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Growth by the Heat Exchanger Method and Characterization of Multi-crystalline Silicon ingots for PV

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Abstract - *Multi-crystalline silicon ingots of 44 cm square cross section, weighing 80 kg, have been produced by a modified Heat Exchanger Method in which a graphite insulation and heat exchanger block move down from the heater during crystal growth to facilitate heat extraction from the bottom of the crucible. Wafers of 300 μm thickness and 1.2 Ω-cm resistivity, have shown consistency and uniformity in the properties required for large-scale production. The interstitial oxygen concentration varies from 1.6 to 3.6 ppm, whereas the substitutional carbon concentration is assessed to be below 10 ppm.*

Résumé - *Nous avons utilisé une variante de la technique de l'échangeur thermique (HEM) pour élaborer des lingots de silicium multicristallin à usage photovoltaïque. Au lieu d'utiliser l'hélium comme agent d'extraction de la chaleur, la solidification directionnelle est, dans notre cas, provoquée par l'abaissement, durant le cycle de croissance, du bloc de graphite situé sous le creuset. Le matériau obtenu semble présenter les propriétés requises à une production à grande échelle.*

Keywords: Multi-crystalline silicon – Characterization - Directional solidification - Photovoltaic.

1. INTRODUCTION

The photovoltaic industry is presently growing at 40 % per year, largely due to government subsidised programs. A recent market survey reports that, of all solar photovoltaic module sales in 2002, 36 % were based on mono-crystalline silicon wafers, similar to those used in microelectronics. A further 52 % were based on lower-quality multi-crystalline silicon wafers. These are large-grained polycrystalline wafers produced by slicing from large ingots of directionally solidified silicon, an approach developed specifically for photovoltaic [1].

With increasing expectations for the solar cell market, a shortage of the silicon material is forecasted [2]. This tendency will continue into the near future. Since silicon wafer costs constitute a large portion of the total cost, several technologies have been competing for the low-cost production of silicon wafers. The Czochralski (CZ) technology is considered to be the first one to meet this goal. However, in terms of yield and productivity, CZ technology has the drawback of the labour-intensive ''seeding'' step. Heat exchange method (HEM) is the other strong candidate for low-cost production [3]. The process control for the production of large multi-crystalline silicon ingot is easier than in CZ technology.

Another advantage is the in situ annealing of the ingot after growth. This in situ annealing reduces the thermal stresses which cause dislocation generation in the ingot. Originally, HEM technology was developed to grow single-crystalline materials with seeding. However, multi-crystalline silicon crystal grown in small size with HEM without seeding is found to have almost the equivalent electrical property as mono-crystalline silicon for solar cells [4-6]. This is due to vertically oriented grains which transport the carriers without hindrance in the crystal grown with HEM. In this study, 80 kg multi-crystalline ingot is grown with fully automated HEM furnace. The quality of the ingot is assessed with both Etch-Pits Density (EPD) analysis and Fourier Transform Infrared (FTIR) spectroscopy.

2. EXPERIMENTS

2.1 Crystal growth

In this experiment, a HEM furnace manufactured by GT-Equipment Technologies Inc. (Nashua, USA) is employed (Fig. 1). The furnace is well insulated. The graphite resistance heating element provides heat so that there are no significant temperature variations during the melt down of the silicon charge. The feedstock used for this charge was virgin solar grade poly-silicon, having Acceptors concentration (Boron) < 0.3 ppb, Donors concentration (Phosphorus) < 0.5 ppb and intrinsic Carbon concentration < 0.7 ppm.

