallographic orientations alternate and they share a  
 618 common {111} plane. The fact that crystallographic orientations are found successively can be  
 619 explained by the orientation of both seed and first twin grain. The stereographic projection of {111}  
 620 planes of both the seed and first twin grain (green and pink color in Figure 5.c, respectively)



621 corresponding to Figures 6.c and 7.b is shown in Figure 7.c. These two stereographic projections are  
622 sufficient to describe the grains of the entire twinning zone because only two crystallographic  
623 orientations are successively repeated. The seed (Figure 7.c left) presents four {111} planes, two with  
624 a vertical projection parallel to the growth direction, and two {111} planes presenting a horizontal  
625 projection perpendicular to the growth direction and facing the liquid. The first nucleus initiated at  
626 the left edge of the sample nucleates on the {111} facet having a horizontal projection (Figure 7.c right).  
627 This is confirmed by the existence of a common {111} plane between the seed and the horizontal twin.  
628 Then, as a subsequent step, the first twin has only one {111} plane presenting a horizontal projection  
629 perpendicular to the growth direction and facing the liquid. The next  $\Sigma 3$  twin nucleating on this {111}  
630 facet has the same orientation as the initial seed so that the crystallographic orientation is alternately  
631 retrieved.

### 632 3.2.3 Twin growth

633 Once a twin nucleus appears at the sample edges on a {111} facet, it grows laterally as shown by  
634 the *in situ* radiography and topography images. Twin grains grow towards the central part along  
635 their respective {111} facets until they meet the grain that took over from the seed or other twinned  
636 grains (Figure 6). Indeed, the progress of the pristine grain issued from the seed can be stopped by  
637 the competition with twinned grains as for example in Figures 6.a and b. This is in fact totally  
638 controlled by the relative orientation of the seed that determines the orientation of the {111} facets  
639 initiating twinning as can be seen on the sketch showing the {111} facet orientations of the seeds in  
640 Figure 6 (bottom line) and as studied by Trempa *et al.* [7].

### 641 3.3 Grain competition and higher order twin boundaries

642 The encounter of twinned grains with other grains creates grain boundaries, which leads to the  
643 formation of grain boundary grooves at the solid-liquid interface (see as well supplementary  
644 material). The grain boundary type formed is directly linked to the adjacent grain orientations. As  
645 seen above, the  $\Sigma 3$  type twinned grains are the only ones to nucleate during growth so, higher order  
646 twin boundaries such as  $\Sigma 9 \langle 110 \rangle$  and  $\Sigma 27a \langle 110 \rangle$  are in all the experimental cases (FZ or Cz seeds)  
647 only the result of grain encounter and competition. A statistical analysis on the percentage of the  
648 different types of twin boundaries in relation to the total number of twin boundaries was obtained  
649 from EBSD measurements after the last solidification experiment on several samples from FZ seeding  
650 to exclude the influence of impurities. It is clearly seen that the majority of twin boundaries are of  $\Sigma 3$   
651 type (typically more than 90 %). Whereas the proportion of  $\Sigma 3$  twin boundaries is regularly retrieved  
652 for these pure seed samples, the proportion of higher order twin boundaries depends on the growth  
653 and nucleation events. As the samples grow, more  $\Sigma 3$  twin grains nucleate so that encounters are  
654 more likely to occur increasing the amount of higher order twin boundaries. The experimental results  
655 shown in Figures 2 and 6.a have been recently simulated using a 3D cellular automaton model of the  
656 grain structure [77]. The dynamics of {111} facets and the nucleation, growth and competition of  
657 grains in twin relationship could be modelled and compared successfully to the experiments. The  
658 application of this model to larger scale ingot solidification is foreseen. It is worth noting that a  
659 different behaviour was observed in samples containing higher levels of impurities for which  
660 although the predominance of  $\Sigma 3$  twin grains is still maintained, other grain nucleation events can  
661 take place [54].

