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Improvement of Minority Carrier Life Time in *N*-type Monocrystalline Si by the Czochralski Method

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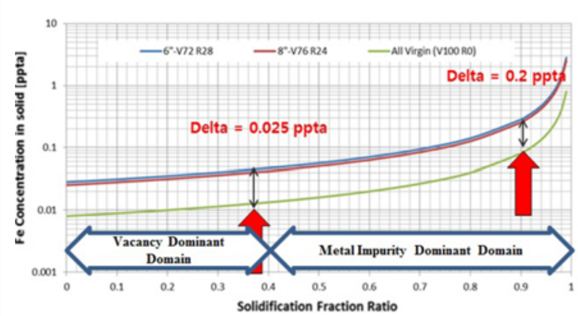
The installation amount of solar power plants increases every year. Multi-crystalline Si solar cells comprise a large share of the market of solar power plants. Multi-crystalline and single-crystalline Si solar cells are competing against one another in the market. Many single-crystalline companies are trying to develop and produce *n*-type solar cells with higher cell efficiency than that of *p*-type. In *n*-type wafers with high cell efficiency, wafer quality has become increasingly important. In order to make ingots with higher MCLT, the effects of both poly types related to metal impurities and pull speeds related to vacancy concentration on minority carrier life time were studied. In the final part of ingots, poly types related to the metal impurities are a dominant factor on MCLT. In the initial part of ingots, pull speeds related to vacancy concentration are a dominant factor on MCLT.



Keywords: MCLT, Czochralski, silicon, solar cells, *n*-type wafer

1. INTRODUCTION

Environmental issues such as global warming have increased interest in renewable energies such as solar and wind power. In 2014, solar power plants producing as much as 40GW of power were installed all over the world.[1,2] The installation amount of solar power plants is expected to increase continuously and approach 50GW in 2020.[3] The solar power plants are made up of 50% of multi-crystalline Si [MCS] solar cells and 30% of single-crystalline Si [SCS] solar cells.[4] Because MCS and SCS compete with one other in terms of both price [Watt/$] and cell efficiency, the prices of each of them have decreased continuously. Recently, the cell efficiency of a high-performance *p*-type MCS has been improved and come close to the cell efficiency of a *p*-type SCS.[4] Therefore, many SCS solar cell companies have tried to move *n*-type SCS solar cells, which have higher cell efficiency than *p*-type SCS solar cells. Last year, Panasonic developed an *n*-type hetero-junction SCS solar cell that has both a back contact structure and the highest cell efficiency in the world of 25.6%.[4]

In *n*-type SCS solar cells with high cell efficiency, the quality of *n*-type SCS wafers has become increasingly important. The wafer with higher Minority Carrier Life Time (MCLT) shows higher cell efficiency of solar cells.[5,6] The wafer with higher oxygen concentration generates many oxygen precipitates during solar cell diffusion processes with high-temperature heat treatments.[7] The oxygen precipitates strongly degrade solar cell efficiency.[7]

The MCLT of wafers mainly depends on metal impurities in wafers.[8] Most metal impurities in wafers come from poly silicon as a raw material. Another factor of the MCLT of wafers is a vacancy concentration as a function of both the pull speed and the axial temperature gradient of a Si ingot in the Czochralski (Cz) method.[9] When a vacancy meets a metal atom located at an interstitial site, the interstitial metal atom is converted into a substitutional metal atom that has a

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different energy level in the bandgap of Si in comparison with the interstitial metal atom.[10] The substitutional metal atom traps fewer electrons than does the interstitial metal atom.[10] This is called “vacancy passivation”.

The higher pull speed induces a higher vacancy concentration.[11] Owing to the segregation phenomena in the Cz method, the concentration of metal impurities in a Si ingot is lower than the concentration of metal impurities in poly Si as a raw material. However, while cropping a Si ingot into a few cylindrical bricks and slabbing a cylindrical brick into a square brick, the contact surface of recycled polys from a Si ingot is contaminated by metal blades. The concentration of metal impurities in recycled polys is higher than the concentration of metal impurities in virgin poly Si. The companies producing SCS wafers use recycled polys in order to reduce cost and to try to increase the pull speed of a Si ingot in order to improve productivity. However, the interaction effect that originates from both poly metal impurities and pull speed has not been researched very deeply. In this paper, we researched the MCLT of a SCS ingot as a function of both poly metal impurities and pull speed, and we investigated the interaction effect of both poly metal impurities and pull speed.

