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Silicon purity controlled under electromagnetic levitation (SPYCE): influences on undercooling

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Abstract The rapid evolution of photovoltaic Si production induced a shortage of high purity silicon raw material. The use of lowest purity silicon has a strong effect on the casting conditions and ingot structure and properties. During solidification, solute rejection at the growth interface leads to an increase of the impurities concentration in the liquid phase and then to the precipitation of silicon nitride and silicon carbide. As a consequence, the grain structure of the ingot changes from columnar to small grains, also known as grits. A new electromagnetic levitation setup which has been developed in order to measure the undercooling versus impurity concentration is presented. The impurity concentration in the levitated Si drop is controlled by the partial pressure of nitrogen or hydrocarbon gas. As nucleation is a random phenomenon, statistical measurements are presented, from samples which showed numerous heating/melting and cooling/solidification phases. The effect of carbon impurities on the undercooling of silicon droplet is discussed.

Introduction

Multicrystalline silicon is intensively used in photovoltaic industry. Due to a rapid increase of silicon demand, the main source of pure Si raw material decreased. Previously, the microelectronic scraps, with impurities in the ppb(a)–ppt(a) range, were used to produce cells, now silicon with impurities in the ppb(a)–ppm(a) range becomes a typical feed material [1]. This permits to decrease the total production cost but leads to less "perfect" cells.

Changes in the morphological multi-crystalline structure have been observed through the solidification process. Instead of columnar grains which permit converting a maximum of photons to electron–hole pairs some areas are composed with small grains, also known as "grits" [2]. These small grains are characterised by a large concentration of carbon and small precipitates of silicon carbide (SiC) were observed [3]. These areas not only induce a decrease of the cell efficiency, but also cause the breaking of wire saws.

Precipitation of SiC occurs if a given supersaturation of carbon is reached. Knowing this value, it would be possible to predict when a classical, preferred, columnar structure will change to an undesired, equiaxed, grit structure. However, there is no way to measure the supersaturation of a given impurity during the solidification process.

It has been observed since years that an increase of impurity concentration provokes a decrease of undercooling. This means that impurities became nucleation sites which diminished the barrier energy to create the first silicon nuclei. To study this phenomenon, it is necessary to conceive an experimental setup which could certify that the only heterogeneous nucleation sites come from impurities which has been intentionally and precisely injected. In that way, a new electromagnetic levitation setup has been developed which permits to control the concentration of impurities by controlling the partial pressure of an ammoniac or hydrocarbon gas.

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Theoretical approach

Supersaturated solution metastability is a characteristic phenomenon of solidification in solution. It is possible to measure the supersaturated length as it is linked to nuclei apparition. Parameters which are taken in consideration are the temperature, the solute concentration or impurity concentration. Generally, the metastable zone is determined by the polythermal method [4] when the first nucleus is visually detected or thanks to instruments. When the material is opaque, like the silicon, it is not possible to observe the first nuclei with conventional techniques. Figure 1 permits to see that there is a link between supersaturation and undercooling. For a given solute concentration C_0, the first nuclei should have been appeared in A, but it doesn't. It can be explained by the thermodynamic laws where critical barrier energy has to be over cross. So the temperature continues to decrease following to E and the supersaturation ΔC of the solution increase as the undercooling ΔT. When the point B is reached, the first nuclei appear, at this point the supersaturation is given by ΔC^* with an undercooling ΔT^* which are the maximum value of supersaturation and undercooling. The apparition of the first nuclei leads to a latent heat exchange as a new phase appears. In case of silicon solidification, this latent heat is exothermic, consequently the temperature increase up to the point A, this phenomenon is also known as recalescence.

Consequently, measuring the nucleation undercooling will permit to obtain supersaturation values and if it is done for various concentrations it is possible to obtain the solubility and the metastable curves of the Si–C and Si–N phase diagram.

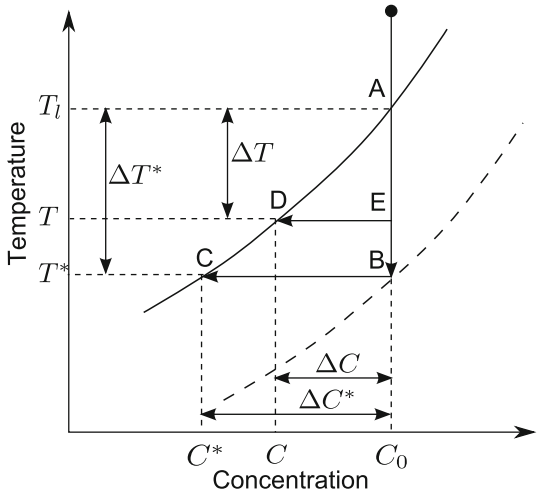

Fig. 1 Illustration of the polythermal method in order to measure the supersaturation versus undercooling