### 662 3.4 Strain building during growth

663 The study of local strain development during growth (deformation) is of great importance as  
664 local deformations can lead to the formation of dislocations, which are major defects affecting the  
665 material electrical properties as seen in the introduction. On the one hand, dislocations can develop  
666 during the cooling down of the sample following the solidification due to the Alexander–Haasen  
667 model [89]. On the other hand, the local nucleation of dislocation clusters is expected to take place  
668 during crystal growth [90, 91].

669 Before presenting results on strain building, it is important to specify that during the heating  
670 segment of the experimental procedure, dislocations appear in the sample as described in [72] and  
671 remain in the seed kept after partial melting. During solidification, these dislocations develop,  
672 usually along the growth direction and can encounter grain boundaries. Dislocations can be stopped  
673 and accumulate, unless they are able to cross-slip at the level of a grain boundary which is most likely  
674 to occur at  $\Sigma 3$  type twin boundaries because of the presence of a  $\{111\}$  possible gliding plane [38]. For  
675 example, in nickel [92], coherent  $\Sigma 3$  twin boundaries act as effective barriers to slip except in the case  
676 of screw dislocations which can direct or cross slip across the boundary using the  $\{111\}$  boundary  
677 plane itself. During growth, dislocations can propagate or cross slip and propagate along the  $\{111\}$   
678 planes until they reach a free surface or meet another interface.

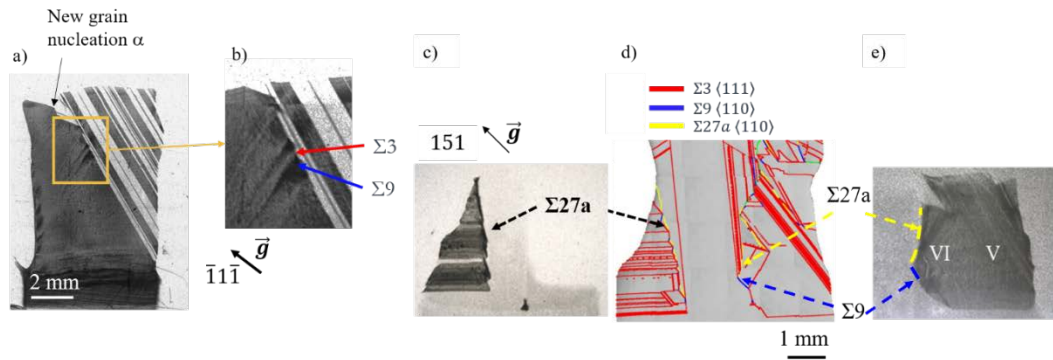
#### 679 3.4.1. Strain and $\Sigma 3\{111\}_{1,2}$ twins

680 Strain is observed at the location of twin nucleation as can be clearly seen on the topographs in  
681 Figures 2.d and 3. It is revealed by the increased black contrast observed at the location of twin  
682 nucleation. Although the apparition of these contrasts is concomitant to twin nucleation and  
683 beginning of growth, it is not possible up to determine if the deformation is present just before or just  
684 after the nucleation event. This is one aspect that will be studied in more details in the future. A video  
685 of topographs showing twinning and strain formation during solidification in the experiment  
686 corresponding to Figure 3 is provided as supplementary material. As explained in Section 2,  
687 dislocations can be clearly evidenced as well as their interaction with twin boundaries. Besides, a  
688 black contrast observed at the level of twin nucleation (Figure 2) is retrieved on the projected image  
689 of the solid-liquid interface. It can be associated to the gliding of dislocations along the  $\{111\}$  facets  
690 that exit at the solid-liquid interface confirming that dislocations can in some cases glide along these  
691 planes as also seen in [38].