2. EXPERIMENTAL PROCEDURE

There were two quartz crucible sizes: 20-inch diameter and 24-inch diameter. Poly Si of 106 kg and 164 kg were charged with *n*-type dopants in a 20-inch crucible and a 24-inch crucible, respectively. The charged 20-inch crucible and 24-inch crucible were moved into 20-inch and 24-inch SCS growing chambers, respectively. The SCS growing chambers were pumped to a vacuum state, and electrical power was provided to graphite heaters in order to melt poly Si in quartz crucibles. After melting poly Si perfectly, a SCS seed was dipped into Si melt. The SCS seed was pulled upward and a SCS ingot was grown. The diameters of SCS ingots were 6 inches and 8 inches in a 20-inch crucible and a 24-inch crucible, respectively. The crucible rotation was 5-8 rpm and in the counter-clockwise direction, and the crystal rotation was 10-12 rpm and in the clockwise direction. The flux of Ar was 30-50 lpm, and the pressure of SCS growing chambers was 10-30 torr. After the removal of SCS ingots from SCS growing chamber, the ingots were cropped into cylindrical bricks for measuring MCLT, and a few slugs were cut for measuring oxygen and carbon concentrations. MCLT values were measured at the center of cropped surfaces of cylindrical bricks by a Sinton tool (Sinton BCT300, USA). The interstitial oxygen (Oi) and substitutional carbon (Cs) concentrations were measured at the center of polished slugs by FT-IR (QS2200, Nanometrics, USA).

There are three variable factors: the poly type, which is related to the concentration of impurities (virgin poly Si 100% and mix poly Si (virgin poly + recycled poly)); the pull speed (low pull speed and high pull speed); and the diameter of an ingot (6” and 8”). Table 1 shows a list of sample names and an explanation of corresponding variable factors.

Table 1. A list of sample names and an explanation of corresponding variable factors.

No	Sample name	Poly type	Pull speed
1	6”-LPS-V72 R28	Virgin: 72% Recycled: 28%	Low Pull Speed
2	6”-LPS-V100 R0	Virgin: 100%	Low Pull Speed
3	6”-HPS-V72 R28	Virgin: 72% Recycled: 28%	High Pull Speed
4	6”-HPS-V100 R0	Virgin: 100%	High Pull Speed
5	8”-LPS-V100 R0	Virgin: 100%	Low Pull Speed
6	8”-HPS-V76 R24	Virgin: 76% Recycled: 24%	High Pull Speed

3. RESULTS AND DISCUSSION

Figure 1 shows the relative pull speeds of 6” diameter ingots as a function of the solidification fraction ratio, which means the ratio of solidified Si weight to initial liquid Si weight. Red and yellow lines represent high pull speed ingots, and green and blue lines represent low pull speed ingots. However, below a 0.2 solidification fraction ratio, the relative pull speeds of both blue and green lines are higher than the relative pull speeds of both red and yellow lines. This is attributed to the mismatch between the real temperature profile for a constant diameter and the feed-forward temperature profile for a constant diameter. Hence, below a 0.2 solidification fraction ratio, the actual pull speed is not in accordance with our intention. However, above a 0.2 solidification fraction ratio, the high pull speed ingots have 5-10% higher relative pull speed than that of the low pull speed ingots.

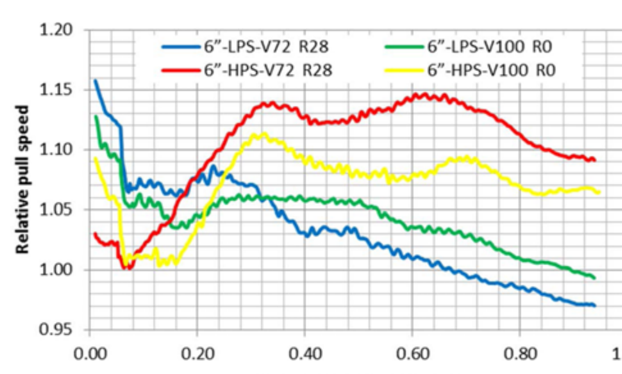

Fig. 1. The relative pull speed of 6” diameter ingots as a function of the solidification fraction ratio.

