Continuous melting and directional solidification of silicon ingot with an electromagnetic cold crucible

***Huang Feng, Chen Ruirun, Guo Jingjie, Ding Hongsheng, Su Yanqing, Yang Jieren, and Fu Hengzhi**

(School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China)

Abstract: In order to avoid contamination from the crucible and to modify the structures, a new solidification method based on cold crucible technology was used to prepare silicon ingots. A silicon ingot with square cross section was directionally solidified with a cold crucible. The mechanism of the cold crucible directional solidification of silicon ingot was revealed. Due to the induction heat that was released in the surface layer and the incomplete contact between the crucible and the melt, the lateral heat loss was reduced and the silicon ingot was directionally solidified. The structures, dislocation defects and the grain growth orientation of the ingot were determined. The results show that neither intergranular nor intragranular precipitates are found in the ingot, except for the top part that was the last to solidify. The average dislocation density is about 1 to 2 × 10^6 cm^{-2}. The grains are preferentially <220> orientated.

Key words: directional solidification; silicon ingot; grain growth; cold crucible

CLC numbers: $TG136^+.1$ Document code: A Article ID: 1672-6421(2012)01-024-04

The photovoltaic (PV) industry has expanded considerably, resulting from the desire to replace fossil fuel based energy sources with renewable energy sources. The average growth rate has been greater than 50% over the past five years [1]. Today, about 90% of solar cells are made from crystalline silicon. Silicon single crystals yield high conversion efficiency but also have high cost; and, therefore, low cost silicon multi-crystals fabricated by a casting method are currently used as substrates for most of solar cells.

At present, multi-crystalline silicon for solar cells is usually cast by directional solidification of high purity silicon in silica crucibles. During this process, although most of the impurities entering the melt will segregate to the top of the solidified ingot, impurities that diffuse into the solid silicon are difficult to remove, which makes the crucible and coating important contamination sources. This additional contamination reduces the conversion efficiency, and leads to increased wire sawing defects on the wafered ingots as hard inclusions are introduced, such as SiC and Si_3N_4 [2]. Also, the crucible is not reusable and the crystal growth rate is slow. Electromagnetic continuous casting (EMC) is another technique for silicon preparation, which enables rapid continuous growth of multi-crystalline silicon with low crucible contamination and consumption [3]. However, as reported by Gallien et al. [4], the solid/liquid interface during casting is concave; and the grain growth deviates from the pulling direction. In this paper, a new directional solidification technique based on the cold crucible technology [5] is proposed for silicon casting. The structures, dislocation defect and the growth orientations of grains for the cast ingot were investigated.

***Huang Feng**

Male, born in 1982, Ph.D candidate. His research interests mainly focus on the design of cold crucible and directional solidification of solar grade multi-crystalline silicon.

E-mail: ruirunchen@hit.edu.cn (corresponding author)

Received: 2010-09-04; Accepted: 2011-11-11

1 Experimental procedure

The experiment was carried out on the multi-functional EM-solidification apparatus, which was originally designed and fabricated by our research group for directional solidification of titanium alloys. The schematic diagram is shown in Fig. 1. The cold crucible was designed with a taper, which is used for continuous casting and solidification expansion of silicon [6]. The detailed experimental procedure is described as follows: a graphite base that is fixed on the pulling pole is inserted 62 mm into the crucible; and 30 g of silicon is set on top of it. The chamber is evacuated and then filled with argon until a pressure of 300 Pa is established. The electrical power is gradually stepped up until it reaches 50 kW. During this process, the graphite base is heated inductively by the alternating electromagnetic field [7]. The silicon that is on the base is preheated and melted by the heat exchange from the base. The feeder is activated as the silicon is completely melted to expand the pool. After a liquid dome in a suitable shape is formed, the continuous casting is started with the feeder working at a corresponding speed, according to the withdrawal velocity. In this paper, the withdrawal velocity is set at 1.5 mm·min^{-1}, the raw material is 99.4% silicon in the form of granules and the electrical frequency is 50 kHz. The cross section of the ingot is about 60 mm × 60 mm and its length is over 120 mm.

