Migration behavior and aggregation mechanism of SiC particles in silicon melt during directional solidification process

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Abstract: SiC inclusions in a multicrystalline silicon ingot have a negative effect on the performance of solar cells. The migration behavior and aggregation mechanism of SiC particles in the silicon melt during the directional solidification process was studied. Results show that SiC particles collide and aggregate in the melt due to the effect of melt flow. Larger aggregation of SiC particles is easily deposited at the bottom of the melt, whereas smaller SiC particles are pushed to the top of melt. Meanwhile, the particles migrate to the edge of melt under the effect of electromagnetic force. Furthermore, the enrichment region of SiC particles can be controlled by adjusting the temperature field distribution of the melt. With an increase of the melt temperature, the SiC particles are enriched at the top of the silicon ingot, indicating that SiC particles can be effectively separated from silicon.

Key words: polycrystalline silicon; SiC; directional solidification; migration

CLC numbers: TG146

Document code: A

Article ID: 1672-6421(2021)06-550-07

1 Introduction

With the rapid development of the photovoltaic industry, large-sized crystalline silicon produced by directional solidification attract more and more attention for its lower production cost^[1,2]. However, the introduction of impurities such as carbon cannot be avoided due to the volatilization of graphite parts during the production process. These impurities will concentrate on the top of the silicon ingot due to the segregation effect, resulting in the waste of a large amount of silicon ingots^[3-5]. Meanwhile, the recycling of silicon scrap is greatly limited due to its higher content of SiC inclusion, which can cause defects on the surface of the wafer and reduce the performance of solar cells^[6-9]. Therefore, the effective removal of SiC inclusion has great significance for the recycling of the silicon scrap.

Considerable efforts have been made to separate SiC

inclusions from silicon^[10-13]. Centrifugal stirring, as a pretreatment method, can separate SiC particles from the wafer cutting slurry, but it is limited in industrial applications due to its inefficiency^[14]. Zhang et al.^[15] tried to separate SiC particles from molten silicon by filtering, but the removal effect for fine particles is not ideal. Electromagnetic separation and directional solidification, as an effective and clean method, has been used to purify polysilicon^[16-21]. It has been found that the SiC inclusions tend to enrich at the edge of the melt due to the effect of electromagnetic force. However, the influence of electromagnetic field on the aggregation mechanism of SiC particles has not been discussed in detail. Liu et al.^[22] revealed the distribution of SiC inclusions in a polycrystalline silicon ingot during the directional solidification process, but the effective removal of SiC has not been achieved. In general, the distribution of SiC in the silicon ingot has been widely studied, but the migration behavior and aggregation mechanism of SiC particles have not been revealed systematically, which limits the removal efficiency of SiC inclusions.

In this study, the distribution of inclusion particles in a silicon ingot under the combined action of electromagnetic field and directional solidification was investigated. Meanwhile, combined with the numerical simulation by COMSOL Multiphysics, the effect of the

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Received: 2021-05-30; Accepted: 2021-08-03

temperature field on the migration behavior of SiC particles was studied. Furthermore, a model was established to describe the migration behavior and aggregation mechanism of SiC particles in silicon melt.

2 Experimental procedure

The experiment was carried out in a MTQZ-15-60 induction melting furnace, which is mainly composed of electric control system, induction system, cooling system, vacuum system and gas protection system, as shown in Fig. 1. A thermocouple (TC) was used to measure the temperature at the bottom of the graphite crucible. Silicon in the furnace was heated by the eddy current in a graphite crucible induced by high-frequency power under protective atmosphere conditions (Ar).

Fig. 1: Internal structure of induction furnace

Twenty-five gram high-purity Si and 25 g polysilicon scraps were used as raw materials for each experiment. The silicon scraps were placed at the bottom of the Al_2O_3 crucible. To observe the migration behavior and distribution of SiC in the silicon melt under different temperature fields, the TC temperature and the induction coil height, h (distance from the center of coil to the bottom of crucible, as shown in Fig. 1) were changed. The detailed experimental parameters are shown in Table 1. During the directional solidification process, the pulling mechanism was drawn at a speed of $10.8 \text{ mm} \cdot \text{h}^{-1}$, and the vacuum degree in the furnace was maintained at 0.5 atm.

