



HAL
open science

Undercooling measurement and nucleation study of silicon droplet solidification

Maria G. Tsoutsouva, Thierry Duffar, Christian Garnier, G. Fournier

► **To cite this version:**

Maria G. Tsoutsouva, Thierry Duffar, Christian Garnier, G. Fournier. Undercooling measurement and nucleation study of silicon droplet solidification. *Crystal Research and Technology*, 2015, 50 (1), pp.55-61. 10.1002/crat.201400165 . hal-01121276

HAL Id: hal-01121276

<https://hal.science/hal-01121276>

Submitted on 20 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Undercooling measurement and nucleation study of silicon droplet solidification

M.G. Tsoutsouva^{1,2}, T. Duffar^{2,}, C. Garnier², and G. Fournier²*

The most efficient method to investigate nucleation phenomena is to measure the undercooling temperature at the beginning of the solidification process since it gives information about whether or not a certain substrate favors the heterogeneous nucleation. In this work a suitable experimental setup has been designed and developed for the study of nucleation phenomena, where a silicon droplet is directly placed and melted on a substrate. The melting-solidification process was filmed and the undercooling temperature was simultaneously measured by monochromatic and bichromatic pyrometers. For all the studied substrates the melting process started from the bottom of the sample where there was a contact with the substrate. In the case of zirconium and fused silica substrates, on which we focus in the present paper, the temperature profile of the silicon sample presented a temperature plateau during melting and a typical cooling curve showing undercooling, recalescence and a plateau denoting that solidification occurred under isothermal conditions. It was also found that the nature of the substrates influences the measured undercooling values and the shape of the solidified silicon droplets.

1 Introduction

The most popular commercial method for producing silicon based solar cells involves a process in which molten silicon is directly cast into a mould and allowed to solidify into an ingot. However, the fact that molten silicon reacts with almost every known material creates severe obstacles to the photovoltaic (PV) technology. The interfacial interactions between the molten silicon and the mould and the subsequent heterogeneous nucleation that takes place on the crucible surface are determinant for the beginning of solidification. Grains nucleate on the crucible walls and elongate from the periphery towards the center

of the ingot, leading to a polycrystalline material. Grains and grain boundaries play a crucial role in PV technology since they directly determine the electrical performance of the solar cell.

In literature there are some research teams who have investigated the silicon-crucible interaction by measuring the wetting angle between a silicon droplet and the nucleating substrate (sessile drop experiments) [1–3]. This technique gives interesting information mainly about adhesion and infiltration phenomena rather than nucleation. Unfortunately there has not been found yet a way to directly relate the nucleation process to the wetting results.

Concerning the investigation of nucleation phenomena, a more efficient method is to measure the undercooling temperature during the solidification process since it gives information about whether or not a certain material favors the heterogeneous nucleation. In bibliography there are some research works dealing with undercooling measurements in an electromagnetic levitation setup either concerning pure silicon or silicon containing a controlled percentage of impurities. Those kinds of experiments give information about the role that the presence of nucleation centers, inside the droplet, has on the final microstructure of silicon but do not take under consideration the role that the substrate (crucible or mould walls) plays on the nucleation of silicon [4–9].

The influence that the substrate has on the undercooling of silicon has not been studied thoroughly, but some investigations in the area have been done. Appapillai et al. [10, 11] determined the nucleation properties using differential scanning calorimetry to measure the undercooling below the melting temperature of molten

* Corresponding author: e-mail: thierry.duffar@grenoble-inp.fr,
Phone: +33 4 76 82 52 13

¹ European Synchrotron Radiation Facility, 6 Rue Jules Horowitz,
Grenoble 38043, Cedex 9, France

² SIMaP-EPM, PHELMa, BP75, Saint Martin d’Heres 38402, France

silicon in contact with silicon oxides and nitrides. Various coatings on the silicon samples were tested for their influence on nucleation. Both dry and wet oxides coatings presented higher interfacial stability resulting in higher undercooling values than the nitrides coatings. However the undercooling measurements presented significant variations probably due to the coatings non-uniformity and the overall samples deformations during melting and solidification process.