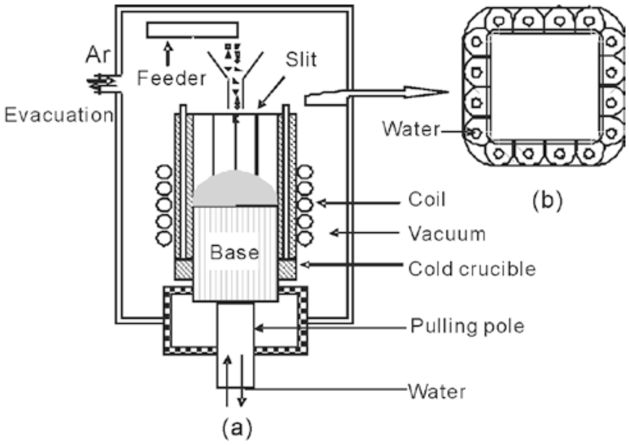

Fig. 1: Schematic diagram of experimental apparatus: (a) overview of equipment, and (b) cross section of cold crucible

2 Results and discussion

2.1 Macrostructure of ingot

The cast ingot was sectioned longitudinally and transversely, polished and etched using 20% NaOH. Its macrostructure is shown in Fig. 2. As the whole macro-structure graph is formed from the macro-graphs of individual slices, the grains in one slice do not seem to match those of the adjacent slices because some small parts of the ingot between the two slices might have fragmented during sawing. Figure 2 shows that the ingot mainly consists of columnar grains orientated approximately parallel to the pulling direction, which indicates that the solidification occurred directionally. Resulting from the intense cooling of the cold crucible wall, shull is formed at both sides; in which the grains are fine and grow perpendicularly to the crucible wall. Due to the pulling of the base, the columnar grains become thicker as a result of the decreased cooling rate and the coalescence of grains. A large columnar grain exceeding one centimeter in width is formed in the top, which is close in size to that cast by conventional directional solidification and is much larger than that cast by EMC.

Directional solidification requires a unidirectional heat flow in the samples and the heat transfer through the crucible wall must be reduced or even avoided. As discussed by Ding et al. [8], the contact between the melt and the crucible wall is incomplete because of the existence of magnetic pressure. Meanwhile, as the induction heat is mainly released in the skin layer of the melt, the typical solid/liquid interface bends upward in the peripheral areas and changes to convex in the middle at lower withdrawal velocities. It changes from convex to planar and eventually to concave as the withdrawal velocity is increased. As the resistivity of silicon at lower temperature is much higher than that of metals, the induction heat is mainly released in the melt inside the skull, not the shell itself as in induction melting metals. A skull that contacts incompletely with the crucible wall will then play a role of insulator between the melt and the cold crucible wall, which is beneficial to further reduce the lateral heat loss and permit a higher withdrawal velocity to directionally solidify silicon. As the directional solidification of titanium alloys is successfully realized at a speed of 1.0 mm·min^{-1} by this method, in this study the withdrawal velocity is set at 1.5 mm·min^{-1}, and the result shown in Fig. 2 confirms that the silicon can be directionally solidified at this speed.

2.2 Microstructure of ingot

Microstructures of the samples cut from different parts of the ingot are shown in Fig. 3. As shown in the figure, there are neither intergranular nor intragranular precipitates in the bottom and middle parts. This is beneficial to reduce the wire sawing defects and to increase the electron life because the