The obtained silicon ingot of $\Phi 24 \text{ mm} \times 40 \text{ mm}$ was cut lengthwise down the middle. The detected area is the yellow section shown in Fig. 2. The methods used for microscopic analysis included electron probe X-ray microanalysis (EPMA),

Table 1: Experimental parameters

Experiment	Coil height h (mm)	TC temperature (K)
1	22.5	1,623
2	42.5	1,623
3	22.5	1,723

Fig. 2: Sampling position

scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Meanwhile, Image-Pro software was used to measure the particle size at different positions of the ingot.

Thermal and flow fields in the melt were numerically simulated by COMSOL Multiphysics 5.5 based on the experimental process parameters. In addition, the silicon melt was regarded as incompressible Newtonian viscous fluid, and the flow state was regarded as laminar flow in order to simplify the simulation process.

3 Results and discussion

3.1 Macrostructure and microstructure

Figure 3(a) shows the macroscopic morphology of the longitudinal section of the silicon ingot obtained by directional solidification at 1,623 K, and the coil position $h=22.5 \text{ mm}$. It can be seen that the particles are distributed mainly at the top and edges of the ingot, with a few particles deposited at the bottom. The particle enrichment regions were selected for SEM analysis. Figures 3(b) and (c) show the microstructure of particles at the top and bottom of the ingot, respectively. The particles at the bottom of the ingot are aggregated, while the particles at the top are relatively dispersed.

EPMA analysis on the particle enrichment region was further performed to observe the element distribution, as shown in Fig. 4. The particles with dark colors were identified as SiC, while

Fig. 3: Macromorphology (a) and micromorphology (b and c) of particles enrichment region along longitudinal section: (b) top of ingot; (c) bottom of ingot

Fig. 4: EPMA mapping of elements distribution on particles enrichment region: (a) EPMA image; (b) N; (c) Si; (d) C

the bright-colored particles were detected as Si₃N₄, which was derived from polysilicon scraps. According to previous study^[23], α -SiC is unlikely to exist below 2,000 K, so the SiC particles are β -SiC which is stable in the experiment.

3.2 Migration behavior and aggregation mechanism of SiC particles

The distribution of SiC particles is closely related to their precipitation, migration and aggregation behaviors. During the melting process, the SiC particles dissolve, which increases the concentration of C in the melt. During the directional solidification process, the C concentration in the melt is further increased due to its low segregation coefficient. If the C concentration in the melt exceeds its solid solubility, SiC will precipitate onto the hard particles or the crucible. Figure 5 shows a schematic diagram of the precipitation of SiC particles in the silicon melt from 1,685 K to 1,735 K^[22], where the solubility limit of carbon in the silicon melt $C_L(T)$ can be expressed as a

Fig. 5: Diagram of precipitation of SiC particles in silicon melt^[22]

polynomial function approximately^[22].

$$C_L(T) = 8.625 \times 10^{-4} T^2 - 2.7643T + 2222.9 \quad (1)$$

where T is the melt temperature, K.

It can be calculated that when the melt temperature is 1,685 K–1,735 K, the solid solubility of carbon in the silicon is between 11 and 19 ppmw.

To analyze the migration behavior of the SiC particles in the melt, numerical simulation on the temperature field and flow field of the silicon melt were carried out using COMSOL Multiphysics 5.5 software. Figure 6(a) shows the temperature field distribution of the melt at 1,623 K of TC temperature and 22.5 mm of coil height. It can be seen that the temperature at the center of the melt is higher than that at the bottom and top. Due to the inhomogeneous temperature distribution and the introduction of electromagnetic field, the flow of silicon melt is unstable, as shown in Fig. 6(b). The melt flows from the center of the crucible to the periphery, and the flow velocity (v) at the

Fig. 6: Temperature field (a) and flow field (b) distribution of silicon melt

center of the crucible is lower than the bottom and top, which leads to the appearance of vortex in the melt. These vortices cause the continuous movement of SiC particles in the melt and the enrichment of SiC particles in certain areas.

Figure 7 shows the distribution diagrams of SiC particles at 0 min and 15 min during melting process. It shows that SiC particles are uniformly distributed throughout the entire melt at the beginning of melting (0 min). After melting for 15 min, SiC particles are gradually enriched at the side, bottom and top of the crucible. The motion trajectory is consistent with the flow pattern of the melt. The SiC particles are forced to migrate to the side of the crucible due to the effect of electromagnetic force.

