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Control of grain size and -orientation in multi-crystalline silicon ingots

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Abstract

Two different cooling rates have been imposed during the early solidification of two multi-crystalline silicon ingots with 250mm diameter and 100mm height in a pilot scale directional solidification furnace. This has been done by opening a variable heat leak system below the crucible in order to achieve a high initial cooling rate in one of the ingots. The grain-structure and -orientation of these two ingots have been investigated by light microscopy (LM) and electron backscattered diffraction (EBSD), and their electrical properties by quasi-steady state photo-conductance (QSSPC) and surface photovoltage (SPV) method. The ingot with the high initial cooling rate shows predominantly grains which are significantly larger than what is usually found in mc-Si. The minority carrier diffusion lengths measured on the large grains in the ingot with high cooling rate show higher values than those measured on the ingot with smaller grains. These results indicate that principles of grain size and –orientation control in mc-Si ingots can be applied to a pilot scale furnace, and the potential for up-scaling to industrial ingots with improved electrical properties and, thus, higher solar cell conversion efficiency.

Introduction

The major challenge of today's photovoltaic (PV) industry is to increase the solar cells conversion efficiency while decreasing production costs. Solar cell conversion efficiency is largely dependent on the impurity content and crystal defects of the multi-crystalline silicon (mc-Si) used for the solar cells, as well as on the grain structure and –orientation of the grown material. Researchers have reported that if impurity content is reduced, conversion efficiency can be largely increased [1-5] with consequent economical benefit. Ingots with larger grains will have lesser grain boundaries and, thus, lesser sites for metallic impurities to precipitate [6,7].

Recently, a research group in Japan [8,9] has shown, in small scale (crucible of 50mm diameter) casting experiments, that mc-Si ingots can be produced with less defects and higher conversion efficiency than in standard directional solidified mc-Si by rapid cooling of the crucible to achieve high undercooling in the melt. This high undercooling was used to force dendritic growth of silicon crystals at the bottom of the crucible where each crystal covers large sections of the bottom of the solidification crucible. During subsequent slow directional solidification, these crystals grew vertically with a planar front. The early dendritic growth always appears in well defined crystallographic directions. The conversion efficiency of the solar cells produced by this method was 16% compared to 17% efficiency of mono-crystalline silicon wafers grown by the Czochralski process [9].

Nucleation and early growth at high undercooling, therefore, present a possibility to control both grain size and –orientation, and, accordingly, enhance the electrical properties of the semiconductor materials.

In this work, we aimed at reproducing these results on a pilot scale directional solidification furnace in order to prove if the principles of control of grain size and –orientation in multi-crystalline silicon could be applied to larger scale ingots.

Experimental

Two mc-Si ingots were cast in a Crystalox DS 250 pilot scale directional solidification furnace at SINTEF/NTNU. The ingots were 12kg in weight, 250mm in diameter and approximately 100mm in height. The furnace consists of a graphite support ring and support plate, a susceptor, carbon fibre insulation and a variable heat leak (VHL). The VHL system, which is located underneath the crucible, allows for adjusting the heat flow through the bottom of the crucible. A schematic representation of the furnace main components and VHL is shown in Figure 1. The furnace is provided with thermocouples for temperature measurements. For both ingots, the pedestal temperature, i.e. the temperature measured at the bottom of the ingot, and the furnace power were recorded. A more detailed description of the furnace and casting procedures is given in reference [10].

The same type of feedstock, crucible and coating materials was used to produce the two ingots. Both were doped with the same amount of boron in order to produce p-type materials with resistivity in the typical range of 0.8-1.2 Ohm cm. The thickness of the crucible was 16 and 8 mm for the first and second casting (named BCD-1 and BCD-2), respectively. To obtain forced cooling of the silicon melt in