#### 692 3.4.2. Strain building due to competition

693 Local strain heterogeneities are also created due to grain competition. This is clearly evidenced  
694 in the topographs shown in Figure 8. Comparing the CSL map (Figure 6.a) with the respective  
695 diffraction image (Figures 8.a and b), it can be concluded that no local strain accumulation occurred  
696 at the level of  $\Sigma 3$  twin boundaries except at the nucleation location as discussed above. On the  
697 contrary, a localized strain field is characterized at the position of  $\Sigma 9$  twin boundaries as evidenced  
698 by the black contrast on the topograph (Figure 8.b). This is expected as in the case of  $\Sigma 9$  twin  
699 boundaries, cross slip is unlikely. Only the dislocations having the Burgers vector directions of a  
700 common rotation axis  $\langle 110 \rangle$  to build a symmetric grain boundary can cross slip; for other rotation  
701 axes, cross slip is not possible. As a consequence, dislocations and strain accumulate at the level of  
702 the  $\Sigma 9$  twin boundary. The same observation is made each time  $\Sigma 3$  and  $\Sigma 9$  twin boundaries are  
703 formed due to competition for all successive twins. Moreover, it is worth noting that the strain created  
704 by the grain competition seems to propagate over longer distances in the samples. This can be seen  
705 in the few millimeters wide expansion of the black contrast from the competition zone on the right  
706 side of the sample (Figure 8.b).

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**Figure 8:** (a) Topograph for the experiment in Figures 2, 5.a and 6.a, (b) Close up at the level of competing twin grains, (c) topograph for the experiment in Figures 5.b, 6.c and 7.b-c, (d) corresponding coincidence site lattice map and (e) topograph of a grain on the right side.

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This observation is not a single observation corresponding to a particular experiment but was repeatedly observed during solidification. In successive twinning configuration, due to the alternated twin crystallographic orientations, the same grain boundary types are retrieved alternately. In the experiment presented in Figures 8.a-b,  $\Sigma 3$  and  $\Sigma 9$  twin boundaries are formed and are observed in sequence which means that local deformations are built successively according to the grain boundary type. On the experiment shown in Figures 8.c-e,  $\Sigma 3$  and  $\Sigma 9$  twin boundaries are also formed and are observed in sequence as well as  $\Sigma 27a$  type twin boundaries. For the later grain boundary type, high strained zones (Figures 8.c-d) are created which could be due to the accumulation of already present dislocations that cannot cross slip or to the emission of dislocations from imperfect grain boundaries from the crystallographic point of view. Dislocation emission is clearly observed at the level of a  $\Sigma 27a$  type twin boundary (Figure 8.e).

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### 3.4.3. Grain nucleation related to strain accumulation

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Strain building during growth has a high impact on the generation of dislocations but it is also associated to spontaneous new grain nucleation. In the experiment shown in Figures 8.a-b, after twin nucleation, the grain boundary formation at the encounter of twins coming from both sides continues regularly until a new grain nucleates in the grain boundary groove. This grain nucleation event happens regularly at the encounter between twin grains and the central grains. The nucleation of grain  $\alpha$  (Figures 8.a and 9) is of particular interest. This grain has a different crystallographic orientation compared to the seed and to the twins on the right and left as evidenced by the topograph in Figure 8.a and by the inverse pole figure map in Figure 9.a. However, it is a twinned grain that nucleated on the left  $\{111\}$  facet of the grain boundary groove as shown by the  $\Sigma 3$  twin boundary on its left hand side (Figure 9.b).