Fig. 7: Numerical simulated distribution of SiC particles at different melting times: (a) 0 min; (b) 15 min

Compared with the morphology of the ingot shown in Fig. 3(a), it can be found that the simulation results on distribution of SiC particles are consistent with the experimental results.

During the melting process, SiC particles in the silicon scraps are separated out and entrained into the melt, meanwhile the particles aggregate with each other due to melt convection, as shown in Fig. 8(a). The large aggregation of SiC particles will sink and deposit at the bottom of the melt due to the effect of gravity, whereas the individual particles continue to move through the melt, as shown in Fig. 8(b).

Figure 8(c) shows that SiC particles are subjected to multiple forces under the action of the melt and solid-liquid interface, such as lift force (F_L), interface force (F_I), gravity (F_G), electromagnetic force (F_P) and drag force (F_D). Li et al.^[24] discussed the relationship between these forces and the migration behavior of SiC particles. They calculated the critical flow velocity (v_c) of the SiC particles as follows^[24]:

$$v_c = \frac{\sqrt{6}d_{\min}}{3\mu R_p} \left(\frac{d_{\min}}{R_p} \right)^{0.423} \left(\frac{k_L}{k_p} \right)^2 [\Delta\gamma_0 \left(\frac{a_0}{a_0 + d_{\min}} \right)^2 \frac{k_L}{k_p} + \frac{3.23}{\pi} \mu V_{\text{rel}} R_p \sqrt{\frac{\rho_L}{\mu}} \left(\frac{dV_{LX}}{dy} \right)_{\text{avg}} - \frac{2}{3} g R_p^2 (\rho_p - \rho_L)] \quad (2)$$

where g is the gravity acceleration, R_p is the radius of the particle, ρ_p and ρ_L are the density of the particle and melt, k_p and k_L are the thermal conductivity of the particle and melt, $\Delta\gamma_0$

Fig. 8: Schematic diagram of migration behavior of SiC during directional solidification

is the interfacial energy difference between the solid/particle and liquid/particle, a_0 is the diameter of an atom in the liquid metal, $d_{\min}$ is the gap width between particle and interface, μ is the dynamic viscosity of the liquid, V_{rel} is the velocity of the particle relative to the liquid, $(\frac{dV_{LX}}{dy})_{\text{avg}}$ is the averaged velocity gradient within the momentum boundary layer.

The equation indicates that the migration rate of the particles decreases with the increase of particle size. At the beginning of solidification, the aggregation of SiC particles in the melt is easily engulfed by the solid-liquid interface, with the smaller-sized particles being pushed away. As the solid-liquid interface pushes forward, the SiC particles in the melt continues to collide and form aggregation, which are gradually engulfed by the solid-liquid interface during the directional solidification process. Meanwhile, the SiC particles are enriched at the edge of the melt due to the effect of electromagnetic force.

At the later stage of solidification, a great number of SiC particles are enriched at the top of the melt. The particles collide and aggregate with each other by irregular thermal motion in the residual silicon melt, as shown in Fig. 8(d). Once an aggregation occurs around a particle, the number density

of particles in its neighborhood area will decrease, with the result that SiC particles in the melt migrate to the aggregation. In addition, the aggregation mechanism of SiC particles may involve Ostwald ripening^[25]. Carbon in the melt diffuses from smaller particles to larger particles due to the concentration gradient between SiC particles. Finally, a large aggregation of SiC particles is formed at the top of the ingot.

3.3 Control of particles enrichment region

Based on the migration behavior and aggregation mechanism mentioned above, the temperature field affects the flow state of the melt, and then changes the migration behavior of particles in the melt. Furthermore, the enrichment region of the particles can be controlled by adjusting the melting temperature and coil position. As shown in Fig. 9, the ingots were produced in different temperature fields. The particles are mainly enriched at the bottom when the temperature and coil position are 1,623 K and 42.5 mm, respectively, as shown in Fig. 9(a-c). The enrichment regions of SiC particles will move up with the TC temperature increase and coil position decrease, as shown in Fig. 9(d-f). However, the micromorphology shows that the aggregation tendency of particles decreases with the increase of ingot height even at different temperature fields.