A scientific research closely related to the present work has been done by Brynjulfson and Arnberg [12]. They studied the nucleation undercooling phenomena during the solidification of silicon on SiO_2 , coated with oxidized Si_3N_4 , and Al_2O_3 by the sessile drop method. Substrates provided by the commercial crucible producer for photovoltaic applications, Vesuvius, were also investigated. They concluded that the coating parameters such as thickness, roughness and the amount of oxygen in the coating have no significant influence on the undercooling of silicon. However they used a thermocouple placed below the sample holder in order to measure the undercooling temperature and this method cannot give such precise values of the undercooling. In the present work, it is planned to improve these experiments in three directions: a silicon piece is placed and melted directly on a substrate (this avoids the problems of non-uniformity of the coating and the deformation of the sample), use of pyrometers for measuring the temperature directly on the silicon and in addition the melting-solidification process is visualized in-situ. The final crystalline structure of the solidified silicon droplet is also investigated.

In order to perform these experiments a special installation has been designed, developed and optimized and is presented extensively in the experimental part. Representative results concerning the solidification of silicon on zya-rock and silica substrates are discussed in the second part of the article.

2 Experimental procedure

A special experimental setup has been implemented, as shown in figure 1, to measure the undercooling temperature and give access to the investigation of the nucleation phenomena during the solidification of silicon on a substrate. An electronic grade silicon square piece is placed on a substrate which is housed in a silica crucible. The silica crucible has been chosen among other materials since it is known that it does not favor silicon nucleation [13]. The substrate is held and centered on the bottom of the crucible and its dimensions are 10

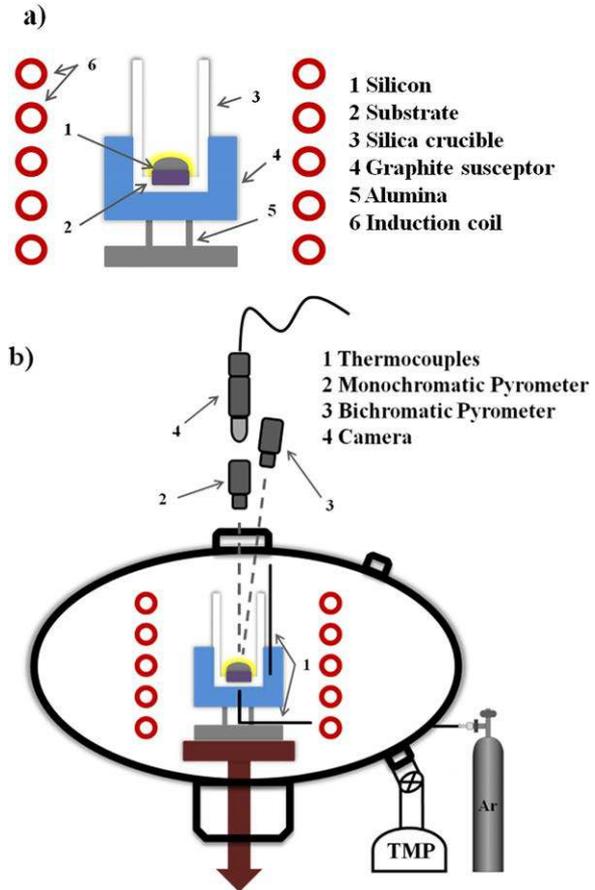


Fig. 1 Schematic illustration of the experimental set-up. a) Central part of the setup. b) General view of the experiment with measurement facilities.

