Simulation study on 300mm monocrystalline silicon celerity single crystal

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Abstract. Since entering the 21st century, the survival and development of mankind are faced with great challenges and great opportunities. With the decrease of petroleum, coal, natural gas and other resources, a large number of harmful products generated in the combustion process of fossil fuels have caused incalculable adverse effects on human living environment. Thermal stress in crystals is one of the key factors affecting the properties of solar level monocrystalline silicon. In this paper, the relationship between the heat loss mode and the stress in crystal is studied. If carbon is introduced into the crystal growth process, it will promote the formation of oxygen precipitation and SiC precipitated phase, resulting in increased stress in the crystal, thus affecting the quality of monocrystalline silicon. The distribution of carbon impurities in the melt is closely related to the convection behavior of the melt. The carbon atoms in the atmosphere diffused into the melt mainly through the free surface area near the crucible wall. By adjusting the structural parameters of symmetric magnetic field and asymmetric magnetic field, the convection intensity in the carbon atom doped region can be suppressed, the thickness of carbon atom diffusion layer can be increased, and the oxygen content and distribution uniformity in the crystal can be controlled by magnetic pull technology to improve the crystal quality.

Keywords: Monocrystalline silicon; Czochralski single crystal; simulation study.

1. Introduction

With the integration of semiconductor industry, the demand for large-diameter and high-quality Czochralski monocrystalline silicon is increasing, so the demand for improving the performance and quality of crystalline silicon is increasingly prominent [1]. Monocrystalline silicon is widely used in the fields of semiconductor and solar power generation. With the strategic needs of environmental resources protection and sustainable development, our demand for renewable energy is constantly increasing. In the early stage of crystal growth, the heat in the crystal is mainly exchanged through seed crystal heat transfer, shoulder surface heat dissipation and side surface heat dissipation of the crystal [2]. Therefore, there are large stress areas under the crystal seed, under the shoulder and on the side surface of the crystal. At the initial stage of crystal growth, the heat in the crystal is mainly exchanged by seed heat transfer, shoulder surface heat dissipation and side surface heat dissipation. Therefore, there are large stress areas under the crystal seed, under the shoulder and on the side surface of the crystal. Therefore, it is necessary to strengthen the quality control of Czochralski silicon, and the demand for renewable energy is increasing, which requires the quality of Czochralski silicon to be further improved [3]. If the thermal stress in the crystal is large, the crystal will have defects such as dislocation slip and crystal breakage. If monocrystalline silicon is heated unevenly, it will produce a large temperature gradient in the crystal, which will produce a large stress. Single crystal manufacturing is the foundation of the rapidly developing photovoltaic industry. The strong market demand urges the development of monocrystalline silicon manufacturing technology towards more efficient, more economical and higher quality. Czochralski method is used as the main manufacturing method by the majority of single crystal hanging manufacturers for its rich energy transmission efficiency. The influence of different hook-shaped magnetic field structures on the content and distribution of carbon impurities in the melt was simulated by CGSim crystal growth software. By adjusting the magnetic field intensity ratio (MR) and the height (H) of the coil position from the ground, the relative position between the zero

Gaussian plane (ZGP) and the growth interface can be controlled, and the optimized melt convection can be obtained.

2. Model

2.1 Mathematical model

CGSim can realize laminar or turbulent flow, heat conduction and convection, passive material transport, and calculation of solid-liquid interface shape with or without magnetic field in 2D/3D simulation area of Czochralski monocrystalline silicon in fluid. Lorentz force generated by magnetic field inhibits the flow in melt and changes the intensity of melt convection. Slow down the flow rate of the melt below the crystal, and make the boundary layer below the growth interface thicker, thus reducing the concentration of carbon diffusion in the silicon melt into the crystal, which is conducive to obtaining high-quality silicon crystal. Monocrystalline silicon is widely used in photovoltaic power generation systems and microelectronics technology, and the rapid development of the industry puts forward higher requirements for the quality of monocrystalline silicon [4]. And impurity defects are the two main determinants of crystal quality, among which impurities mainly include metallic impurities and nonmetallic impurities. At the same time, the market competition of solar-grade monocrystalline silicon is becoming increasingly fierce. How to occupy a favorable position in the market competition should make a breakthrough in the following two aspects: first, reducing the production cost, and second, improving the performance of products. In order to study the heat exchange behavior of the crystal, the grid at the side, shoulder, growth interface and seed crystal of the crystal is refined, and the rest is divided by free triangular grid. The physical parameters used in the simulation process are shown in Table 1.