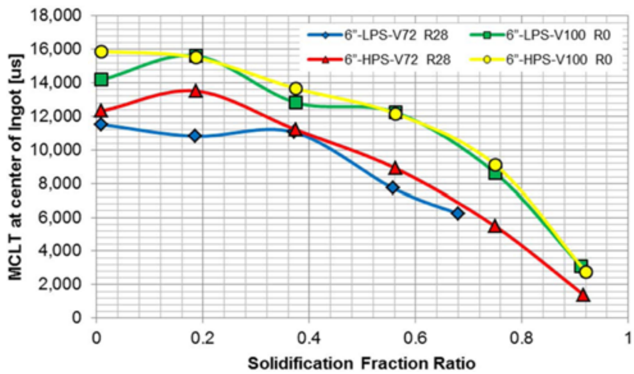

Fig. 2. The ingot Center MCLT of 6" diameter ingots as a function of the solidification fraction ratio.

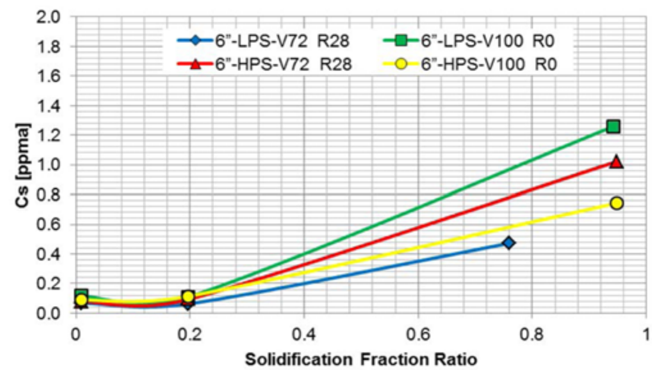

Fig. 4. The substitutional carbon (Cs) concentration profile as a function of the solidification fraction ratio.

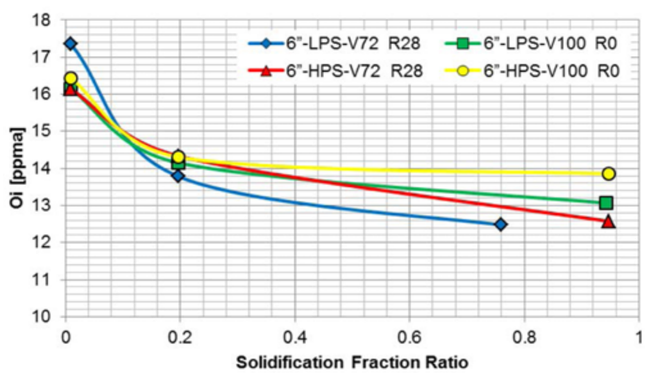

Fig. 3. The interstitial oxygen (Oi) concentration profile of 6" diameter ingots as a function of the solidification fraction ratio.

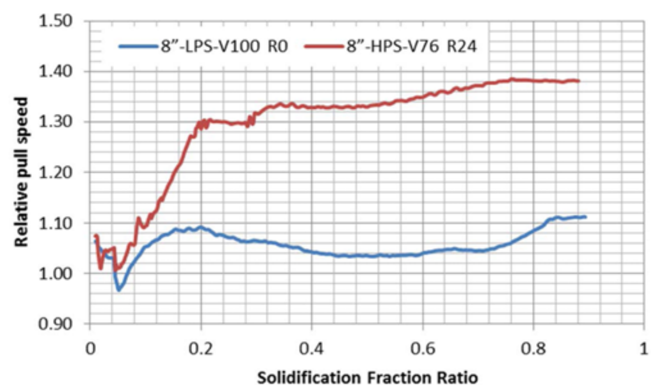

Fig. 5. The relative pull speeds of 8" diameter ingots as a function of the solidification fraction ratio.