$\times 10$ mm. The silicon mass is 0.8 ± 0.2 gr, depending on the material of the substrate so as after total melting it becomes hemispherically shaped and covers the whole surface of the substrate. This is in order to keep the Si/substrate area constant from one experiment to another. The heating and thus the melting of silicon is realized by electromagnetic induction with the aid of a Celes Generator with 50 kW power operating at 50 kHz. Since silicon and silica are bad conductors of electricity at room temperature, a graphite susceptor is used in order to heat the silicon by conduction through the silica crucible and the substrate and also by radiation through the crucible. As it can be seen in figure 1a the height of the graphite susceptor is smaller than the height of the silica crucible. This choice has been made for the two following reasons: i) C propagation inside the silica crucible, that would cause silicon sample pollution, should be avoided. It is well known that C interacts with Si leading either to the precipitation of SiC or to carbon solidification in interstitial positions in the silicon, affecting the

nucleation process in both cases [14]. ii) Graphite crucible radiates when heated above 700 °C. The reflection of the graphite radiation on the surface of the hemispherical melted silicon affects the temperature measurement by pyrometers as will be discussed below. The decrease of the graphite height eliminates this non desired vertical reflection of the radiation on the silicon surface, allowing the measurement of the exact Si temperature during the whole process.

The above described system is housed inside a water cooled stainless steel vacuum chamber evacuated to a pressure of 3×10^{-6} mbar with a turbomolecular pump (TMP on figure 1b) and backfilled with ultra high purity argon gas (99.999%) to a pressure of 1000 mbar (figure 1b). The temperature inside the graphite crucible is measured during the whole process by two mobile type C thermocouples (W5%Re – W26%Re) operating in the range of temperature 0 °C to 2320 °C. As already mentioned, these thermocouples are placed too far from the silicon sample to measure precisely the rapid temperature recalcence significant of nucleation. Then, silicon temperature during the melting-solidification process and the undercooling is measured in parallel by means of an IRCON Modline 5 52–2020 monochromatic pyrometer operating in the temperature range 600 °C to 2000 °C (spectral range 0.85 μm to 1.1 μm) and an IRCON Modline 5 5R-1810 bichromatic pyrometer operating in the temperature range 700 °C to 1800 °C (spectral range 0.75 μm to 1.05 μm). They are both placed on a window at the top of the vacuum chamber. The use of two different pyrometers helps in estimating accurately the actual temperature of the silicon. A monochromatic pyrometer gives the mean temperature value, influenced by the emissivity factor specified to the pyrometer [15]. In case of silicon the temperature value given by the monochromatic pyrometer can vary significantly since the emissivity of solid silicon is 0.6, greater than that of liquid silicon, 0.2 [16]. In these experiments, the emissivity of the monochromatic pyrometer has been adjusted to 0.6. On the other hand a bichromatic pyrometer gives the maximum sample temperature value without having to take into account the emissivity variation [15].

From the first experiments, it became obvious that the silicon surface change, from solid to liquid and vice-versa, influences significantly the temperature values given by the pyrometers. Thus a camera was installed above the monochromatic pyrometer as shown in figure 1b and the whole melting-solidification process has been recorded in real time, through the pyrometer viewing window.

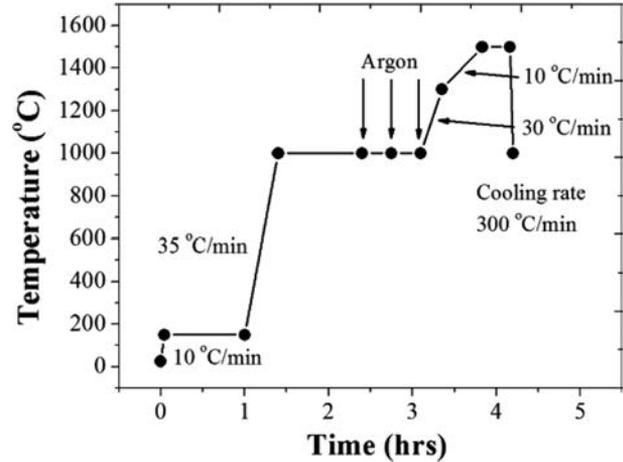


Fig. 2 Schematic temperature profile as measured by the thermocouple placed inside the graphite susceptor.