Table 1 Physical parameters of materials

	Thermal conductivity	Specific heat	Density	Radiation coefficient
Graphite	4.62	2200	2500	0.7
Crucible of Shi Ying	4.1	1680	2620	0.6
Thermal insulation carbon felt	2.7	1050	2010	0.5
Hot screen	121	2300	2400	0.4
Silicon (melt)	78	1100	2840	0.2
Silicon (solid)	34	980	2950	0.6

The simulation of the thermal stress field in the crystal can be realized in the post-processing operation based on the above operation. Besides, in the axisymmetric growth model, the heat radiation exchange can be calculated. The governing differential equations of heat conduction, mass transport, magnetic field and solute transport used in the model are:

$$\frac{\partial p}{\partial t}+\nabla \bullet \left(pu\right)=0 \tag{1}$$

$$\frac{\partial\left(pc_pT\right)}{}+\nabla \bullet \left(pc_puT\right)=\nabla \bullet \left(\lambda_{eff}\nabla T\right)-\nabla \bullet q_{rad}+S_T \tag{2}$$

$$p=\frac{p_{0m}}{R_gT} \tag{3}$$

Inorganic carbon impurities have an important influence on the quality of silicon single crystal. During the annealing process of silicon single crystal, carbon impurities can promote the formation of oxygen precipitation and increase the concentration of point defects in silicon single crystal, such as the formation of oxidation-induced stacking faults and other defects, which greatly affects the photoelectric conversion efficiency of silicon single crystal. The oxygen in the crystal mainly comes from the dissolution of Shi Ying crucible during crystal pulling, in which 99% of the oxygen volatilizes from the melt surface in the form of Si O and is taken away by argon flow, while the rest enters the crystal. Among them, Czochralski method is the most commonly used method to manufacture monocrystalline silicon at present. By growing crystal from seed crystal in melt, it has many advantages such as fast growth rate, low cost, high purity and good integrity [5]. During the growth of monocrystalline silicon, the thermal field in the furnace changes with time, and the temperature gradient in the crystal also changes. For silicon crystals with different equal diameter stages, heat exchange occurs between the crystal and the surrounding environment, the temperature in the crystal is constantly changing, and its thermal stress also changes. Turbulence is characterized by the transmission of momentum, energy and solute through velocity pulsation. Because of the small scale and high frequency of these flows, direct linear simulation (DNS) will greatly consume computer resources. In addition, carbon impurities can also reduce the yield of silicon single crystal and make the leakage performance of devices worse. The carbon mainly comes from the chemical reaction between the high-temperature graphite device in the furnace and the Si O volatilized from the melt, resulting in CO gas.

2.2 Oxygen in Czochralski monocrystalline silicon

The main reason for the high and low oxygen content distribution is that during the growth process, the melt with silicon content has decreased, the reaction zone and contact area with Shi Ying crucible have been decreasing, and the reaction with the length of crystal growth causes the amount of stannum to continue to decrease. During the growth process of monocrystalline silicon, heat transfer occurs between the connected seed crystal and protective gas, while the crystal surface undergoes heat exchange by radiation [6]. There are some details missing in the geometry of CGSim operation interface, such as the meniscus at the three-phase point, the junction between seed crystal and ingot, and the bending part of Shi Ying orange pot, which need to be properly corrected according to the actual situation. Therefore, by reducing the content of CO diffusing from the free surface of the melt into the melt and optimizing the convection behavior of the melt, the carbon content migrating into the crystal can be reduced. In general, the flow in the melt can be changed by changing the crystal pulling process parameters such as crystal rotation and crucible rotation. However, the volatile surface of silicon melt is unchanged, and the volatile liquid of silicon dioxide on the silicon surface is basically unchanged during the whole growth process, which leads to oxygen entering the crystal, reducing and increasing the crystal length. The high temperature of seed crystal indicates that heat transfer between seed crystal and crystal is also one of the main ways of crystal heat loss [7]. With the increase of crystal pulling length, the temperature of seed crystal decreases gradually, which means that the proportion of heat transfer between seed crystal and crystal in the heat loss of crystal decreases gradually. During the growth process, the meniscus appears at the triple point at the junction of the crystal and the melt. The next stage of geometry file adjustment will create the melt curve around the crystal. This part of the curve is lost during the initial introduction of the geometry. The meniscus curve can be obtained by using the automatic meniscus creation function, and its size can be adjusted to fill in the geometry of the furnace body. On the one hand, applying transverse magnetic field and hook magnetic field to the melt can also change the flow behavior in the melt [8]. After the magnetic field is applied, Lorentz force is generated in the conductive melt to inhibit the melt flow, thus changing the thickness of the boundary layer below the growth interface and reducing the doping of carbon in the crystal. Convection intensity of Si O evaporation rate from the melt surface. The distribution of oxygen in Czochralski single crystal is that the single crystal head has high content, low tail content, high center and low edge.

