Influence of growth rate on minority carrier lifetime of multicrystalline silicon ingot

Xiufan Yang\textsuperscript{1*}, Dianxi Zhang\textsuperscript{1}, Zhongzheng Guo\textsuperscript{1}, Wanjun Yan\textsuperscript{1} and Houyong Zhang\textsuperscript{2}

\textsuperscript{1}School of electronics and information engineering, Anshun University, Anshun, Guizhou, 561000, China
\textsuperscript{2}Guizhou Anji Aviation Precision Casting Co., Ltd, Anshun, Guizhou, 561000, China
\textsuperscript{*Corresponding author’s e-mail: xnmdyxf@163.com}

Abstract. Multicrystalline silicon was grown by directional solidification method, and different growth rates was obtained by optimizing the growth process. The influence of the growth rate on the minority carrier lifetime of the multicrystalline silicon ingot was studied. The results show that the infrared image of the middle and lower part of the silicon block with an average growth rate of 1.0 cm/h has a lighter shade. The area with minority carrier lifetime of the silicon block is less than 4 us accounts for about 50%, and the average minority carrier lifetime is 5.28 us. Reduce the growth rate to 0.94 cm/h, the infrared image of the crystal is pure and the crystal grains are coarse, the average minority carrier lifetime of the silicon block is increase to 5.65 us. When the growth rate is further reduced to 0.87 cm/h, the crystal growth deviates from the vertical direction. The area of silicon block less than 4 us accounts for about 40%, and the average minority carrier lifetime is reduced to 5.39 us. The phase field method is used to calculate the growth of multicrystalline silicon. The results show that the greater the flow rate, the faster the growth of crystal nucleus and the easier the formation of competitive growth, which is in good agreement with the experiment.

1. introduction

Multicrystalline silicon ingot occupies an important share in the field of solar cell materials due to its high production efficiency and low production cost\cite{1}. In 2019, China's multicrystalline silicon output will be about 260000 tons, an increase of 2.8%. The production scale will continue to expand, and the global photovoltaic market will maintain a high level. With the rapid development of photovoltaic industry, the demand for multicrystalline silicon products is increasing, and higher requirements for the quality of multicrystalline silicon products are put forward\cite{2}. The performance of multicrystalline silicon has an important impact on the conversion efficiency of silicon cell, and the minority carrier life is the key factor affecting the conversion efficiency of silicon wafer cell \cite{3-4}. The Influence of impurities, defects, solid-liquid interface, undercooling and temperature on the properties of multicrystalline silicon are reported in literature \cite{5-8}. In order to obtain high performance multicrystalline silicon, it is necessary to grow crystals with large grains, low crystallographic defects and low impurity content. The growth rate of multicrystalline silicon affects the segregation of impurities in the ingot \cite{9-10}, also affects the size and quantity of grains, which has an important impact on the crystal performance. In the process of crystal growth, we can control the growth rate by optimizing the ingot process, reduce the crystal crystallographic defects, reduce the impurities, and improve the minority carrier lifetime of the crystal.
2. experiment
The same GT ingot casting furnace is used for ingot casting, and the raw and auxiliary materials such as crucibles and polysilicon materials are from the same manufacturer and the same batch. There are 7 steps in the crystal growth process, and three silicon ingots with different growth rates are obtained by optimizing the crystal growth process. The upper surface temperature of the silicon ingot is controlled by the top and side wall heaters, fed back by the top thermocouple temperature $T_{C1}$, and the bottom temperature of the silicon ingot is given by equation (1) [1]:

$$T = \left( RT_m + \frac{X T_{C2}}{K_s} \right)(R + \frac{X}{K_s})^{-1}$$  

In formula (1), $R$ (m$^2$. K / W) is the contact thermal resistance between the quartz crucible, the graphite guard plate and the directional solidification block, $T_m$ (k) is the melting point of silicon, $T_{C2}$ (k) is the bottom thermocouple temperature, $X$(m) is the height of solidified silicon ingot, and $K_S$ (w / (mK)) is the thermal conductivity of solid silicon. The crystal height is measured by inserting a quartz rod into a small hole at the top of the ingot furnace every 1 h after the ingot process enters the crystal growth. The ratio of the crystal height difference to the interval time h is the crystal growth rate. After ingot casting, the multicrystalline silicon ingots was broken and sliced to obtain a polycrystalline silicon chip with a thickness of about 0.18mm and a thickness of 156mm × 156mm. Irb30 infrared flaw detector was used to scan the silicon block after ingot casting, and WT-2000 minority carrier lifetime tester was used to measure the minority carrier lifetime.