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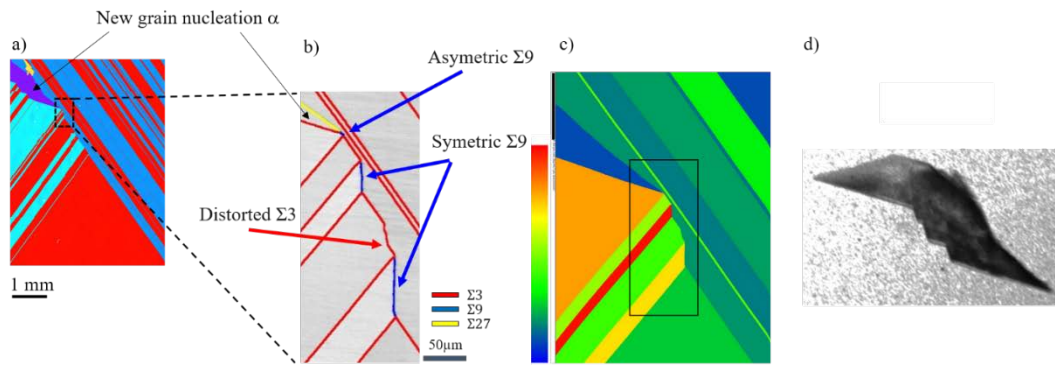
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Several phenomena are at the origin of the nucleation of this particular grain at the level of the grain boundary groove. The first reason is that the undercooling inside a grain boundary groove is higher than at the level of the solid-liquid interface as discussed in section 3.1 and in our previous work [48] which facilitates grain nucleation in this area. However, it is not a sufficient reason to explain the nucleation at this particular instant as a grain boundary groove was repeatedly formed at the encounter between twins nucleating from the left and right during the experiment. In fact, the grain competition dynamics imposes the formation of twin boundaries non-symmetric or of distorted grain boundaries and induces at the same time accumulation of crystal structure deformation both described in the following for this particular experiment.



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**Figure 9:** (a) Inverse Pole Figure (IPF) map along the growth direction (same experiment as in Figures 2, 5.a, 6.a and 8.a-b), (b) high resolution CSL map of the competition region, (c) GOS map of the region of the new nucleated grain ( $\alpha$ ), (d) Topograph of the grain ( $\alpha$ ).

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The growth dynamic competition between twin grains coming from the left and right leads to the formation of a distorted  $\Sigma 3$  twin boundary (Figure 9.b) at first twin encounter. This distorted  $\Sigma 3$  twin boundary gradually evolves to the ideal orientation and straightness of a symmetric  $\{111\}$   $\Sigma 3$  twin boundary during growth. Besides, due to the relative crystallographic orientations of the twin grains,  $\Sigma 3$  and  $\Sigma 9$  twin boundaries are alternately formed. Due to the competition and growth dynamics, some of the  $\Sigma 9$  are forced to adopt an asymmetric configuration  $\{111\}/\{115\}$  (Figure 9.b). The  $\Sigma 9$  twin boundary asymmetric configuration corresponds to a higher grain boundary energy [94]. In fact, it was reported by TEM (Transmission Electron Microscopy) studies coupled to DFT (Density Functional Theory) [94] that on the contrary to the  $\Sigma 9 \{122\}_{1,2}$  grain boundary, the atomic structure of the asymmetric  $\Sigma 9 \{111\}/\{115\}$  one shows strong distortions. Its energy is about twice as high as that of the symmetric  $\Sigma 9 \{122\}_{1,2}$ . As a consequence, this situation is unstable from an energetic point of view and not favourable. Just before the nucleation of grain  $\alpha$ , at the level of the encounter with a new twin grain from the right, a tiny asymmetric  $\Sigma 9 \{111\}/\{115\}$  twin boundary is created. As seen above, non-symmetrical grain boundaries are deformed at the atomic scale [94] and offer greater resistance for dislocation crossing, thereby creating higher strain [92] and structure deformation, promoting dislocation emission. Indeed, the competition goes along with an increasing accumulation of strain when  $\Sigma 9$  twin boundaries are present which is revealed by both diffraction images *in situ* during growth and grain orientation spread map (GOS) determined from *ex situ* EBSD measurements after cooling down of the sample (Figure 9.c).