3. Simulation study on growth characteristics of Czochralski single crystal silicon

3.1 Basic characteristics of solid-liquid interface in the growth of Czochralski single crystal silicon

In the growth process of monocrystalline silicon, the profile curve of solid-liquid interface is shown in Figure 1.

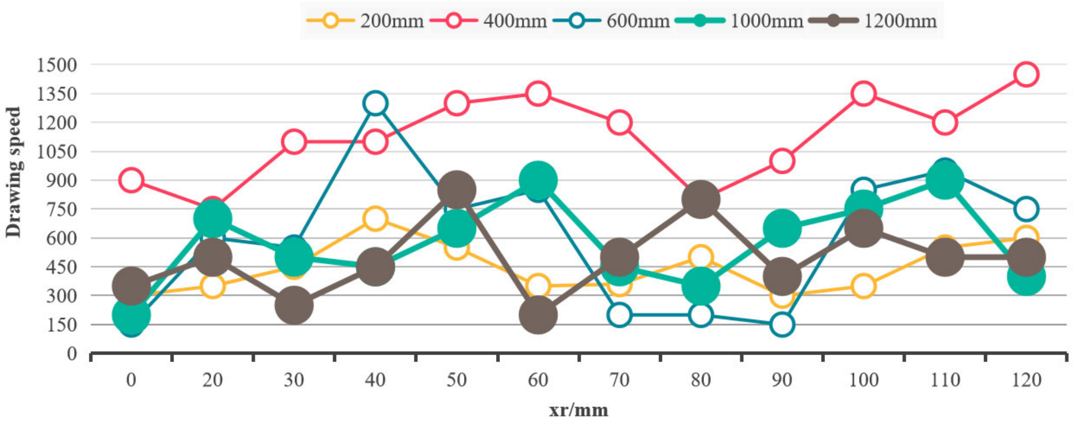

Figure 1 Profile curve of solid-liquid interface of 300mm monocrystalline silicon at the casting speed of 0.8mm/min

The carbon concentration in magnetic field crystal pulling was measured by Photoluminescence spectrometer. It was found that by increasing the flow rate of argon, CO in silicon melt could be evaporated and the doping of CO could be controlled. However, there is little research on the carbon concentration in the crystal growth process under the hook-shaped magnetic field structure. In the process of optimizing the hook-shaped magnetic field structure, the variation law of carbon impurity concentration in Czochralski single crystal silicon was studied, and finally the optimized magnetic field structure was determined [9]. In the early stage of crystal pulling process, the height and volume of the crystal rod are low, and the axial temperature gradient near the solid-liquid interface in the crystal rod is large, so the central area of the solid-liquid interface rises, and the shape gradually changes from flat to typical convex. In the final stage of crystal pulling, the volume of melt in citrus fruit decreases significantly, the temperature in the melt increases and the axial temperature gradient decreases, and the average temperature of the melt near the free surface and triple point increases obviously, as shown in Figure 2.

