Research and preparation of high quality and high utilization polycrystalline silicon ingot

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An improved furnace was designed to reduce the carbon and oxygen impurity of multicrystalline silicon during unidirectional solidification process. The flow pattern of impurity gas at the top of the silicon melt can be significantly improved under the small cover conditions and the impurity gas eddy currents can also be avoided. The number of silicon block containing inclusions significantly reduces under the conditions of small cover plate. Meantime the carbon content at the head and tail of ingot reduced from 10.2 ppma and 4.52 ppma to 7.78 ppma and 2.1ppma, and the oxygen content at the head and tail of ingot reduced from 0.7ppma and 12.96ppma to 0.46ppma and 11.3 ppma, respectively. The utilization of the entire ingot has also been improved from 70.1% to 72.1%, which is significantly higher than that of the ordinary ingot under small cover condition.

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1. Introduction

Today, multicrystalline silicon has now become the main material in the photovoltaic market because of its low production cost and because of the relative high conversion efficiency of solar cells made from this material. It is well known that the efficiency of mc-Si solar cell is strongly dependent on the quality of the mc-Si wafers, which are cut from massive mc-Si ingots. The quality of the as-grown ingots is affected by the impurity content and concentration from the feedstock, and the dissolution that occurs in the crucible and heating apparatus during growth [1-2]. Directional solidification systems (DSS) are frequently employed to fabricate large-size multicrystalline silicon (mc-Si) ingots for use in solar cells. Today, it is common for companies to produce mc-Si ingots with a weight of 420kg. Similar to the Czochralski method, the unidirectional solidification is connected with transport of impurities [3].

Carbon is one of the major impurities in multicrystalline silicon. The carbon concentration in the silicon crystal is lower than the one in the silicon melt, because the segregation coefficient of carbon is less than one [4]. Silicon carbide (SiC) particles will precipitate as the carbon concentration rises beyond the solubility limiting the silicon melt [5]. It can cause severe ohmic shunts in solar cells and result in nucleation of new grains in silicon ingots. Pizzinietal showed that the density and electrical activity of dislocations in a mc-Si ingot is strongly dependent on the carbon concentration [6].Therefore, the carbon content in the silicon feedstock must be kept as low as possible. Oxygen impurity is another one of the most significant types of impurities affecting solar cell wafers and may cause light-induced degradation or creation of thermal donors in solar cells [7-8]. Oxygen precipitation is known to act as intrinsic gettering sites for impurities and to affect the mechanical strength of the wafer. The oxygen in a DSS mainly originates from the heated quartz crucible and the feedstock. Some of the dissolved oxygen in the melt reacts with Si atoms to form silicon oxide at the free surface, which is carried away by the argon gas above the surface, and the remaining quantity is incorporated into the ingot[9-12].Therefore, the oxygen content in the ingot also need to be strictly controlled.

In this study, an improved unidirectional solidification furnace was suggested to produce silicon crystals with lower carbon and oxygen concentration. A global simulation including melt convection, argon flow, solid conduction and thermal radiation was carried out and the ingot experiment was done under different conditions simultaneously. The gas flow above the free surface of the silicon melt could be changed by improving the size and position of quartz crucible cover. It can reduce the interaction time between the impurity gas and the silicon melt surface by adjusting crucible cover, thereby obtaining a lower carbon and oxygen concentration high quality of polycrystalline silicon ingot.

2. Experiments

A typical directional solidification system for mc-Si ingots is sketched in Fig. 1. It consists of graphite heaters, fused silica crucible with graphite susceptor, heat exchange block and insulation material, etc. The production of mc-Si starts with the melting of Si feedstock in a silica crucible (coated with Si_3N_4 on its inner surfaces) in a protected atmosphere of Ar (600mbar). The growth cycle of ingot include five stages as follow: heating, melting, crystallization, annealing and cooling, respectively. The whole growth period is about 60 hours. Growth starts by moving the side insulation upwards and lowering the heating power after the silicon has melted. Silicon growth from the bottom of the crucible, the growth rate is about 10 mm per hour which is determined by the gap opening and power of the heaters. When the silicon melt crystallization after all, program went into the annealing stage, after a few hours annealing, it went into the cooling phase, Ingot can be removed from the casting furnace when the temperature drops to 300 degrees and the whole casting process of ingot were completed finally.