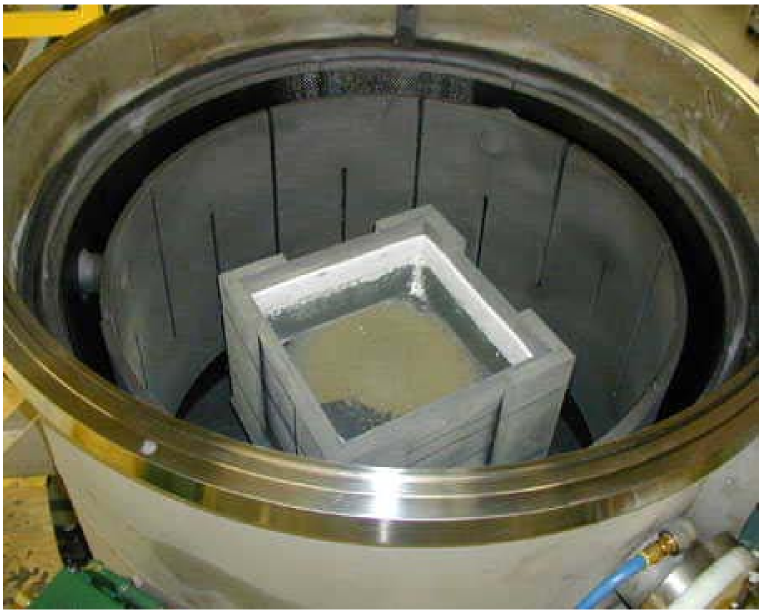

Fig. 1: Interior of the UDTS / HEM furnace

During growth, the crucible is lowered in the heat zone to further facilitate heat extraction from its bottom and to maintain low gradients. As can be seen (Fig. 2), the power is maintained for 24 h during growth cycle. In this experiment, the growth rate averages 12mm/h, which is very close to that in the CZ process. The result is a large block of crystallised silicon ingot (Fig. 3). This ingot is evaluated to see its acceptability in the solar cell production.

2.2 Wafer processing

The obtained ingot is cut into sixteen 100 x 100 mm bricks by using a diamond wire saw. After a crooping operation of 2 cm from top and bottom of all bricks, wafers with a thickness of 300 μm are obtained by a multi wire saw machine using a mixture of silicon carbide with glycol.

Batch of selected wafers from ingot are used to measure interstitial oxygen $[O_i]$ and substitutional carbon $[C_s]$ concentrations, using FTIR spectroscopy. The resistivity of the wafers is determined by mean of four probe technique. Other batches are used to determine the EPD dislocation of the material.

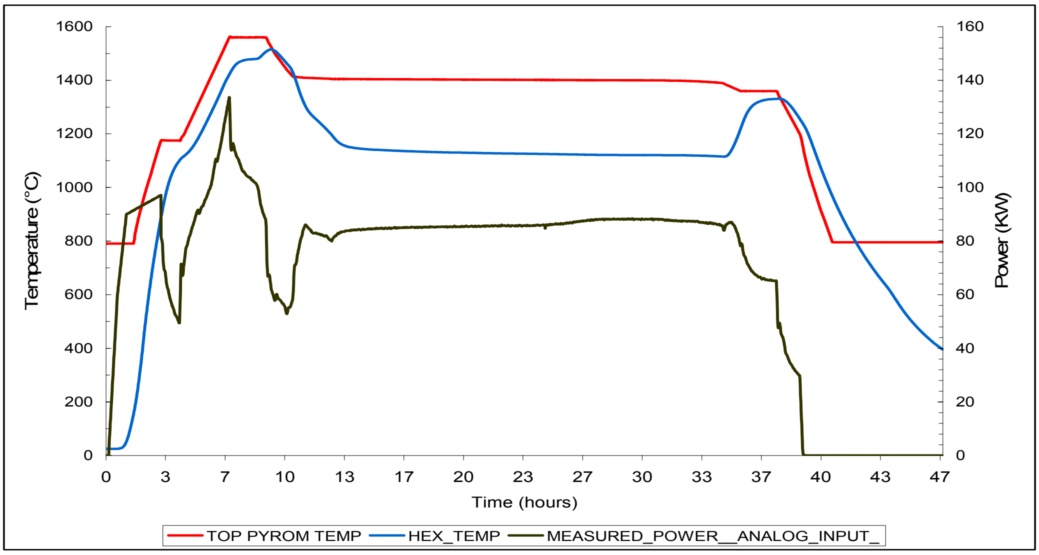

Fig. 2: Main Process parameter data for a 44 x 44 x 18 cm silicon ingot

Fig. 3: 44 cm square cross section multi-crystalline silicon ingot

3. RESULTS AND DISCUSSION

3.1 Ingot evaluation

As can be seen in Fig. 3, cracks are not observed on the surface of the ingot. The top surface is very smooth and, as suited, slightly convex. These observations indicate that a strong unidirectional solidification takes place during the growth of this silicon crystal.