Fig. 9: Macromorphology and micromorphology of particles enrichment area at different experiment conditions: (a, b, c: 1,623 K, $h=42.5$ mm; d, e, f: 1,723 K, $h=22.5$ mm)

All sizes of SiC particles (including individual particles and aggregated particles) are counted using Image-Pro software, and most of the SiC particles are between 20–400 μm in size. The maximum and average sizes of SiC particles are measured and calculated, as shown in Table 2. It can be found that the maximum and average sizes of SiC particles decrease with the increase of ingot height, which means that the larger particles are more easily deposited at the bottom of the ingot during the directional solidification process.

Based on the experimental results (Fig. 3 and Fig. 9), the proportions of the enrichment regions of SiC particles at different ingot heights were calculated. As shown in Fig. 10, the distribution of the SiC particles is changed in different

temperature fields. At 1,623 K and coil position of 22.5 mm, a few particles deposit at the bottom of the ingot. However, the particles at the bottom disappear and enrich at the upper of the ingot as the TC temperature is increased. This phenomenon indicates that the increase of melt temperature promotes SiC particles to migrate to the top. However, it can be found that the enrichment region of SiC particles is mainly located at the bottom as the coil position moves up.

Figure 10 shows that the enrichment region of SiC particles in the silicon ingot varies significantly under different temperature fields. At 1,623 K, with a coil height of 22.5 mm, the melt is completely in the action zone of electromagnetic field due to being in the coil. The aggregation of SiC particles

Table 2: Size of SiC particles in ingot

TC temperture (K)	Coil height (mm)	Area	Maximum diameter (μm)	Average diameter (μm)
1,623	22.5	Bottom	657.9	126.8
1,623	22.5	Top	191.8	55.7
1,623	42.5	Bottom	471.51	143.4
1,623	42.5	Middle	260.5	73.1
1,723	22.5	Middle	367.0	99.8
1,723	22.5	Top	316.7	68.0

Fig. 10: Cumulative area distribution of SiC inclusions at different heights of ingot

in the melt are deposited on the bottom, while individual SiC particles migrate to the top of the ingot. As the coil height moves up ($h=42.5$ mm), the turbulence of the upper melt is more intense due to the higher intensity of the electromagnetic field. The turbulence causes individual SiC particles to collide with each other, forming the aggregation of SiC particles. However, with the particles moving down, the lift force on the SiC particles decreases. While, the action of gravity makes the SiC particles sink and deposit at the bottom of the melt.

When the temperature is increased to 1,723 K, the flow velocity of the melt is accelerated. The SiC particles are uniformly distributed and continuously move in the melt. During the solidification process, it is difficult for the SiC particles to form aggregation. They will be repelled to the top of the melt by the solid-liquid interface. Finally, the SiC particles form an enrichment region at the top of the ingot. This means that the SiC particles can be effectively separated from silicon scraps.

4 Conclusions

The migration behavior and aggregation mechanism of SiC particles were discussed systematically, and the following conclusions are obtained:

(1) The SiC particles move continuously and collide with each other due to the effect of melt convection. The particles tend to form aggregation by collision and Ostwald ripening mechanism.

(2) Larger aggregation of SiC particles is easily entrapped by the solid-liquid interface, while the smaller SiC particles are repelled to the top of melt. Some particles are captured near the crucible inside wall under the action of electromagnetic force.

(3) With the increase of the melt temperature, the enrichment region of SiC particles moves upward due to the accelerated melt flow. In addition, the particles can be deposited at the bottom by adjusting the electromagnetic field.

This work proves that the enrichment region of SiC particles can be controlled by adjusting the temperature field distribution of the melt. The particles can be effectively separated from the silicon scraps by alternating electromagnetic fields and directional solidification.

Acknowledgements

This study was financially supported by the Specialized Research Fund for the National Natural Science Foundation of China (51974057), the Open Project of State Key Laboratory of Advanced Special Steel, Shanghai Key Laboratory of Advanced Ferrometallurgy, Shanghai University (SKLASS 2019-19), and the Science and Technology Commission of Shanghai Municipality (No. 19DZ2270200), and the Innovation Team Project for Key Fields of Dalian (Grant No. 2019RT13).

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