Figure 2 presents the experimental melting-solidification procedure giving the heating and cooling rates in the different process steps.

Two degassing steps are taking place, the first one at 150 °C and the second one at 1000 °C. At 1000 °C the chamber is rinsed twice and then is backfilled to atmospheric pressure with Ar in order to start the melting process. Approaching the silicon melting temperature the heating rate is decreased in order to detect the melting plateau due to the enthalpy of melting absorbed by the Si. After melting the residual power gives an increase of temperature up to [110 °C to 200 °C] which depends on the material of the substrate. Then the sample is maintained about 5–10 min at this temperature in order to assure its full melting. The electrical power is cut abruptly and the silicon droplet starts to cool down at 300 °C/min, reproducibly from one substrate to the other.

In summary, the output of each experiment is the two recorded temperature profiles, the video film showing the melting and solidification process and the solidified silicon droplets samples. In the frame of this research different substrates (oxides, carbides, borides and nitrides) have been studied, however, in the present paper we focalize on the results obtained after the solidification of Si on zyarock and fused silica substrates. Zyarock is the standard material used for the industrial crucibles in the photovoltaic industry. It is a fused silica product with the following typical composition: silica 99.6%, alumina 0.12%, iron oxide 0.10%, titania 0.027%, magnesia 0.013% sodium oxide 0.008%, calcia 0.007% and potassium oxide 0.005% [17].

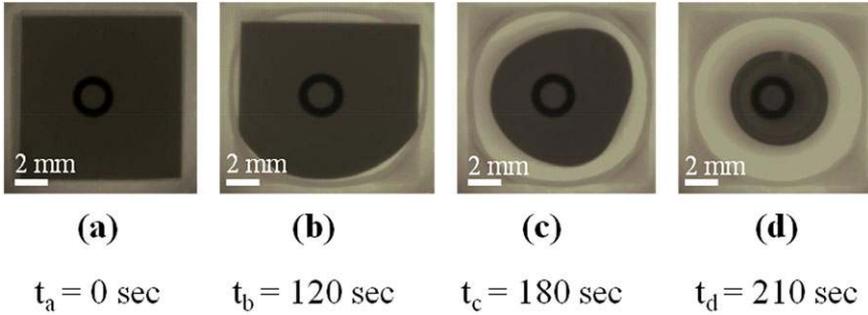


Fig. 3 Melting process of silicon on a zyarock substrate as recorded by the camera.

3 Results and discussion

Figure 3 illustrates a top view of the melting process of silicon on a zyarock substrate as recorded by the camera. Since the camera looks at the sample through the pyrometer window, the black ring that appears in all images is the monochromatic pyrometer measurement spot. The solid Si appears in black, the liquid silicon in white and the square substrate in grey. As it can be seen in the second image (b) the melting process starts from the bottom where the sample is in contact with the substrate. In the third image (c), a floating solid piece of silicon can be seen on the top surface of the droplet. In the last image (d) when the specimen is totally melted it can be remarked a bright zone around the black spot in the middle of the droplet. Silicon in a liquid state behaves as a mirror and thus this bright zone is due to the vertical reflection of the graphite radiation on the droplet surface. On the contrary, the dark central circle is the reflection of the crucible opening. It can be seen in image (d) that the pyrometer spot is inside this circle, assuring the correctness of the temperature measurement values. The whole melting process of silicon was found to be the same in the case of the fused silica substrates.

Figure 4a shows a representative temperature profile of the silicon sample during the melting and solidification process on a zyarock substrate as recorded by both the monochromatic and the bichromatic pyrometers.