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The nucleation in presence of strain accumulation can be triggered by energetic reasons as well as by the existence of the associated dislocations [46]. Indeed, dislocations can favour nucleation by decreasing the nucleation undercooling as discussed in section 3.1. On Figure 9.d showing a topograph corresponding to grain  $\alpha$ , it can be seen that the highest strain level (darker contrast) is localized at the position of its nucleation and beginning of its growth. During its growth, the strain level decreases as evidenced by the lighter contrast on the top left side (Figure 9.d). However, inside the grain  $\alpha$ , local strain and dislocation emission are observed on the right upper region (Figure 9.d). It is due to another phenomenon namely, to the competition between grains on the right and this newly nucleated grain that tends to extend in the solidification direction. Due to the relative crystallographic orientations of both grains, a  $\Sigma 27$  twin boundary is formed. This type of twin boundary is prone to crystal structure deformation and associated dislocation emission as seen above and in [38, 95].

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Generally, the new type  $\alpha$  grain nucleation contributes to obtain a better crystalline quality in the upper part of the ingot. A lower strain level is observed in the upper growing grains as can be seen in the GOS map (Figure 9.c). Grains above this nucleation event are generally less deformed at the scale of the grain structure and more locally inside the grain that nucleated (Figure 9.d). Strain redistribution cannot be invoked in our experimental case as the existing strain field built during growth remains localised. Yet, the nucleation of grain  $\alpha$  did contribute to a lower strain level in the following of growth. In summary, the nucleation can be triggered by energetic reasons discussed

786 above, by grain competition space constraints as well as by the existence of a high density of  
787 dislocations that can favour nucleation by decreasing the nucleation undercooling value. This result  
788 can be generalized because in other samples with the same crystallographic orientation, processed  
789 under similar conditions, comparable grain structures and similar nucleation events to those of grain  
790  $\alpha$  are observed. It is worth noting that the nucleation of grain type  $\alpha$  is never observed at early growth  
791 stages but later during growth when strain has accumulated.

792 Besides, despite the subsequent deformations that can be expected and that are observed at the  
793 scale of the sample during cooling down [46], the local strain variations created during growth and  
794 due to grain nucleation, competition and strain building during growth are retrieved after cooling  
795 down as can be seen on the GOS map that was recorded *ex situ* and with rocking curve imaging in  
796 our previous work [38]. These deformed regions remain in the material and can be already associated  
797 to dislocations but can be at the origin of further dislocation emissions in subsequent steps of the  
798 solar cell fabrication process.

#### 799 4. Conclusions

800 The combination of X-ray radiography and topography imaging achieved *in situ* during the  
801 solidification of Si using the GaTSBI tool has proven its efficiency to unveil crystal growth  
802 mechanisms. Time-resolved phenomena that occur during crystal growth such as grain nucleation,  
803 grain competition, twin formation, defect generation and their evolution and interaction with grains  
804 are followed and investigated in real time.

805 The growth of {111} facets at grain boundary grooves and at the edges of the sample was  
806 investigated. Nucleation of twin crystals are found to occur preferentially on {111} facets at the edges  
807 of the sample where solid – liquid – vapor triple point lines exist and at the location where the sample  
808 is in contact with the crucible as well. Nucleation can also take place at the level of {111} facets in  
809 grain boundary grooves formed by a grain boundary at the solid-liquid interface. In our growth  
810 parameter range, the undercooling at the level of {111} facets at the edges and in grain boundary  
811 grooves is always lower than 1 K relatively to the solid-liquid interface, which is sufficient for twin  
812 nucleation. Since the undercooling on facets at the edges is higher than the undercooling on facets  
813 inside grain boundary grooves, there is a higher nucleation probability at the edges resulting in  
814 regular and successive twinning from the sides. Additionally, when studying the {111} facet growth  
815 laws, it appears that the experimental results can only be compared reasonably to the quadratic  
816 growth law which relies on the presence of dislocations that enhances growth which is highly  
817 probable considering other experimental results revealing the presence of dislocations during growth.