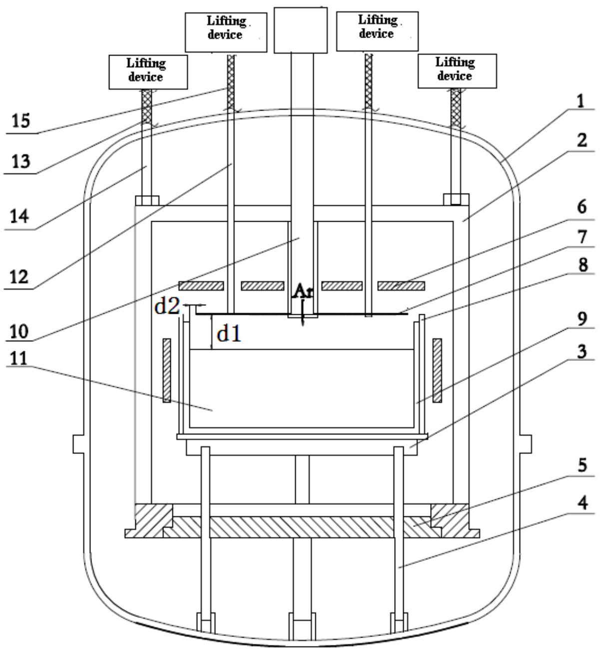


Fig. 1 Structure schematic of polysilicon ingot furnace (1, furnace body 2, insulation cage, 3,heat exchange station 4, pillar 5, insulating substrate 6,heater, 7,cover plate 8, graphite plate 9, quartz crucible, 10, graphite sleeve 11, silicon melt, 12, cover plate boom 13, Insulation cage hoisting bellows 14, Insulation cage lift lever 15, Cover upgrade bellows)

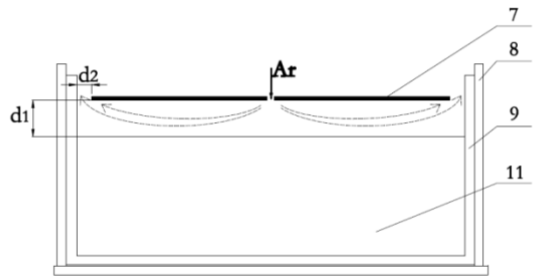


Fig. 2 Structure diagram of small cover.

In order to reduce the contamination of impurity gas on the polycrystalline silicon ingot, the quartz crucible cover is improved in this paper, as shown in Fig.1. The distance between the edge of cover and the inner wall of quartz crucible is d2, it was set at L1 mm and it remains unchanged during the experiment. The small cover also can move up and down by the traction apparatus in Fig.1. The d1 represents the distance between the lower surface of the cover and the upper surface of silicon melt. The d1 distance can be adjusted during the experiment. The specific test parameters are shown in Table 1. Fig.2 shows the relative positions of the small cover and the quartz crucible. The flow pattern of the gas above the silicon melt can be significantly improved and the gas vortex can also be avoided by the movement of the small cover.