Zyarock is the material of the crucible that the PV industry uses but it needs to be mentioned that in the present case it is not coated with the anti-adherent Si_3N_4 coating. During melting the sample absorbs the heating energy, due to the needed enthalpy of fusion, and the temperature remains constant as it can be seen from the presence of a temperature plateau in the bichromatic pyrometer temperature curve. However, in the monochromatic temperature curve the beginning of the melting process is detected by the decrease in the slope of the curve, despite the fact that the heating rate provided by the external supply remains constant. The fact that

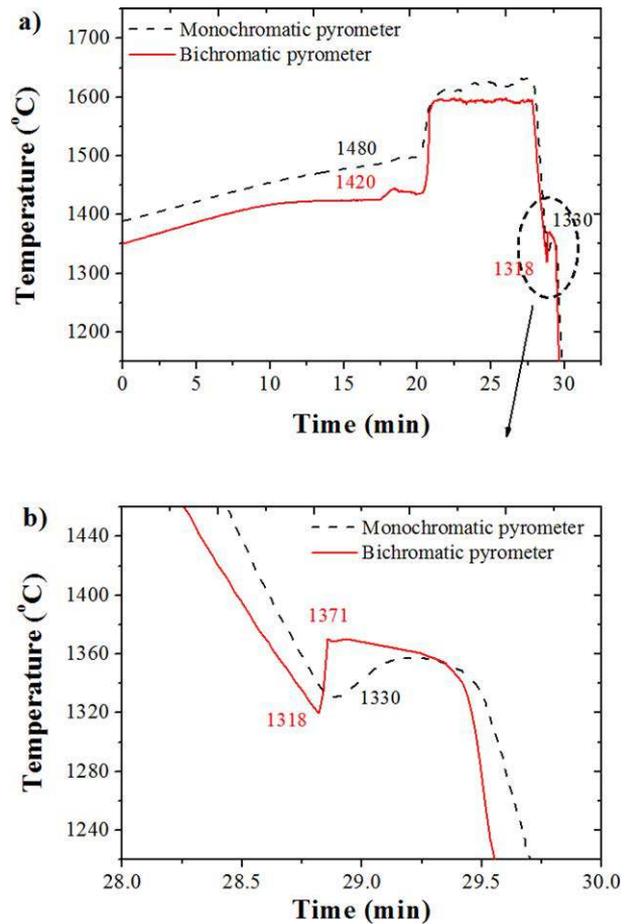


Fig. 4 Temperature profile of the silicon sample during the melting and solidification process on a zyarock substrate.

the monochromatic temperature curve does not present a melting plateau is probably due to the smaller spot size compared to the bichromatic one. This means that the given temperature represents the temperature of the solid silicon that floats on the surface of the liquid, as presented in figure 3c. At the end of the plateau some temperature fluctuations can be observed. As confirmed by the recorded video, this is due to the fact that the non melted solid pieces of silicon are moving on the top of

the droplet and thus the viewing field of the pyrometers is partially occupied with some varying solid and liquid phases.

After complete melting of the solid, a successive temperature increase is detected at about 20 min due to the fact that the enthalpy of fusion is no more absorbed by the sample. The temperature is stabilized and after 7 minutes the electrical power is cut abruptly and the silicon starts to cool down. The abrupt temperature rise observed at 28 min is the recalescence event caused by the latent heat of solidification release during the nucleation and growth of the silicon crystal.