Experimental setup

The experimental setup, named SPYCE, is composed of a chamber which is evacuated to 10^{-8} mbar with a turbo molecular pump and an ionic pump (see Fig. 2). It is filled with a mixture of 6 N pure Argon and 6 N pure Helium gases. Undoped silicon of 6 N purity was used as source material. Lump of silicon about 2.8 g are directly positioned in the experimental setup. To remove impurities on the surface, a chemical treatment with a solution of 20% NaOH at 80 °C is done beforehand while 30 min. As silicon resistivity is too high at ambient temperature up to 1,000 °C to be electromagnetically levitated, it is necessary to decrease its resistivity by increasing its temperature. A two-step heating method was used as described in [5] to levitate pure Si samples. The silicon sample is placed on a fused quartz holder composed of a graphite heating element encapsulated at 10^{-5} mbar to prevent chemical pollution during heating. A levitation coil is placed at the centre of the chamber and is connected to a RF generator with 50 kW power operating at 130 kHz. The graphite is heated by the eddy currents; the resulting heat is conducted into the silicon through the fused quartz. As soon as the silicon is levitated, the encapsulated graphite heater is pulled down and silicon is molten in levitation. The melt is superheated by 200 K during 10 min, and then partial pressure of pollutant gases (CH_4 or N_2) is adjusted in order to obtain impurity concentration in the 1–10,000 ppm (w) range. The sample is maintained to this superheated temperature during 10 min in order to obtain a stationary reactive state between the polluting gas and the silicon.

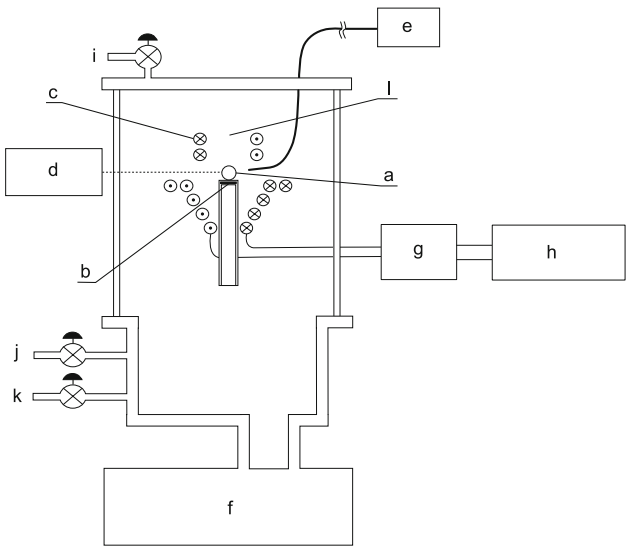

Fig. 2 SPYCE experimental setup. *a* Sample, *b* graphite postheater, *c* coil, *d* two colour pyrometer, *e* OFT, *f* ionic and turbo molecular pumps, *g* capacity, *h* CELES HF generator, *i* vent-hole, *j* Ar/He gas, *k* polluting gas, and *l* light guide sensor

Then, the levitated drop is cooled with an helium flow at cooling rates varying between 2 and 40 K s^{-1}.

Two cameras allow following the evolution of the silicon morphology during the cooling step and any chemical reaction with the polluting gases. A camera at 100 Hz records all the experiment whereas a high speed camera (HSC) at 1 kHz captures 2 s of the precipitate nucleation and growth. They are all both located on the equatorial plan, and the recording is launched through a digital interface. A reference is taken between the camera and the pyrometer to adjust the acquired image with a temperature recording.

The temperature of the sample is measured with a two colour pyrometer on the equatorial plane and by optical fibre thermometry (OFT) on the side, similar to the experiment described by Cröll and coworkers [6–8]. The OFT (monochromatic pyrometer Luxtron M100) is essentially a pyrometric method using a sensor tip as waveguide. The light is guided by the sensor to the outside of the enclosure through glass fibre cable up to the OFT system. The sensor is composed of fused quartz with a 1.5-mm tip diameter. The maximum resolution of the OFT is 0.01 K, and the signal is acquired at 20 Hz. It permits measuring precisely the rapid increase of temperature during the recalescence. Comparatively the maximum resolution of the two colour pyrometer is 1 K and the signal is acquired at 70 Hz. This apparatus permits calibration of the OFT signal that evolves with time.