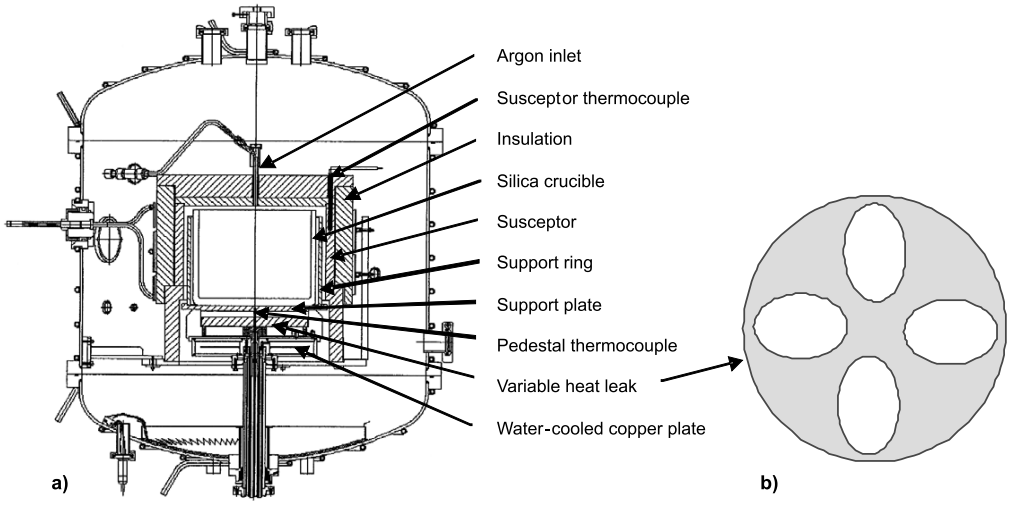

Fig. 1 : Schematic representation of the a) Crystalox DS 250 directional solidification furnace, and b) variable heat leak

the two casting experiments, the VHL was quickly opened just before nucleation started.

Optical microscopy was used for the visual inspection of the two ingots. One central slice from bottom to top was cut for each ingot. These two slices were etched and the grain structure/morphology investigated. The grain orientations were analysed by Electron Back-Scattered Diffraction (EBSD). The electric properties of the materials were investigated by quasi-steady state photoconductance (QSSCP) which measures the minority carrier lifetime, and by surface photo-voltage (SPV) which gives a spatial distribution of minority carrier diffusion length. These electrical properties also give an indication of the solar cell performance.

Results and discussion

Figure 2 shows the pedestal temperature and the power plotted versus time for both castings. The circles show the start of nucleation and the arrows indicate the opening of the VHL. In the first ingot (BCD-1), when the VHL was opened after approximately 14 hours, the temperature measured below the crucible decreased rapidly from 1200 ºC to 1050 ºC. After solidification started, the VHL was closed to reduce the heat flux and obtain a controlled vertical directional growth. In the second casting (BCD-2), a thinner crucible was used in an attempt to obtain an even higher cooling rate before nucleation. The heat transport of this crucible was, however, higher than expected and the melt started to solidify before the VHL was opened. BCD-2 had, therefore, lower cooling rate than BCD-1 at nucleation.

The optical micrographs, in Figure 3, are cross sections through half the ingots. The ingot with high initial cooling rate (BCD-1) has an abnormally large twinned grain extending over nearly the whole section (Fig. 3a). The second ingot (BCD-2) has many small grains and this grain structure is typical for mc-Si ingots produced with standard cooling rate (Fig. 3b)

Figure 4 shows an EBSD-micrograph of the grain orientation of a section from the ingot with the high initial cooling rate (BCD-1). Clearly, there is one large twinned grain (blue/pink) with a growth direction close to <112>. Nagashio and Kuribayashi [8] have shown that the grain orientation of a dendrite changed from <112> to <110> to <100> with increasing degree of undercooling. When the undercooling was lower than 100K, as in this investigation, <112> or <110> dendrites were observed.