Figure 4b shows in more details the solidification period. Concerning the bichromatic pyrometer measurements, it can be seen a typical isothermal plateau during solidification. Nucleation occurs at temperature $T_n = 1318 \text{ }^\circ\text{C}$, at the beginning of the recalescence. After recalescence the sample remains almost isothermal for approximately 35 sec at $T_g = 1370 \text{ }^\circ\text{C}$ until the solidification process is completed. This duration is in agreement with the recorded video during solidification as it will be discussed below. The thermal plateau after recalescence corresponds to the solidification temperature of the nucleated crystals, which is theoretically $1410 \text{ }^\circ\text{C}$. The maximum nucleation undercooling temperature (ΔT) can be approximated as the difference between T_g and T_n and thus in the present experiment $\Delta T = 53 \text{ }^\circ\text{C}$. There should be no further nucleation event after T_n , and further solidification can only be achieved by crystal growth. The experiments have been repeated three times and the measured undercooling values were in the range of $41 \text{ }^\circ\text{C}$ to $53 \text{ }^\circ\text{C}$. In the same figure, the monochromatic pyrometer curve does not present this abrupt increase of temperature caused by the creation of the first nucleus in the melted silicon as observed in the previous case. This is not surprisingly at all since, as it has already been discussed, the monochromatic pyrometer measures the mean value of sample temperature, then averaging the light emitted by the liquid and solid phases. However, there is an obvious correlation between the two curves and both measurements are needed in order to better understand the nucleation and crystal growth phenomena and verify the measured undercooling temperature and solidification time.

The temperature profile is found to present a similar tendency, when the silicon sample is melted and solidified on a fused silica substrate (figure 5). However, the measured undercooling value is $89 \text{ }^\circ\text{C}$ and it is higher in comparison to the case of silicon solidification on a zyarock substrate.

Figure 6 shows the morphologies of the growing crystal during the solidification of silicon on zyarock and

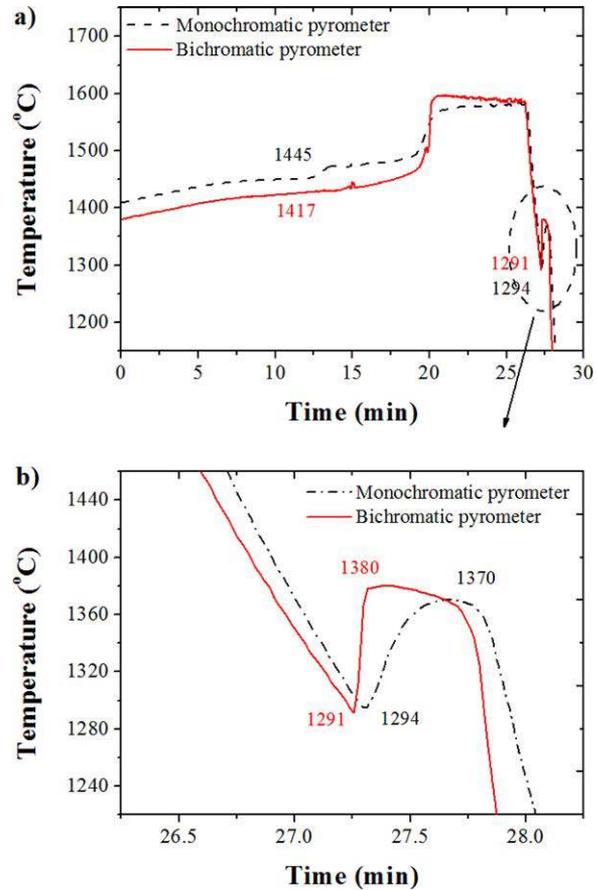


Fig. 5 Temperature profile of the silicon sample during the melting and solidification process on a fused silica substrate.

fused silica substrates as observed by the installed camera. The dark gray and bright parts in the figures are the undercooled liquid and the solid that has been solidified from the undercooled liquid, respectively. At the beginning of solidification, thin solid strips crossing the whole droplet can be observed. They develop to several continuous lines as time goes on. Jian et al. [18] have observed similar structures performing rapid solidification experiments in an electromagnetic levitation setup. They suggested that the crystal growth depends on the nucleation undercooling and in the nucleation undercooling region from 40 to $100 + 10 \text{ K}$ (similar to the present study) the initial crystal seed solidifies as dendrites that form a number of plates. Apparently the process is the same in case of solidification on a substrate. The “horn” appearing at the end of solidification is due to the 10% decrease of density between molten and solid silicon.