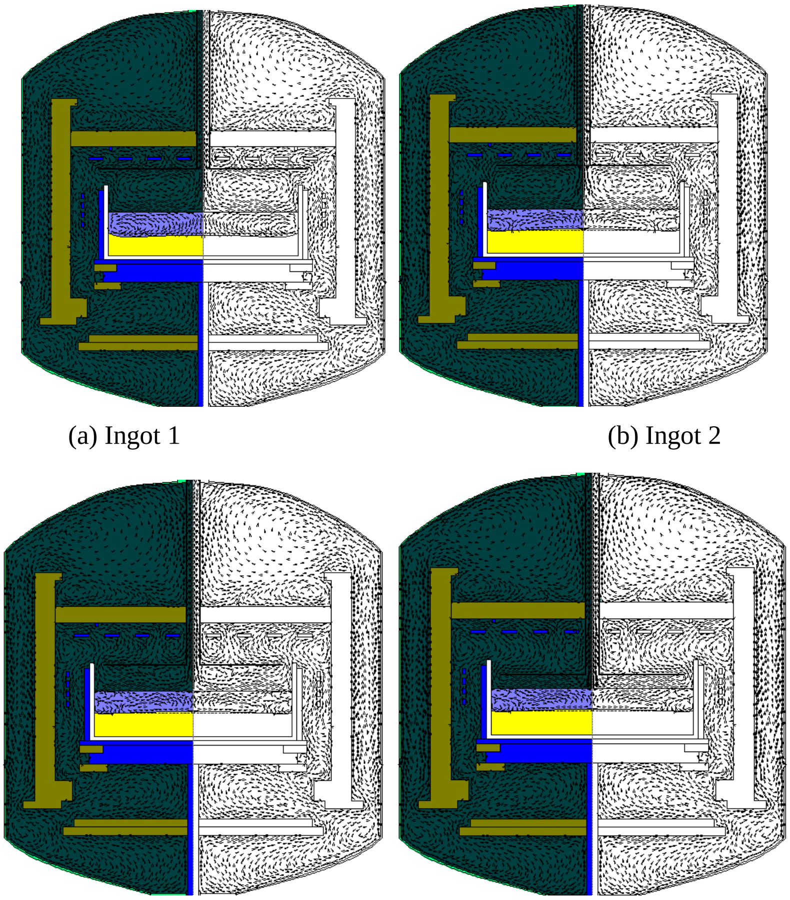
Table 1 Test parameters

Experimental conditions	cover	d1	d2
ingot 1	Conventional	H1 mm	L1 mm
ingot 2	Small	H1 mm	L1 mm
ingot 3	Small	H2 mm	L1 mm
ingot 4	Small	H3 mm	L1 mm

3. Results and discussion

3.1 Global simulation of oxygen and carbon transport

In order to clearly understand the impact of small cover on gas flow in ingot furnace, the gas flow pattern during the ingot growth process will be simulated by CGSim software. Global modeling including melt convection, argon flow, solid thermal conduction, thermal radiation, melt/solid phase change and completely coupled boundary conditions was carried out firstly for a directional solidification furnace. The major assumptions in the model are as follows: (1) the quasi-steady-state assumption is applied, (2) the geometry of the furnace configuration is axisym- metric, (3) radiative surfaces are diffuse-gray, (4) the melt flow is laminar and incompressible, and (5) the argon gas in the furnace chamber is ideal and completely transparent. The gas flow in the furnace was analyzed at the same growth height. Fig 3 shows the schematic diagram of the gas flow in the furnace during ingot growth process under three different conditions.



(a) Ingot 1 (b) Ingot 2

(c) Ingot 3 (d) Ingot 4

Fig.3. Gas flow pattern in crucible internal under different cover conditions

Previous studies have shown that due to the crucible cover is fixed at the top of the quartz crucible and the position cannot be moved at the current structural conditions, eddy currents cause harmful gases long stay inside the quartz crucible, and a longer duration contact with the silicon melt, so that the carbon and oxygen is adsorbed and dissolved into silicon melt, resulting in a high content of carbon and oxygen in the silicon ingot [13-14]. The simulation results of this paper show the same view with other studies. It can be seen from Fig.3 (a) that there are two very distinct gas vortexes above the silicon melt in the crucible. The basic processes of carbon and oxygen incorporation into a crystal are given in the following. First, the silica crucible(SiO_2) is dissolved and the oxygen and silicon atoms enter into the melt; second, the dissolved oxygen atoms are transported to the gas/melt interface and evaporate as SiO gas; third, the SiO is carried away by the argon gas flow to all of the graphite components and reacts with them to produce gas-phase CO; fourth, the resultant CO is transported back to the melt surface by diffusion or convection and then dissolved into the melt and fifth, the C and O atoms are segregated into the crystal [15]. Therefore, when the cover is made from carbon, evaporated SiO gas comes into contact with the hot carbon cover, a ditreacts with them

$$SiO_{(g)} + 2C_{(s)} \leftrightarrow 2CO_{(g)} + SiC_{(s)}$$

Then the product CO gas can be transported back to the gas/melt interface in the argon flow. At the interface, the CO gas dissolves into the melt according to the reaction

$$CO_{(g)} \leftrightarrow C_{(m)} + O_{(m)}$$

Therefore, there are two sources for carbon impurity in a crystal. One is the carbon cover inside the crucible and the other is the graphite components of the furnace outside the crucible [15].