3. results and discussion

3.1 growth rate of multicrystalline silicon ingot
After the multicrystalline silicon ingot process runs to the growth section, through optimizing the process, the crystal height is measured every 1 h, and the average growth rate of G1-G7 in the crystal growth section is calculated, as shown in figure 1.

![Figure 1. Growth rate of multicrystalline silicon ingot](image)

It can be seen from figure 1 that the crystal growth rate is fast at the initial stage of crystal growth, showing a linear increasing trend, and the maximum growth rate reaches 1.5cm/h. In the early stage of crystal growth, in order to provide nucleation driving force for silicon melt, the heater power is reduced rapidly, the temperature of liquid silicon is reduced to about 1432 ℃, and the heat insulation cage is raised to more than 8 cm, so as to reduce the temperature of silicon melt and increase the heat dissipation at the bottom. When the bottom temperature of crucible reaches supercooling, nucleation and growth begin. It can be seen from figure 1 that the growth rate of G1-G3 segment is more sensitive to temperature change, and a smaller temperature change can obtain a larger growth rate. In the middle stage of crystal growth, the growth rate tends to be slow, and the difference between the
three growth rates is more and more obvious. The growth rate of the crystal growth slows down in the later stage, and the fastest growth rate in the early and middle stage is the fastest in the later stage. In figure 1, the average growth rate of growth rate 1 is 1.0 cm/h, that of growth rate 2 is 0.94 cm/h, and that of growth rate 3 is 0.87 cm/h.

3.2 Influence of growth rate on crystal morphology

Irb30 infrared flaw detector is used to scan the multicrystalline silicon blocks after ingot breaking. Figure 2 shows typical infrared images of silicon blocks with three growth rates. Figure 2 (c) shows the infrared image with an average growth rate of 1.0 cm/h. There are small areas of shadow at the bottom and middle lower part of the silicon block. The shadow in the infrared image of silicon block is mainly caused by impurity enrichment or microcrystalline [11-12]. It can be seen from the figure that the shadow area of the silicon block is small, the color is light, and there is no disordered and fine dendrite around it. Therefore, it is speculated that the shadow of silicon block is caused by the enrichment of impurities. Figure 2 (b) shows the infrared image of silicon block with an average growth rate of 0.94cm/h. The infrared image of crystal is pure, the crystal grain is relatively thick, and the growth direction is basically along the vertical direction. It shows that the crystal with strong grain and consistent growth direction can be obtained under this growth rate.

Figure 2. Infrared image of Multicrystalline Silicon with different growth rates

Figure 2 (a) shows the infrared image of silicon block with an average growth rate of 0.87cm/h. The infrared image of crystal is pure and the grains are coarse. However, most of the grain growth directions deviate from the vertical direction and close from the bottom to the top. At this time, due to the low crystal growth rate, the shape of the solid-liquid interface changes from flat to concave, and the crystal growth deviates from the vertical direction [13].

3.3 Influence of growth rate on minority carrier lifetime

3.3.1 minority carrier lifetime of crystals with different growth rates.

WT-2000 minority carrier lifetime tester is used to measure minority carrier lifetime of silicon block after ingot breaking. The average minority carrier lifetime of all silicon blocks is taken as shown in Table 1.

| Average growth rate of multicrystalline silicon (cm/h) | Average minority carrier lifetime of silicon block (us) |
|------------------------------------------------------|--------------------------------------------------------|
| 0.87                                                  | 5.39                                                   |
| 0.94                                                  | 5.65                                                   |
| 1.0                                                   | 5.28                                                   |

It can be seen from table 1 that the maximum minority carrier lifetime of multicrystalline silicon with a growth rate of 0.94cm/h is 5.65us. Too high or too low growth rate is not conducive to
improving the minority carrier lifetime of the crystal. The purpose of increasing the minority carrier lifetime of the crystal can be achieved by adjusting the crystal growth rate.