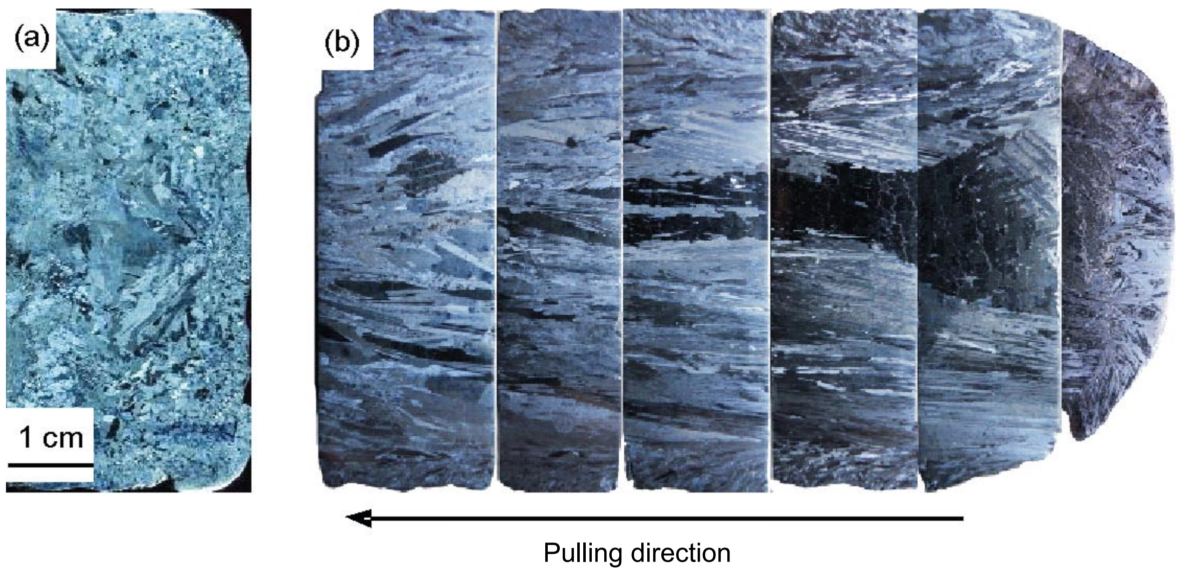

Fig. 2: Macrostructure of ingot: (a) cross section, and (b) longitudinal section

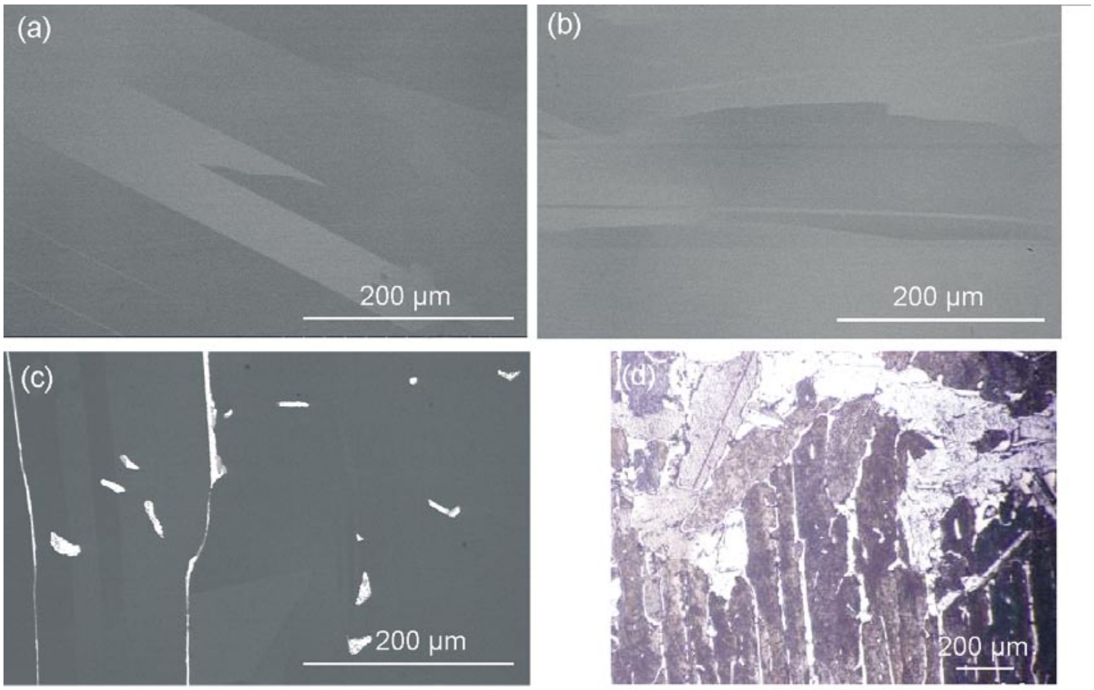

Fig. 3: Microstructure of ingot: (a) SEM image of the bottom part, (b) SEM image of the middle part (c) SEM image of the top part, and (d) optical microscopy image of solid/liquid interface

precipitates act as recombination centers [9]. But in the top area, which solidified last, precipitates were observed, especially in front of the solid/liquid interface, which is cellular in this experiment (see Fig. 3d). Meanwhile, the SEM images suggest the existence of more than one type of intermetallics, shown by different tones of grey. The electron microprobe analysis (EDS) of the precipitates reveals different contents of the following elements: Si, Fe, Al, Ti, Ca and Ni; all of which were also found by M. A. Martorano [10] in conventional directional solidification of Mg-Si alloy. The samples cut from the middle of the ingot were measured by X-ray fluorescence spectrometry. The results show that all the impurities are below the detection limit, which means the raw material is purified above 99.9% during this continuous directional solidification process.

In addition to grain boundaries and impurities, the dislocation is another important defect that affects the conversion efficiency of the cast silicon. In this paper, Secco etching process combined with optical microscopy examination was applied to observe and study dislocation. The result indicates that the average dislocation density in the middle part of the ingot is about (1 to 2) × 10^6 cm^{-2}, which is in the middle range of the results reported by other researchers [11]. Besides the influence of high concentration of impurities in the raw material, an annealing furnace under the crucible needs to be installed to control the cooling conditions of the cast ingot and then eventually reduce the dislocation density.