Results

Pure silicon

Numerous experiments have been managed with pure silicon. Cooling and heating cycles are successively repeated on the same levitated silicon sample to obtain statistical results. It has been observed a good repeatability of pure silicon undercooling with a mean deviation of the normalised temperature T/T_m equal to 0.016 (Fig. 3). Even if nucleation is a statistical phenomenon which is described by classical thermodynamic laws there is no significant variation of the nucleation undercooling. From this, it is postulated that repeating numerously the same experiment under the same conditions with the same sample should lead to undercooling measurement with low deviation. Even for cooling–heating cycles repeated during hours, no contamination and significant undercooling disparity have been observed.

Same experiments has been managed numerous times to check the reproducibility of the experimental setup. Samples prepared with the same conditions have shown low differences in undercooling, permitting to conclude that all parameters are well controlled.

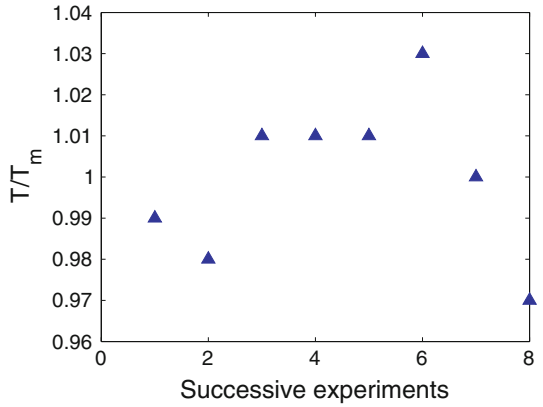

Fig. 3 Nucleation temperature of successive experiments, normalized by the mean nucleation temperature

Maximum undercooling obtained with this experimental setup is ~308 K (Fig. 4). As each experiment requires to control accurately external contamination, the reference undercooling is defined as higher than 250 K.

The growth velocity of pure Si has been measured for different undercoolings with the HSC. Figure 5 shows a 12-mm diameter pure Si drop undercooled by 120 K. The dark and bright parts are, respectively, the undercooled melt and the solid phase releasing latent heat. Thanks to the gap of emissivity between solid and liquid semiconductors, this permits to outline the solid–liquid interface which is continuously observed with the HSC. The bright shadows observed on the silicon surface are reflections of the drop on the coils. The growth velocity of this sample was measured as 2.1 m s^{-1} with facetted dendrites which is coherent with results obtained in the literature (Fig. 6).

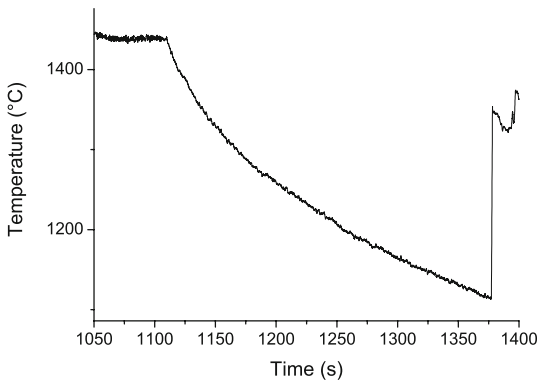

Fig. 4 Maximum undercooling of ~308 K obtained in the SPYCE experimental setup

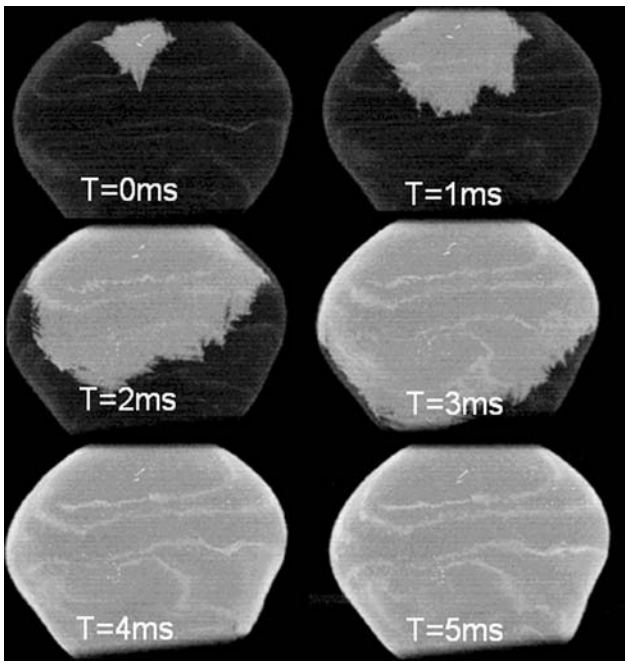

Fig. 5 The solid–liquid interface on the surface of a Si drop (1.2-mm in diameter) is observed with a HSC. The undercooling immediately before solidification is 120 °C and the interval between the frames is 1 ms