3.3.2 Influence of growth rate on minority carrier lifetime distribution of multicrystalline silicon block. Figure 3 shows the area ratio of minority carrier lifetime in multicrystalline silicon block. Figure 3 (a) shows the minority carrier lifetime distribution of silicon blocks with an average growth rate of 1.0 cm/h, with values ranging from 0-5.4us, mainly distributed in the range of 1.88-4.52us. The minority carrier lifetime regions below 4us account for about 50%. Figure 3 (b) shows the minority carrier lifetime distribution of silicon block with an average growth rate of 0.87cm/h, with values ranging from 0-7us, mainly distributed in the range of 2.28-5.82us. Figure 3 (c) shows the minority carrier lifetime distribution of silicon block with growth rate of 0.94 cm/h, with values ranging from 0-8.4us, mainly distributed in 2.72-6.98us, and the region with minority carrier lifetime of 8 accounts for about 23%.

The main factors affecting minority carrier lifetime of multicrystalline silicon are impurities and crystal defects. Impurities with segregation coefficient greater than 1 are concentrated at the bottom of the crystal, while impurities with segregation coefficient less than 1 are pushed to the top of the crystal.

Effective segregation coefficient of impurities [14]:

$$K_{\text{eff}} = K_0 + (1 - K_0)e^{-V_D \delta}$$

In formula (2), V is the growth rate, D is the solute diffusion coefficient and \( \delta \) is the thickness of solute diffusion boundary layer. If the growth rate increases, the effective segregation coefficient of impurities will increase, and the impurities tend to accumulate at the solid-liquid interface and solidify into the solid phase with crystal growth, which will become the composite center of minority carriers and reduce the minority carrier lifetime. According to the infrared image of silicon blocks, only about 25% of the silicon blocks with a growth rate of 0.94 cm/h have a minority carrier lifetime of less than 4, and the low minority carrier lifetime region is small, and the highest average minority carrier...
The lifetime value is 5.65. Reducing the growth rate is conducive to the impurity segregation into the liquid phase, and finally solidifies to the top of the silicon ingot through the liquid phase, thus increasing the minority carrier lifetime of the crystal.

4. Simulation of multicrystalline silicon growth by phase field method
The phase field method is used to simulate the growth of multicrystalline silicon. The anisotropy coefficient is 0.05, the undercooling degree is 0.55, the grid is divided into 1200 × 1200, and the flow rates are -1.0, -1.5 and -2.0 respectively. The calculation results with 1500 steps are shown in figure 4.

![Figure 4. simulation results of phase field method](image)

Figure 4 (a), (b) and (c) show the simulation results of flow velocity -1.0, -1.5, and -2.0 phase field method. It can be seen from the calculation results that the inner and outer temperature gradient of the polysilicon crystal core with a flow rate of -2.0 is large, and the crystal core tip grows faster. Under the same calculation step, it is easier to produce competitive growth. It can be seen that the faster the growth rate of the crystal, the competition between the crystal nuclei is easy to produce, which makes the impurities easier to solidify into the crystal, thus affecting the minority carrier lifetime. Therefore, the proper growth rate is beneficial to increase the minority carrier lifetime.

5. Conclusion
The higher growth rate makes the impurities in the polycrystalline silicon crystal can not be fully removed, resulting in impurity enrichment and reducing the minority carrier lifetime of the crystal. The lower growth rate will make the crystal growth deviate from the vertical direction, increase the crystallographic defects and reduce the minority carrier lifetime. When the average growth rate is 0.94 cm / h, the infrared image of polysilicon is pure, the grain size is coarse, and the minority carrier lifetime value of silicon block is 5.65us. The results of phase field simulation show that the higher the flow rate, the faster the crystal growth, which is easy to form competitive growth, which is not conducive to improving the minority carrier lifetime of the crystal. The conclusion is in good agreement with the experiment. Therefore, a suitable growth rate can improve the minority carrier lifetime of the crystal.

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