Through the above analysis it can be seen that silicon monoxide gas will be quickly discharged outside the crucible if certain measures was taken. It can reduce the interaction between carbon monoxide and silicon melt if the formation of gas vortex was avoided, which can reduce the carbon and oxygen impurity content in silicon ingot. The size and position of cover in the ingot furnace is improved in this paper, the purpose is to enhance the quality of ingot. Fig 3 (b), Fig 3 (c) and Fig 3 (d) shows the flow pattern of the gas inside the crucible under the conditions of small cover. The strength of the vortex does not change if only the size of the cover is changed without changing the position of it, as shown in Fig 3 (b). Gas flow patterns has been significantly changed by changing the size and position of the crucible cover as can be seen from the Fig 3(c), large gas vortex does not exist anymore, but it still be able to find at local. Simulation results show that the gas flow above the silicon melt inside the crucible was completely changed when the position of the small cover was further reduced as shown in Fig 3 (d). All of gas vortex has already disappeared and the action of the impurity gas generated flows in one direction under the protective gas. The change of gas flow pattern can greatly reduce the contact probability of the silicon melt with the impurity gas, thus reducing the reaction chance between of them; it can greatly reduce carbon and oxygen impurity content and improve the ingot quality.

3.2 Experimental results

3.2.1 Ingot and Inclusion number

Fig.4 gives the physical map of 420 kg ingot. After the around shield and quartz ceramic crucible were removed, the ingot is divided into 25with silicon blocks cross-sectional dimensions of 156 x 156 mm as shown in Fig.4. The silicon with lower carrier lifetime or inclusion such as the top and bottom regions and the four sides of the mc-Si ingot is cut off after infrared testing and minority carrier test, and then the residual silicon blocks were cut into silicon wafers. Each of the mc-Si blocks is wire-sawed into a number of mc-Si wafers of certain thickness such as 200um. After being etched, cleaned, selected, and packaged, the mc-Si wafers are shipped to solar cell manufacturers.

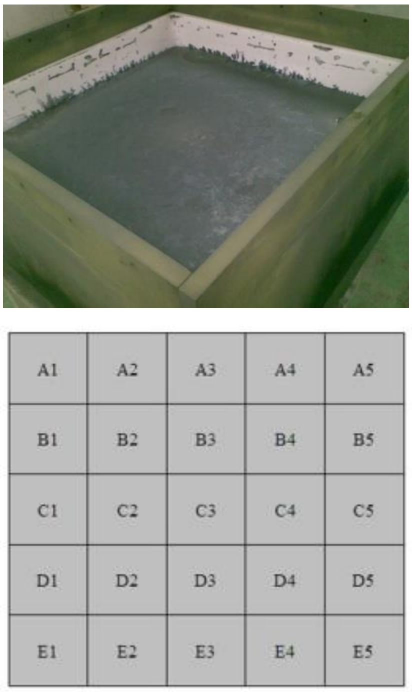


Fig.4 Physical map and prescribing mark of 420 kg ingot

	1	2	3	4	5
A	◆	◆	◆	◇	◇
B	◆	◆	◇	◇	◆
C	◇	◇	◆	◇	◆
D	◇	◆	◇	◇	◆
E	◇	◇	◆	◆	◆

(a) Ingot 1

	1	2	3	4	5
A	◇	◆	◇	◇	◇
B	◇	◇	◇	◇	◇
C	◇	◇	◆	◇	◇
D	◇	◇	◇	◇	◇
E	◆	◆	◇	◇	◇

(b) ingot 3

	1	2	3	4	5
A	◆	◇	◇	◇	◇
B	◇	◇	◇	◇	◇
C	◇	◆	◇	◇	◇
D	◇	◇	◇	◆	◇
E	◇	◇	◇	◇	◇

(c) ingots 4

Fig.5 The number and distribution of inclusions silicon block for different ingot

Fig. 5 shows quantities of silicon block which contains silicon carbide inclusions. The results showed that the number of silicon carbide inclusions in ingots 1 and 2 are basically the same, which is similar to the simulation results, so we chose ingot1, ingot 3 and ingot 4 for comparative analysis. It can be seen that the number of silicon block containing inclusions in conventional ingot is 13, but the number of silicon blocks containing silicon inclusions significantly reduce at the small cover conditions, the number of inclusions silicon blocks is 4 and 3 in ingot 3 and ingot 4, respectively. The number of inclusions silicon block reduce indicates that the content of carbon in the silicon melt has been reduced. The flow pattern of containing impurity gases above the silicon melt is significantly changed by adjusting the size and position of the small cover plate. Gas eddy can be avoided and the residence time of the impurity gas in the crucible can be also significantly shortened, thereby reducing interaction time between the impurity gas and the silicon melt and thus reducing the risk of impurity gas into the silicon melt[13]. Therefore significantly reduced carbon content in the melt and the quantity of silicon carbide inclusions is also supported due to the reduction of the carbon content in the melt.