Figure 2 shows the ingot center MCLT of 6" diameter ingots as a function of the solidification fraction ratio. The MCLT of the ingots with 100% virgin poly Si is higher than the MCLT of ingots with mix poly Si (72% virgin + 28% recycled poly Si) by about 2000 micro seconds. Below a 0.2 solidification fraction ratio, the MCLT of the high pull speed ingot is higher than the MCLT of the low pull speed ingot by about 2000 micro seconds in 100% virgin poly Si ingots. Below 0.4 of solidification fraction ratio, the MCLT of the high pull speed ingot is higher than the MCLT of the low pull speed ingot by about 1000-2000 micro seconds in mix poly Si ingots. The MCLT of four ingots decreases as the solidification fraction ratio increases because of the impurity accumulation through a segregation phenomenon.

Figure 3 shows the interstitial oxygen (Oi) concentration profile as a function of the solidification fraction ratio. Besides the ingot (6"-LPS-V72 R28, blue line), the other three ingots have Oi concentration of around 16 ppma at a solidification fraction ratio of 0. The Oi concentration decreases as the solidification fraction ratio increases owing to the reduction of the contact area between a Si melt and a quartz crucible.

Figure 4 shows the substitutional carbon (Cs) concentration profile as a function of the solidification fraction ratio. The Cs of all ingots is below 1.2 ppma along the whole solidification fraction ratio. The Cs concentration increases with the solidification fraction ratio because of the carbon accumulation through a segregation phenomenon.

Figure 5 shows the relative pull speeds of 8" diameter ingots as a function of the solidification fraction ratio. The red line represents a high pull speed ingot, and the blue line represents a low pull speed ingot. In comparison with the relative pull speeds of 6" diameter ingots, the actual pull speed is in accordance with our intention along whole solidification fraction ratio. The high pull speed ingot has about 30% higher pull speed than that of the low pull speed ingot.

Figure 6 shows the ingot center MCLT of 8" diameter ingots as a function of the solidification fraction ratio. Below a 0.4 solidification fraction ratio, in spite of the impurity difference from the different poly type, the MCLT of the high pull speed ingot (red line) is higher than the MCLT of the low pull speed ingot (blue line). Above a 0.4 solidification fraction ratio, the MCLT values of the two ingots are reversed.

Table 2 shows the Oi and Cs of 8" diameter ingots

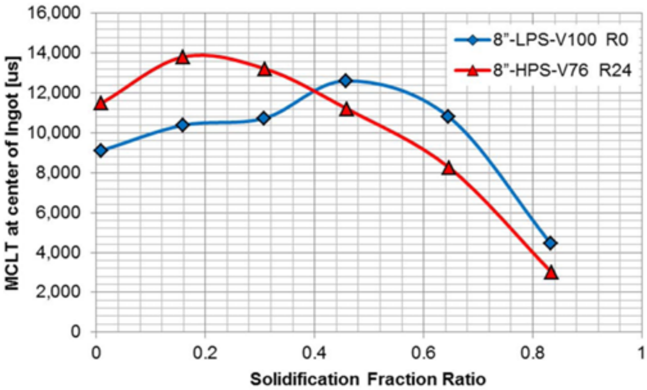

Fig. 6. The ingot Center MCLT of 8” diameter ingots as a function of the solidification fraction ratio.

Table 2. The Oi and Cs of 8” diameter ingots depending on ingot positions.

	8”-LPS-V100 R0		8”-HPS-V76 R24	
	Oi	Cs	Oi	Cs
Top of ingot	15.9	0.061	14.5	0.029
Bottom of ingot	9.8	0.507	11.4	0.651

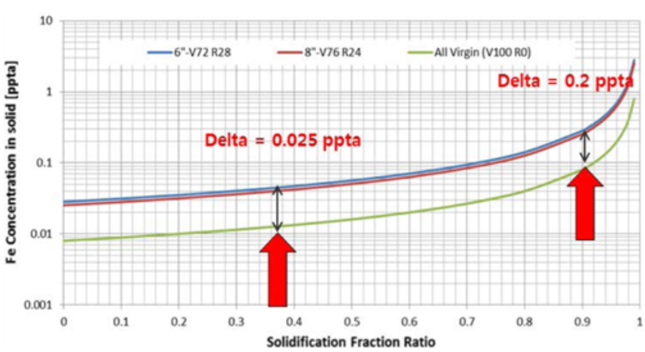

Fig. 7. Theoretical profiles of Fe concentration as a function of the solidification fraction ratio.

depending on ingot positions. The Oi of the two ingots is below 16 ppma, and the Cs of the two ingots is under 1 ppma along whole ingot positions.