Figure 7 shows the macroscopic views of silicon droplets solidified on fused silica and zyarock, substrates.

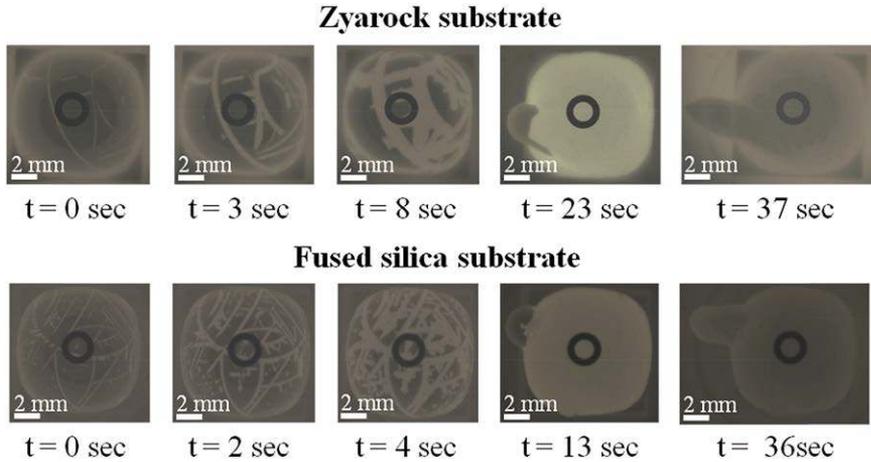


Fig. 6 Morphologies of growing crystals during the solidification of silicon on a zyarock and fused silica substrates.

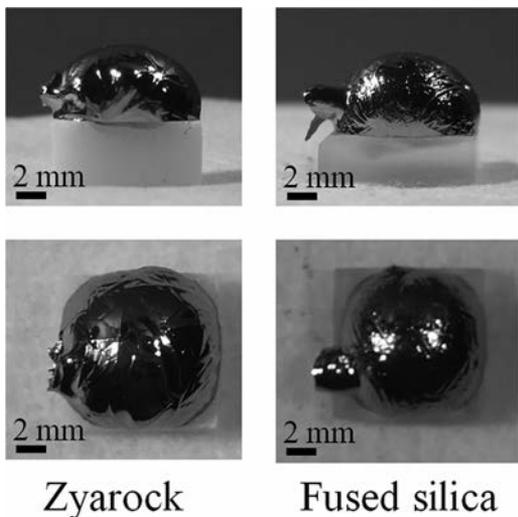


Fig. 7 Macroscopic top/side views of solidified silicon droplets on fused silica and zyarock substrates.

The undercooling measurements for a zyarock substrate ranged from [41 to 49 K], while, in the case of polished fused silica, the range was [45 to 89 K]. It can be seen that the nature of the material of the substrate plays a role on the solidification process and droplet formation. These experiments confirm that silica is a bad nucleating agent for Si, then validating the choice of a silica crucible in order to protect the molten droplet from external contamination. The significantly smaller undercooling in the case of zyarock also shows that the chemical and/or roughness of the substrate impact the nucleation behavior of Si. Experimental results are currently under interpretation. A correlation between the measured undercooling temperature, the microstructure of the solidified droplet, the interactions at the silicon/substrate interface and the precipitation that takes

place and the grain competition during the initial stage of the solidification process of the droplets will be discussed in details in a forthcoming paper.