3.2.2 Carbon and oxygen content at the head and tail of ingot

The top of ingot is the upper surface which does not contacts with the crucible and the tail of ingot is the bottom surface which contacts with the crucible, the solidification of ingot starts from the tail of ingot, the final solidification portion is the top of ingot. After slicing the silicon block, Package the wafer in accordance with the order of the head and tail, sampled and analyzed, respectively, the carbon and oxygen content of the sample from 25 silicon blocks in every ingot is measured, and then averaged. The carbon content of the measurement results shown in Fig.6, the oxygen content of the measurement result is shown in Fig.7.

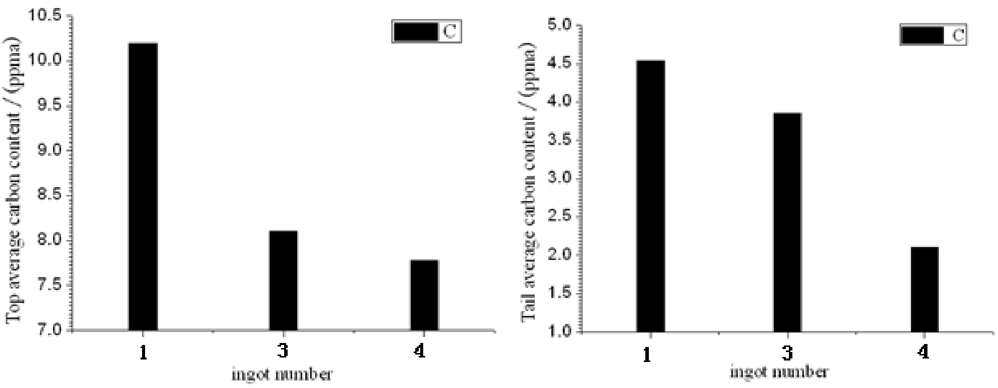


Fig.6 Average carbon content at the head and tail of ingot

Fig.6 shows comparison results of the carbon content at the head and tail of each ingot. As can be seen from Fig.6 the average carbon content at the head of three ingots is 10.2ppma, 8.1 ppma and 7.78 ppma, respectively. The average carbon content at tail of three ingots is 4.52ppma, 3.95ppma and 2.1ppma, respectively. Test results showed that the small cover can significantly reduce the carbon content at the head and tail of ingot. It can influence changes carbon content of the entire ingot by changing the gas flow pattern. Silicon material in the crucible gradually melted from the top and the outer of crucible to the lower and the inner of crucible. The melted silicon liquid flows along the gap between the silicon material to the bottom of the crucible and silicon melt will contact with the impurity contained gas. Gas can be able to be excluded to the outside of the crucible under the condition of small cover, so the degree of contamination on melted silicon is reduced. Meantime, the contamination of impurity gas on silicon melt can also be reduced when the silicon material is completely melted and the entire growth process of ingot by small cover. Therefore the carbon content can be obtained significantly reduced under the small cover conditions whether it is the head or tail of the ingot. It can be seen that average carbon content at the head of ingot is higher than that at the bottom of ingot the reason is because the carbon segregation coefficient is less than 1 in silicon, carbon impurities constantly being pushed into the silicon melt in the ingot growth process, resulting in a high content of head and low content of tail phenomenon [10-14].