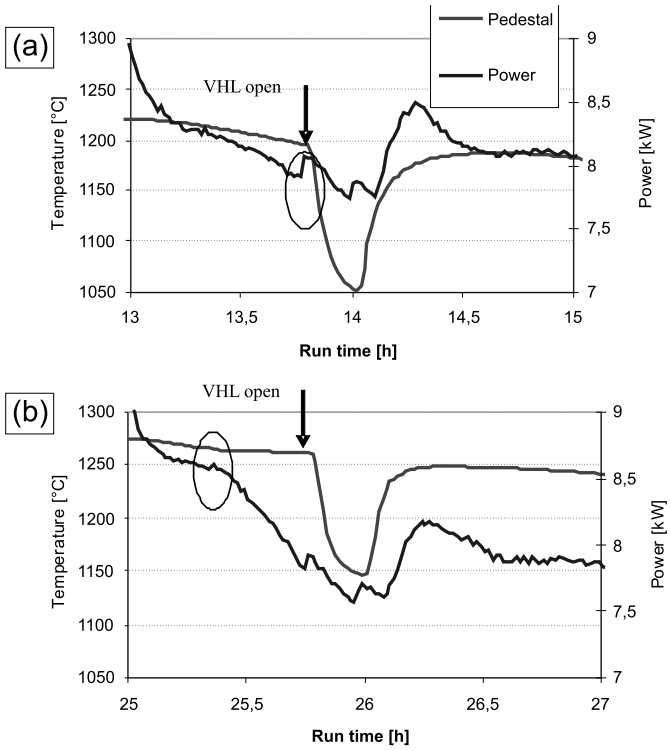

Fig. 2 : Pedestal temperature and power for the two ingots with a) high initial cooling rate (BCD-1) and b) standard cooling rate (BCD-2). The circles indicate the start of nucleation

The QSSPC measurements showed that the ingot with the high initial cooling rate (BCD-1) has higher lifetime than the ingot with standard cooling rate (BCD-2). The lifetime of the large twinned grain in the ingot BCD-1 was approximately 28 μs, while it was approximately 18 μs for the small-grain area. Similar results are shown by the SPV measurements. The minority carrier diffusion length of the ingot BCD-1 was observed to be significantly longer than in BCD-2, with a maximum of approximately 250 μm and 180 μm, respectively (Fig. 5). The longest diffusion length in BCD-1 was measured in the large grain present in this ingot.

Solar cells from the two ingots were not processed. However, it is expected that cells made from the ingot with high initial cooling rate will have higher conversion efficiency.

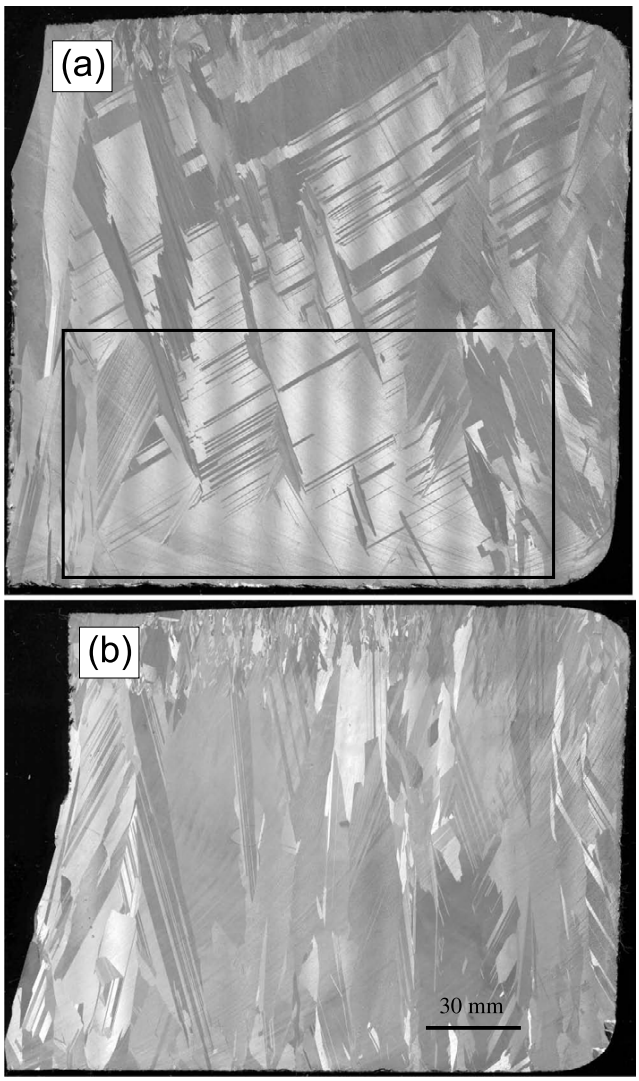

Fig. 3 : Optical micrographs of two ingots with a) high initial cooling rate (BCD-1) which shows one large grain growing from bottom to top of the ingot, and b) standard cooling rate (BCD-2) which shows several grains (different grey tones) growing from bottom to top of the ingot