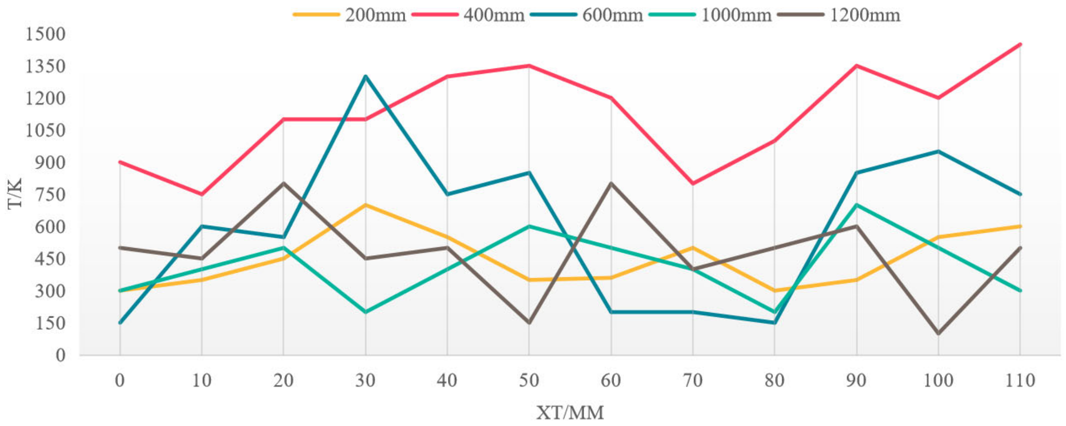

Figure 2 Free surface temperature of 300mm monocrystalline silicon melt when the casting speed is 0.8mm/min

The upper coil and the lower coil are placed outside the single crystal furnace to generate an external magnetic field, and reverse current is passed through the coils to form a hook-shaped magnetic field. The volatilization rate of Si O gas on the free surface of the melt is closely related to the distribution and intensity of the gas flow field. The flow rate of argon rushed into the furnace is fixed, and the change of gas flow field is analyzed by changing the liquid port distance, so as to obtain the best liquid port distance suitable for crystal pulling. The solubility of silicon oxygen varies with temperature. The higher the temperature, the faster it dissolves, while the lower the temperature, the lower the solubility. In the whole processing process, the temperature should be controlled between 850 and 1200℃. The heat loss from the crystal surface within 300 mm above the solid-liquid interface is greater than that from the rest of the crystal surface, indicating that the length within 300 mm above the triple point is the main heat dissipation area. During crystal pulling, the heat convection in the area near the liquid level above the melt is directed from the crucible wall to the center of the crucible in the radial direction, which is just opposite to the flow direction of argon in the area near the liquid level above the melt. Therefore, the flow of argon can suppress the convection in the area near the liquid level above the melt by its shear force in the horizontal direction [10]. Therefore, its concentration will be in a saturated state, in which interstitial oxygen atoms will be formed, and oxygen will precipitate secondary thermal donor defects. Here is the role of oxygen in silicon. The transformation curve of the percentage of thermal radiation in different areas of the crystal under different crystal pulling lengths to the total radiation value is shown in Figure 3.

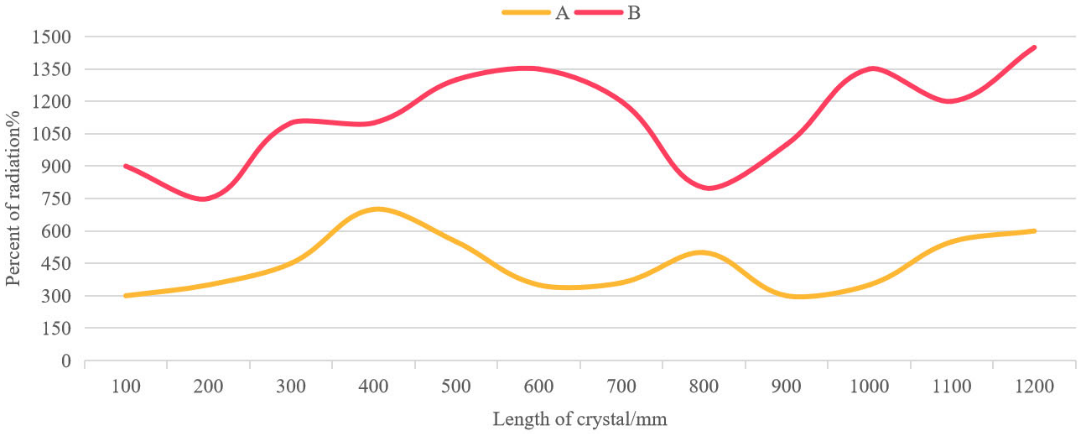

Figure 3 Percentage of thermal radiation value of different crystal areas in total radiation value under the same diameter

The curve B in the figure shows the thermal radiation value in the length above the triple point, and the curve A shows the thermal radiation value in the remaining length (part of the side wall and shoulder). From the calculation results, it can be seen that the heat lost from the crystal surface above the solid-liquid interface is greater than that from the rest of the crystal surface, indicating that the length above the triple point is the main heat dissipation area.