The slightly convex solid-liquid interface is confirmed by observing the circular solid silicon first seen in the centre of the melt at the end of the growth cycle. This fact is due to the temperature gradient created by opening and lowering respectively the insulation first, and then the graphite heat exchanger block which is supporting the crucible. The solidification is initiated by extraction of the superheat from the bottom portion of the melt in the crucible; this is accomplished by setting up the heat flow such that the heat extraction is primarily from the bottom of the crucible and the heat input is such that no grains are nucleated along the sidewalls. This situation is different from the casting process in which the solidification starts from the crucible outside the melt and the crystal grows into the centre part of the melt. The cooling situation in this process is also different from the CZ process where the cooling of the ingot is conducted from outside the crystal, with argon gas flowing from the top of the furnace. From this difference, it is expected that the ingot grown with this HEM furnace will have less residual stress than the ingot grown by the CZ or casting process.

In Fig. 4, the grain morphology of the cross section of a brick is shown. As can be seen in the picture, most of the grains are aligned vertically, i.e., the solidification proceeds in an upward direction from the bottom of the crucible. This observation is coincident with the fact that the top surface of the ingot is very flat. The vertical arrangement of the grains is very favourable for solar cell fabrication because the grain boundary will not act as a barrier for the electrical carriers generated. The other fact that can be seen in the picture is that the size and shape of the grains is uniform throughout the ingot. This fact confirms the possibility that this process is effective in the growth of large ingot. The upper part of the ingot is slightly bigger than the lower part. It is possible that the slight deformation of the silicon crucible is due to the long length of time which this process requires. Another possible explanation of these results might be that the density of the solid silicon is lower than that of the liquid silicon.

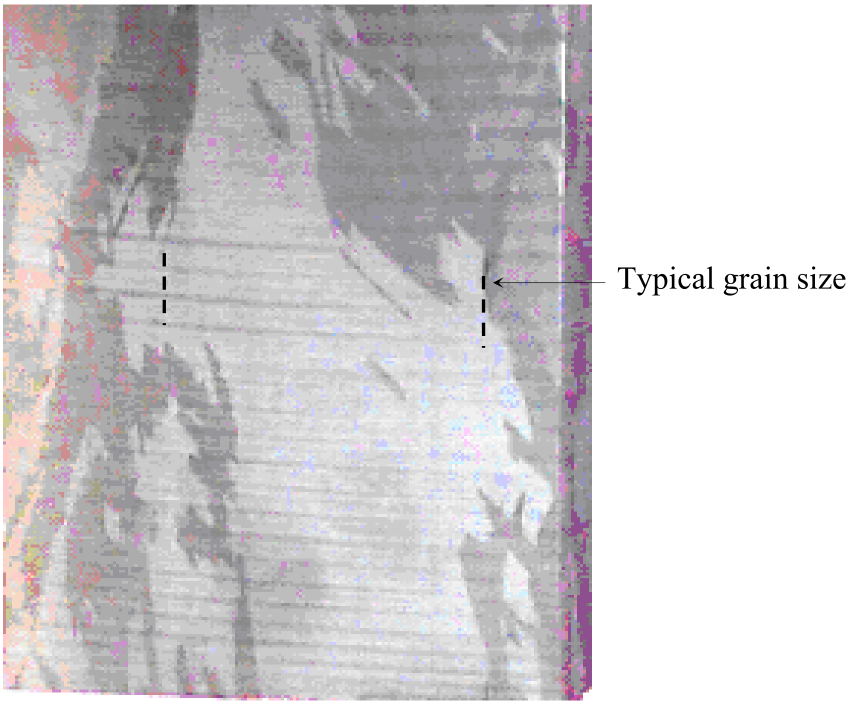

Fig. 4: Vertical cross section of a one brick of 44 cm multi-crystalline silicon ingot (side part)

As solidification proceeds, silicon can cause crucible deformation with increased volume. Further, in the upper part of the ingot, grains nucleated from the side wall of the crucible can be seen. Since the crucible becomes wider with the growth of the crystal, grains nucleated from the bottom of the crucible might not be grown into this area. The grain morphology in this area is not better than that of the grains in the central area of the ingot. However, this part will be removed during the preparation of the square ingot for the slicing.

As can be seen in Fig. 5, the average size of the grains is larger than 1 cm. The huge size of the grains might be due to the lower growth rate of the crystal in this process. In the CZ process, the growing ingot is pulled from the melt and cooled by the flowing of argon gas. However, in this process, the solidified ingot is contained in the hot crucible and cooled down slowly. Although not a single crystal as with CZ technology, the multi-crystalline ingot grown in this process is believed to contain fully grown large grains. Because of these large grains, the grain boundary is not expected to impair the efficiency of the solar cell later.