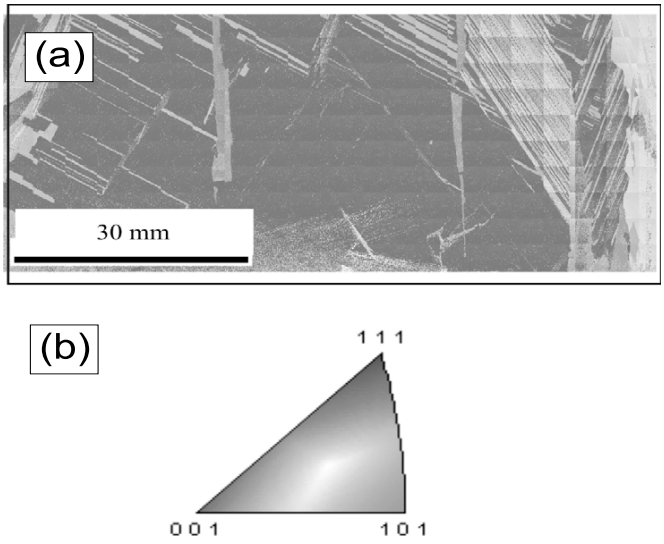

Fig. 4 : a) EBSD orientation map from the ingot with high cooling rate (BCD-1), the analysed area is a mirror image of the area marked in Fig. 3a. b) inverse pole figure triangle (different colours indicate different grain orientation)

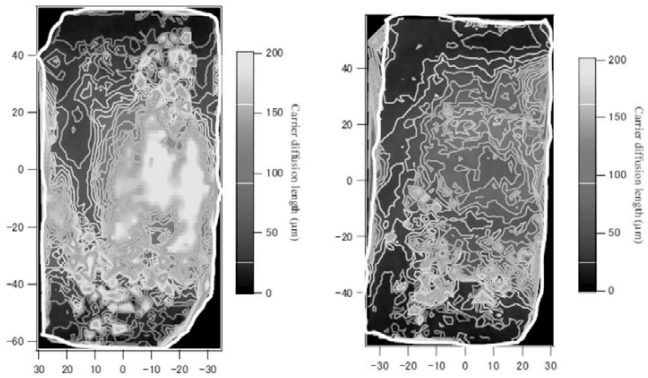

Fig. 5 : Minority carrier diffusion length (µm) from the ingot with high cooling rate (left) and the ingot with standard cooling rate (right)

Conclusions

These results indicate that the control of nucleation and the resultant large crystal grains are beneficial for the improvement of the electrical properties of multi-crystalline silicon ingots.

The investigation also shows that principles of grain size and orientation control in mc-Si ingots, which have been demonstrated on a small laboratory scale, can be applied to a pilot scale furnace, and illustrates the potential for up-scaling to industrial ingots with improved conversion efficiency.

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References

1. Davis R J, Rohatgi A, Hopkins R H, Blais P D, Rai-Choudhury P, McCormic J R and Mollenkopf H C, *IEEE Trans. Elctron. Dev.* ED-27 (1980) 677.
2. Geerligs L J, Manshanden P, Wyers G P, Øvrelid E J, Raanes O S, Wærnes A N and Wiersma B, Proceedings 20th EUPVSEC, 6-10 June 2005.
3. Istratov A A, Buonassisi T, Pickett M D, Heuer M and Weber E R, *Mat. Sc. Eng. B*, **134** (2006) 282-286.
4. Buonassisi T, Istratov A A, Marcus M A, Lai B, Cai Z, Heald S M, Weber E R, *Nature Materials*, **4** (2005) 676.
5. Binetti S, Libal J, Acciarri M, Di Sabatino M, Nordmark H, Øvrelid E J, Walmsley J and Holmestad R, *Mat. Sc. Eng. B,* (2008).
6. Martinuzzi S, Perichoud I, Palais O, *Solar Energy Mat. Sol. Cells,* **91** (2007) 1172.
7. Macdonald D, Cuevas A, Kinomura A, Nakano Y, Geerligs L J, *J. Appl. Phys.,* **97** (2005) 33523.
8. Fujiwara K, Obinata Y, Ujihara T, Usami N, Sazaki G and Nakajima K, *J. Crys Growth,* **266** (2004) 441.
9. Fujiwara K, Pan W, Usami N, Sawada K, Tokairin M, Nose Y, Nomura A, Shishido T and Nakajima K, *Acta Mat.,* **54** (2006) 3191.
10. Mjøs Ø, PhD Thesis at NTNU (2006) 39.
11. Nagashio K and Kuribayashi K, *Acta Mat.,* **53** (2005) 3021.