3.2 Simulation of the effect of crystal pulling rate on the growth of 300 mm Czochralski single crystal silicon

The crystal pulling rate has a decisive influence on the crystal yield. A large crystal pulling rate can significantly shorten the production cycle and improve the production efficiency. However, in actual production, excessive crystal pulling rate will cause a series of problems such as the increase of interstitial atomic point defects and thermal stress in the crystal. Therefore, this trend is consistent with the decrease of magnetic induction intensity of the whole silicon melt during the development of single crystal silicon pulling process. The decrease of the magnetic induction intensity of the melt leads to the weakening of Lorentz force in the melt and the weakening of the inhibition of natural convection in the melt. The flow rate is unevenly distributed in the area above the liquid level, and the gas flow rate is affected by the shape of the flow channel, and the flow rate is higher near the lower edge of the draft tube, that is, the existence of the draft tube helps to increase the flow rate of argon. At the same time, it can be seen that when the argon flow rate in the furnace is constant, with the decrease of the distance between the liquid ports, the argon flow rate above the liquid level of the melt gradually increases. Oxygen in the gap position acts as a pinned dislocation, which can increase the mechanical strength of the crystal and effectively avoid the deformation in the thermal process of the device process. The reasons for the above results are analyzed. The change of crystal growth rate mainly causes the change of advection force in the melt. Advection force is the force caused by crystallization at the solid-liquid interface. When only advection force acts in the melt, there is basically no macroscopic flow in the melt, so it has little influence on the thermal field of Czochralski monocrystalline silicon. The radial component of Lorentz force in the upper part of the melt, especially in the free surface area, is obvious, and its direction points to the side wall of the crucible, which is opposite to the main convection direction in this area of the melt, which can well slow down the melt flow in this area. And its position gradually shifts to the crystal direction, all of which are caused by the change of gas flow channel. At the same time, it can be found that the flow rate near the liquid level is enhanced as a whole, which will be very beneficial to the volatilization of Si O in the melt. The rotation of the Shi Ying can make the impurities evenly distributed in the convection direction of the melt; However, it is caused by rotation and convection in the same direction. This is because the temperature fluctuation in the melt leads to the increase of oxygen concentration in the crystal and the rotation speed of the melt with the Shi Ying crucible. Generally speaking, thermal stress is caused by large temperature gradient. This result proves once again that in the early stage of crystal growth, the heat dissipation in the crystal mainly consists of three ways: seed heat transfer, shoulder surface heat dissipation and crystal side wall heat dissipation. However, the ascending system will keep the position of triple point in three-dimensional space unchanged, so the solid-liquid interface shows the upward convex trend with the increase of crystal pulling rate.

4. Conclusions

In order to obtain high-quality and low-cost large-size solar-grade Czochralski monocrystalline silicon, in short, with the continuous progress of the times and the development of large-size low-oxygen concentration monocrystalline silicon growth technology in the later period, the hook-shaped magnetic field in the magnetic Czochralski method is used, and most of the crystal heat is exchanged through seed crystal heat transfer, crystal shoulder heat dissipation and crystal side surface heat dissipation. In the middle and late stage of crystal pulling, the main heat exchange area is within 300 mm above the triple point. Establish a more perfect and complex 2D model that fits the real single crystal furnace structure, and consider the influence of auxiliary facilities such as draft tube and vent valve to improve the accuracy of quantitative simulation. The radial component near the free surface of the melt becomes larger, which inhibits the melt flow, thickens the diffusion boundary layer of carbon atoms, hinders the diffusion of carbon atoms in the atmosphere, and finally reduces the carbon content in the crystal. At the same time, the change of melt convection makes the oxygen content in the crystal gradually increase; With the increase of the cover distance, the axial temperature gradient in the crucible gradually decreases, which reduces the temperature at the bottom of the crucible. At the same time, the temperature of the crucible side wall gradually decreases, which is beneficial to reduce the oxygen dissolved in the melt during crystal pulling. The transmission way and distribution law of oxygen in Czochralski silicon and the ways to reduce the oxygen content and improve its distribution uniformity were carefully analyzed, which effectively controlled the uniform distribution of oxygen content in Czochralski silicon.

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