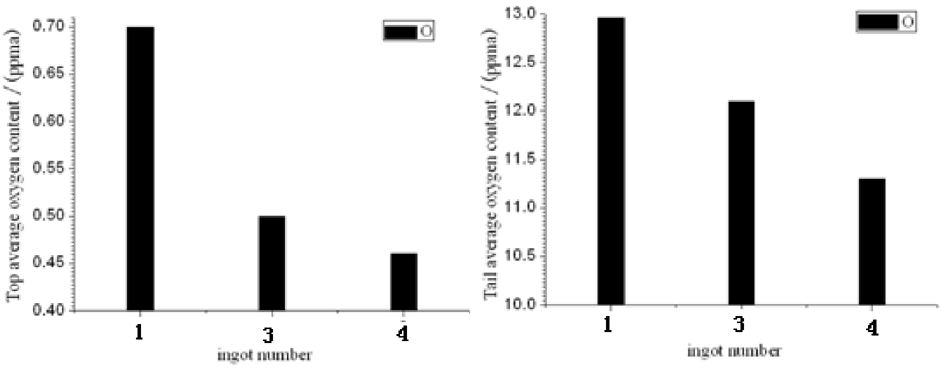


Fig.7 Average oxygen content at the head and tail of ingot

Fig.7 shows the measurement results about the average oxygen content at the head and tail of the three ingots. Average oxygen content at head of the three ingots is 0.7ppma, 0.51ppma and 0.46ppma, respectively. The average oxygen content at the tail of the three ingots is 12.96ppma, 12.1ppma and 11.3 ppma, respectively. The average oxygen content in ingot 3 and ingot 4 is significantly reduced under small cover condition. The reason is the same as the above-described on carbon content reduction. The distribution law of impurity oxygen at the head and tail in three ingots is same, this is because of the segregation coefficient of impurity oxygen is greater than 1 in the silicon, and therefore the content of impurity oxygen at the first solidified portion is higher than that at the later solidified parts ingot.

3.2.3 Ingot utilization

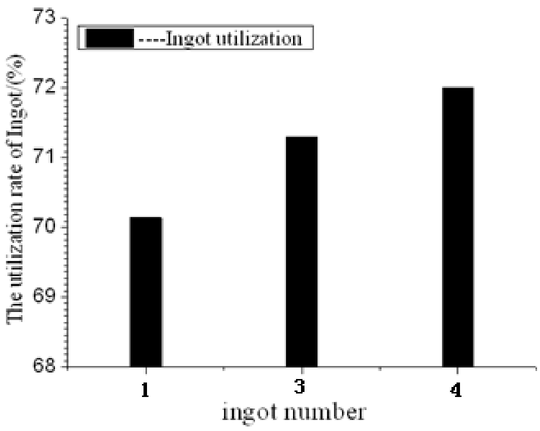


Fig. 8 Utilization of ingot

Fig.8 shows the overall utilization of the three ingots. It can be seen that utilization has also been significantly improved under the conditions of the small cover. The utilization of three ingots is 70.1%, 71.3% and 72.1%, respectively. Ingot utilization is mainly affected by the silicon carbide inclusions as well as the minority carrier lifetime of ingot. The surface of wafer which contains silicon carbide inclusions have serious cutting corrugated and the battery which is made of this wafer will produce severe ohmic shunts. The wafer with very low minority carrier lifetimes cannot be used in the preparation of the battery. From the above analysis shows that the small cover plate can change the gas flow pattern at the top of the silicon melt and it can avoid the formation of gas vortex, and therefore it can significantly reduce the contact time of the impurity gas and the silicon melt, thereby reducing the carbon and oxygen in the silicon melt. So the number of silicon block with inclusions is reduced and the minority carrier lifetime in the silicon block has been improved and thus the utilization of the entire ingot improved.

4. Conclusion

Based on improvement to cover which is changed from the original stationary and bigger cover to the smaller cover and can be move up and down. The following conclusions can be obtained by comparing the test:

1. The flow pattern of impurity gas at the top of the silicon melt can be significantly improved under the small cover conditions and the impurity gas eddy currents can also be avoided. So the impurity gases leave the surface of the silicon melt very quickly, thus reducing interaction time between the impurities gas and the silicon melt and reducing the contamination of impurity gas to the silicon melt.
2. Due to impurity gas contamination to the silicon melt is suppressed under small cover conditions, so the content of impurities in the silicon melt have been improved from silicon material melt to ingot solidification process. The carbon content at the head and tail of ingot reduced from 10.2ppma and 4.52ppma to 7.78 ppma and 2.1ppma. The oxygen content at the head and tail of ingot reduced from 0.7ppma and 12.96ppma to 0.46ppma and 11.3 ppma, respectively. Reduction effect is very obvious.
3. The utilization of ingot mainly depends on the quantity of silicon block with inclusions The number of silicon block containing inclusions significantly reduces under the conditions of small cover plate, therefore the utilization of the silicon block has been significantly improved, the utilization of the entire ingot has also been

improved from 70.1% to 72.1%, which is significantly higher than that of the ordinary ingot.

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