818 Moreover, we show that twinning observed with our processing conditions is a growth rather  
819 than a deformation phenomenon. Only  $\Sigma 3$  twins nucleate during growth, higher order grain  
820 boundaries being solely the result of grain competition. One consequence is that the majority of the  
821 grain boundaries in the solidified ingot are of  $\Sigma 3$  types in samples grown from pure monocrystalline  
822 seeds at least while the competition effect is not dominant. The competition and formation of higher  
823 order twin boundaries go along with deformations and the accumulation of dislocations. The  
824 dislocation behaviour when encountering grain boundaries varies according to the types of grain  
825 boundaries. Lower or no dislocation accumulation and deformation are observed at the level of  $\Sigma 3$   
826 twin boundaries. Indeed, there is a higher probability that dislocations can move along  $\Sigma 3$  twin  
827 boundaries due to the {111} common glide planes that exists at the level of  $\Sigma 3$  twin boundaries  
828 compared to the case of higher order twin boundaries. Strain is observed in all cases at the level of  
829 higher order twin boundaries either because cross-slip of dislocations is not possible and/or because  
830 they are responsible for the emission of dislocations as observed in particular for  $\Sigma 27a$   $\langle 110 \rangle$  grain  
831 boundaries. Such accumulation can be at the origin of significant crystal structure deformations in  
832 the samples. Specifically, areas in which  $\Sigma 27a$   $\langle 110 \rangle$  grain boundaries are present are more distorted  
833 than the average distortion of the sample. It was also observed that dislocations are emitted at the  
834 level of  $\Sigma 27a$   $\langle 111 \rangle$  grain boundary. On top of that, the character of the grain boundary (coherent –  
835 incoherent) and its  $\Sigma$  – type, its deviation from the optimum orientation and the symmetry or non-

836 symmetry of the boundary planes have an impact on the distortion of the formed boundary and on  
837 the emission of dislocations in the vicinity of the surrounding grains as well.

838 Strain building during growth has a high impact on the generation of dislocations but it is also  
839 associated with spontaneous grain nucleation. This kind of nucleation event contributes to the  
840 recovery of a lower strain level in the upper growing grains. The nucleation in presence of strain  
841 accumulation can be triggered by energetic reasons as well as by the existence of associated  
842 dislocations. Indeed, dislocations can favour nucleation by decreasing the nucleation undercooling.  
843 Another main result is that local strain at the grain scale, which is revealed and monitored during  
844 solidification, is retrieved in the ingot after cooling down even though additional strain is created by  
845 the cooling down step. However, no detectable additional twin nucleation is observed during cooling  
846 down.

847 The enhancement of the recording frequency now provides the opportunity to study the  
848 propagation, multiplication and rearrangement of dislocations by interactions with themselves, grain  
849 boundaries and the solid-liquid interface, during the whole process. This includes dislocation  
850 generation and motion in the seed crystal at high temperature up to the melting point as well as  
851 dislocation multiplication and rearrangement during melting, solidification and cooling. In the future,  
852 further experiments will be conducted to develop and deepen the investigation of these phenomena.  
853 Our work clearly shows that local strain can be built during growth and the synchronisation of X-ray  
854 radiography and Bragg diffraction imaging (topography) will allow an enhanced monitoring of strain  
855 building. The impact of impurities is not discussed in details in the present manuscript. However,  
856 the effect of carbon, oxygen and metallic impurities on grain nucleation and competition is in  
857 progress as this is an essential aspect for industrial processes.

858 **Supplementary Materials:** Video S1: Video of radiographs showing the dynamic evolution of the solid-liquid  
859 interface during the experiment corresponding to Figures 2, 5.a and 6.a, Video S2: Video of topographs showing  
860 twinning and strain formation during solidification in the experiment corresponding to Figure 3.

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862 validation, N.M, G.R.1, G.R.2., I.P., J.B.; formal analysis, N.M, G.R.1, G.R.2., J.B., M.B., H.O., T.R.B, M.T.,V.S.,  
863 F.G., L.B., I.P.; investigation, N.M, G.R.1, G.R.2., M.B., H.O., T.R.B, M.T.; resources, J.P.V., A.R., E.B., L.B., F.G.;  
864 data curation, N.M; writing—original draft preparation, N.M.; writing—review and editing, N.M.;  
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