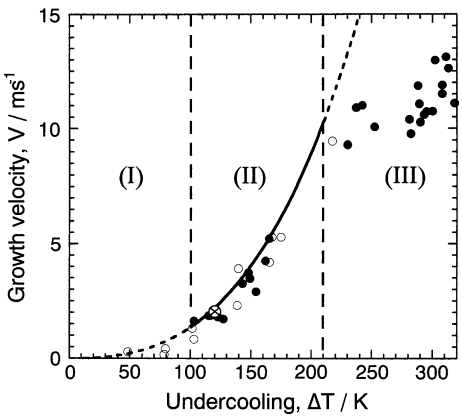

Fig. 6 Growth velocity as a function of undercooling for Si [11]. The cross represents our measured data

Effect of impurities

Chemical reactions between CH_4 or N_2 and Si lead to the following equilibriums:

$$CH_{4(g)} + Si_{(l)} \rightleftarrows SiC_{(s)} + 2H_{2(g)} \quad (1)$$

$$2N_{2(g)} + 3Si_{(l)} \rightleftarrows Si_3N_{4(s)} \quad (2)$$

Therefore, controlling the mole number of CH_4 or N_2 allows, respectively, controlling the number of SiC or Si_3N_4 precipitates in the silicon. This under the hypothesis that the thermodynamically equilibrium is reached during 10 min of superheating. Experiments with superheating times varying from 1 to 10 min have shown stabilisation of the nucleation undercooling for duration higher than 5 min. So if the reaction is longer than 5 min, the thermodynamically equilibrium is supposed.

Electromagnetic field inside the drop leads to Alfven velocity between 0.5 and 2 m s^{-1} [9]. Consequently the temperature in the melt is almost isothermal, and homogeneous in solute concentration which ameliorates the chemical reactions (1) and (2). As the coils give a quadripolar field, there are two mains convective loops which localise the precipitates at the dead zone of flux (Fig. 7).

Due to the Si–SiC surface tension, the precipitates are located at the surface of the drop. Consequently the precipitates are only observed on the convective dead zone. This behaviour has already been simulated: particles smaller than 1 μm remain in the melt and those larger than 10 μm gather at the dead zone [10], the particles between these 1 and 10 μm can be either on the surface or in the bulk. The electromagnetic force is too low to trap small particle, whereas for large particles, they are trapped in a position determined by the balance of buoyancy, drag and the electromagnetic expulsion force. The effect of surface tension also has to be taken in consideration to explain this

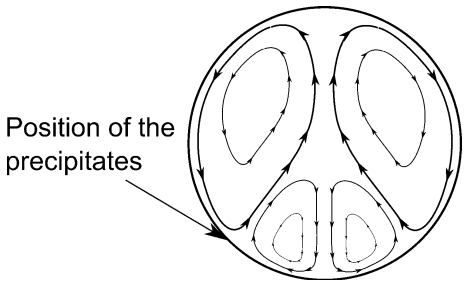

Fig. 7 Schematic representation of fluid flow loops in the drop within an electromagnetic quadripolar field [12]

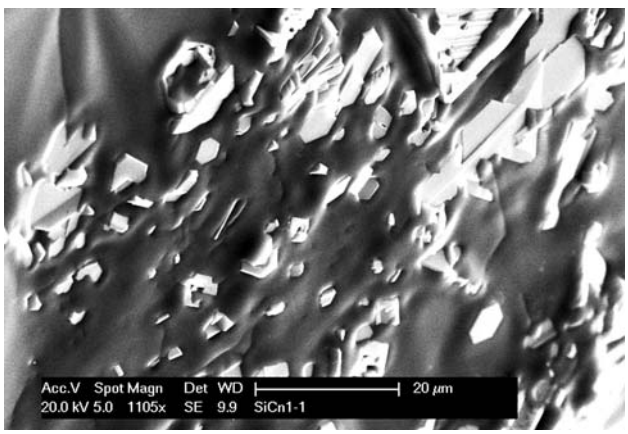

Fig. 8 Scanning electron microscope images of silicon surface showing SiC precipitates

phenomenon. The energy of the liquid-particle system is lower when the precipitate is at the surface.

Figure 8 shows precipitates on the surface of the solid Si obtained after chemical reaction between CH_4 and Si which were located at the dead zone. Raman spectrometer analysis have shown that the precipitates are 3C-SiC polytypes which confirm the reaction between CH_4 and Si.

Conclusion

The experimental setup SPYCE has been validated. The protocol allows obtaining high undercooling with reproducible and repeatable results. The measurement apparatuses (Pyrometers and HSC) give results in agreement with the literature. The SiC and Si_3N_4 precipitation in the liquid silicon can be controlled through the partial pressure of CH_4 or N_2 after a stabilisation time longer than 5 min.

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