4 Conclusions

An experimental setup has been designed and developed in order to investigate the nucleation phenomena during the solidification of electronic grade silicon on different substrates. It has been found that the melting process starts from the bottom of the sample where there is a contact with the substrate. The temperature profile of the silicon sample during the melting and solidification process on a zyarock substrate presented a temperature plateau during melting and a typical cooling curve, with undercooling, recalescence and plateau, during solidification. The thermal plateau after recalescence denotes that the solidification is carried out under isothermal conditions. As during experiments performed under electromagnetic levitation, the formation of continuous strips, presumably dendrite tips intersecting the drop surface, was observed at the beginning of solidification and they develop to several continuous lines as time goes on. Finally, the macroscopic views of the solidified silicon droplets showed the important influence that the material of the substrate has on the nucleation and solidification process. This research is still in progress. The crystalline structure, the microstructure and the grain competition during the initial stage of the solidification process of the droplets is currently under investigation. As the present results show that the set-up and experimental procedure allow emphasizing differences in nucleating power of different substrates, the investigation

will be extended to other substrate materials such as carbides, borides, nitrides and Si₃N₄-coated zyarock.

We strongly believe that the interpretation of the obtained experimental results and sample characterization will give supplementary information to better understand the heterogeneous nucleation of silicon and its impact on the ingot grain structure.

Acknowledgements. Through numerous discussions, Drs. N. Eustathopoulos, B. Drevet and D. Camel took an active part in the design and optimization of the experimental setup and procedure. Special thanks are due to Professor Fukuyama Hiroyuki for his comments on the pyrometric temperature measurements. This research has been funded by the ANR-10-HABISOL-007-03 “Mosaïque” project.

Key words. silicon, solidification, nucleation, undercooling, silica substrates.

References

- [1] I. Brynjulfsen, A. Bakken, M. Tangstad, and L. Arnberg, *J. Cryst. Growth* **312**, 2404 (2010).
- [2] B. Drevet, O. Pajani, and N. Eustathopoulos, *Sol. Energ. Mat. Sol. C* **94**, 425 (2010).
- [3] B. Drevet, R. Voytovych, R. Israel, and N. Eustathopoulos, *J. Eur. Ceram. Soc.* **29**, 2363 (2009).
- [4] T. Duffar, P. Dusserre, N. Giacometti, P. Boiton, J. P. Nabot, and N. Eustathopoulos, *J. Cryst. Growth* **198/199**, 374 (1999).
- [5] C. Panofen and D. M. Herlach, *Appl. Phys. Letters* **88**, 171913 (2006).
- [6] R. P. Liu, T. Volkman, and D. M. Herlach, *Acta Mater.* **49**, 439 (2001).
- [7] M. Beaudhuin, K. Zaidat, T. Duffar, and M. Lemiti, *J. Cryst. Growth* **336**, 77 (2011).
- [8] M. Beaudhuin, K. Zaidat, T. Duffar, and M. Lemiti, *J. Mater. Sci.* **45**, 2218 (2010).
- [9] M. Beaudhuin, K. Zaidat, T. Duffar, and M. Lemiti, *Indian I. Metals* **62**, 505 (2009).
- [10] A. Appapillai and E. Sachs, *J. Cryst. Growth* **312**, 1297 (2010).
- [11] A. Appapillai, C. Shachs, and E. Sachs, *J. Appl. Phys.* **109**, 084916 (2011).
- [12] I. Brynjulfsen and L. Arnberg, *J. Cryst. Growth* **331**, 64 (2011).
- [13] L. Sylla, A. Hodroj, N. Manginck-Noël, and T. Duffar, *European Solar Energy Conference 7–10 June 2004, Paris, France*, p. 3775–3778.
- [14] M. Beaudhuin, G. Chichignoud, P. Bertho, T. Duffar, M. Lemiti, and K. Zaidat, *Mater. Chem. Phys.* **133**, 284 (2012).
- [15] IRCON “Infrared Pyrometry version 3.0”, p. 23–25.
- [16] H. Watanabe, M. Susa, H. Fukuyama, and K. Nagata, *High Temp-High Press.* **31**, 587 (1999).
- [17] <http://www.sflee.co.kr/composites/techcera/tcData/zyarock.pdf>.
- [18] Z. Jian, K. Nagashio, and K. Kuribayashi, *Metall Mater Trans A* **33**, 294 (2002).