Figure 7 shows the theoretical profiles of Fe concentration as a function of the solidification fraction ratio. The assumption is as follows: (1) the only impurities are only Fe atoms, (2) the Fe concentration of virgin poly Si is 1 ppba, (3) the Fe concentration of recycled poly Si is 10 ppba, and (4) the segregation coefficient of Fe is 0.00008. At a 0.4 solidification fraction ratio, the difference of Fe concentration between 100% virgin poly and mix poly (76% virgin and 24% recycled poly) is about 0.025 ppta. At a 0.9 solidification fraction ratio, the difference of Fe concentration is about 0.2 ppta, which is about 10 times higher than the difference of Fe concentration at a 0.4 solidification fraction ratio. In Figure 6, below a 0.4 solidification fraction ratio, the MCLT of the 8”-HPS-V76R24 ingot is higher than the MCLT of the 8”-LPS-V100R0 ingot. This cannot be explained by only metal impurities because the Fe concentration of 8”-HPS-V76R24 ingot is higher than the Fe concentration of 8”-LPS-V100R0 in Fig. 7. There must be another strong factor except metal impurities below a 0.4 solidification fraction ratio. According to A. Black *et al.*,[10] it is possible that “vacancy passivation” could be generated by higher vacancy concentration through high pull speed. The increment of vacancy concentration in comparison with low pull speed ingot is considered to be about 0.025 ppta.

4. CONCLUSIONS

The effects of both the poly types related to metal impurities and the pull speed related to vacancy concentration on the MCLT of SCS ingots were studied. It is generally known that the MCLT of the ingot with 100% virgin poly Si is higher than the MCLT of the ingot with mix poly Si (virgin poly + recycled poly). However, the interaction effect of poly types and pull speeds on the MCLT of ingots has not been researched deeply. In this study, we elucidated the interaction effect of poly types and pull speeds on the MCLT. The higher vacancy concentration induced by high pull speed could cause the “vacancy passivation” phenomenon. The increment of the vacancy concentration through high pull speed corresponds to about 0.025 ppta. Hence, we could increase the MCLT of the initial length of ingots below a 0.4 solidification fraction ratio by increasing the pull speed. The metal impurities from poly Si are a still dominant factor in the final length of ingots above a 0.4 solidification fraction ratio, regardless of the vacancy concentration by high pull speed.

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REFERENCES

1. M. Hosenuzzaman, N. A. Rahim, J. Selvaraj, M. Hasanuzzaman, A. B. M. A. Malek, and A. Nahar, *Renew. Sust. Energ. Rev.* **41**, 284 (2015).
2. K. Y. Kim, H. K. Moon, N. E. Lee, B. H. Hong, and S. H. Oh, *Electron. Mater. Lett.* **11**, 93 (2015).
3. A. K. Pandey, V. V. Tyagi, A. Jeyraj, L. Selvaraj, N. A. Rahim, and S. K. Tyagi, *Renew. Sust. Energ. Rev.* **53**, 859 (2016).

4. S. D. Stranks, P. K. Nayak, W. Zhang, T. Stergiopoulos, and H. J. Snaith, *Angew. Minirev.* **54**, 3240 (2015).
5. H. Wagner, J. Hofstetter, B. Mitchell, P. P. Altermatt, and T. Buonassisi, *Energ. Proced.* **77**, 225 (2015).
6. Y. K. Park, J. G. Lu, J. H. Park, and G. Rozgonyi, *Electron. Mater. Lett.* **11**, 658 (2015).
7. J. Haunschild, I. E. Reis, J. Geilker, and S. Rein, *Phys. Status. Solidi-R.* **5**, 199 (2011).
8. J. Kim, S. Y. Yoon, and K. Choi, *Curr. Appl. Phys.* **13**, 2103 (2013).
9. K. H. Kim, B. C. Sim, I. S. Choi, and H. W. Lee, *J. Cryst. Growth* **299**, 206 (2007).
10. A. Black, J. Medina, A. Pineiro, and E. Dieguez, *J. Cryst. Growth* **353**, 12 (2012).
11. V. V. Voronkov, *J Cryst. Growth* **59**, 625 (1982).