Fig. 5: Grain shape of 10 cm square multi-crystalline silicon wafer

3.2 Wafer characterization

A five minutes treatment with Shimmel etching solution was found to be a good preparation of the samples for detecting dislocations and grain boundaries [7]. For this purpose, EPD measurements have been performed using a light optical microscope combined with a computer assisted image processing system. The data has been checked and corrected manually. For a wafer close to those used for solar cell processing, an average EPD density of $6\ 10^5\ \mathrm{cm}^{-2}$ has been found. Twinned regions, like the one shown in Fig. 6, are typical crystal defects of the investigated poly-Silicon wafers.

Prior to crystal growth, silicon has been doped with boron. Due to segregation phenomena during growth, the measured wafer resistivity increases from 1.1 Ωcm close to the bottom part of the crystal up to 1.3 Ωcm in the upper part, which corresponds to an average doping concentration of $1.8\ 10^{16}$ at/cm^3. FTIR spectroscopy reveals that the interstitial oxygen concentration $[O_i]$ varies from 1.6 to 3.6 ppm, whereas the substitutional carbon concentration $[C_s]$ is below 10 ppm. From these results, we can confirm the good quality of the batch material.

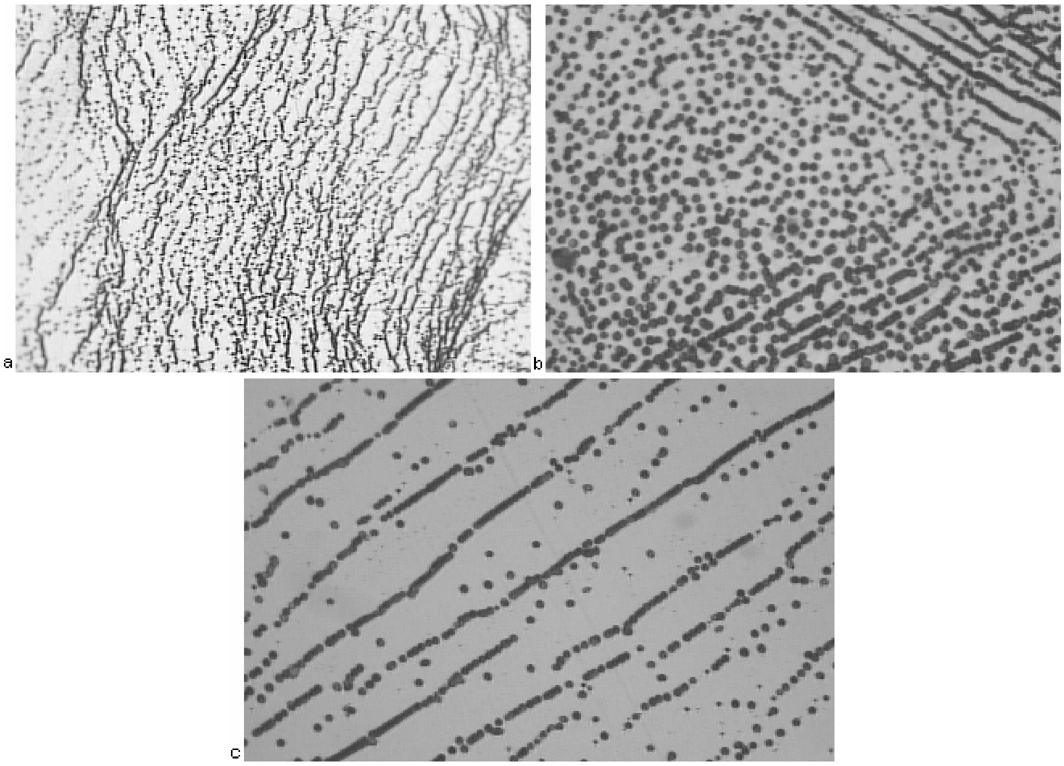

Fig. 6: EPD images obtained on wafers extracted from :
(a, b) upper part (x100, x500 magnifications respectively)
(c) lower part of the ingot (x500)

4. CONCLUSION

Optimized silicon crystal growth process, in which both graphite bottom insulation and heat exchanger block move down from the heater during crystal growth, allows us to get good ingots. The material has shown consistency and uniformity in the properties required for large-scale production, attested by FTIR and EPD analyses. In the near future, the multi-crystalline silicon ingot produced with this technology in UDTS-Algeria should lead to solar cell performance very close to that of mono-crystalline silicon material.

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