2.3 Growth orientations of grains

Figure 4 shows the typical XRD pattern of the sample cut from the middle of the ingot. The detailed data are given in Table 1. As comparison with the standard diffraction data in the powder diffraction files (PDF), only the diffraction peaks corresponding to (220) and (311) crystal planes of cubic silicon were found. In order to determine the preferred orientation, the orientation factor α_{hkl} is introduced, as shown in Equation (1). The calculation results show that α_{220} = 53.76%, α_{311} = 46.24%, confirming that after competitive growing, the cast silicon is preferentially <220> orientated. The reason for that still needs to be explored further because the surface of crystalline silicon growing from melt tends to form (111) crystal plane as a result of minimum of the surface energy.

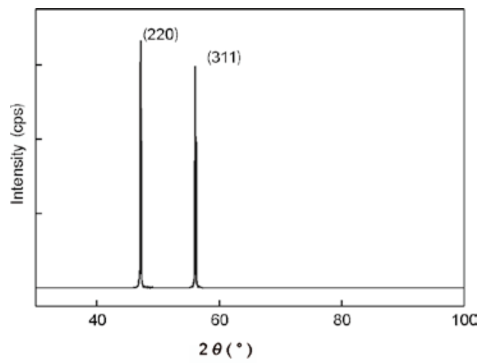

Fig. 4: XRD pattern of sample cut from the middle of ingot

$$\alpha_{hkl} = \frac{I_{hkl} / I_{Ohkl}}{\sum_{hkl}(I_{hkl} / I_{Ohkl})} \times 100\% \quad (1)$$

where I_{hkl} is the measured intensity of diffraction peak from (*hkl*) crystal plane, I_{Ohkl} is the corresponding data given by the PDF, $\sum$ represents the sum.

Table 1: The XRD data of sample cut from middle of ingot

Peak No.	2θ	FWHM	*d*-value	Intensity	I/I_O
1	47.136	0.092	1.9265	266,237	100
2	56.063	0.103	1.6390	239,138	86

3 Conclusions

Silicon can be directionally solidified with a cold crucible at a relatively higher speed (1.5 $mm\cdot min^{-1}$) than titanium alloys. The ingot consists of columnar grains orientated approximately parallel to the pulling direction, except for the skull at both sides. With the pulling of the base, the columnar grains become thicker as a result of the decreased cooling rate and the coalescence of grains. The impurities only precipitate in the top part of the ingot resulting from their accumulation in the melt during this continuous casting process. The average dislocation density is about (1 to 2) × 10^6 cm^{-2}. After competitive growing, the grains are preferentially <220> orientated.

References

[1] Liang Z C, Chen D M, Liang X Q, et al. Crystalline Si solar cells based on solar grade silicon materials. Renewable Energy, 2010, 35(10): 2297–2300.

[2] Du G P, Zhou L, Rossetto P, et al. Hard inclusions and their detrimental effects on the wire sawing process of multicrystalline silicon. Sol. Energy Mater. Sol. Cells, 2007, 91: 1743–1748.

[3] Durand F. Electromagnetic continuous pulling process compared to current casting processes with respect to solidification characteristics. Sol. Energy Mater. Sol. Cells, 2002, 72: 125–32.

[4] Gallien B, Duffar T, Lay S, et al. Analysis of grain orientation in cold crucible continuous casting of photovoltaic Si. J. Cryst. Growth, 2011, 318(1): 208–211.

[5] Chen Ruirun, Ding Hongsheng, Guo Jingjie, et al. Process on Cold Crucible Electromagnetic Casting for Titanium Alloy. China Foundry, 2007, 4(3): 190–193.

[6] Wang Tongmin, Cai Shaowu, Li Jun, etal. Mould taper optimization for continuous casting steels by numerical simulation. China Foundry, 2010, 7(1): 61–67.

[7] Chen Ruirun, Huang Feng, Guo Jinjie, et al. Electromagnetic characteristics of square cold crucible designed for silicon preparation. China Foundry, 2011, 8(2): 206–211.

[8] Ding Hongsheng, Chen Ruirun, Guo Jinjie, et al. Directional solidification of titanium alloys by electromagnetic confinement in cold crucible. Mater. Lett., 2005, 59: 741–745.

[9] Hofstetter J, Lelièvre J F, Cañizo C, et al. Acceptable contamination levels in solar grade silicon: From feedstock to solar cell. Mater. Sci. Eng. B, 2009, 159–160: 299–304.

[10] Martorano M A, Ferreira J B, Oliveira T S, et al. Refining of metallurgical silicon by directional solidification. Mater. Sci. Eng. B., 2011, 176: 217–226.

[11] Ehret E. Characterization of multicrystalline silicon: Comparison between conventional casting and electromagnetic casting processes. Sol. Energy Mater. Sol. Cells, 1998, 53: 313–327.

This research was financially supported by the National Natural Science Foundation of China (No. 50804012) and the Natural Science Foundation of Hei Longjiang Province, China (No. E201002).