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# Redistribution of iron during directional solidification of metallurgical-grade silicon at low growth rate

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**Abstract:** Redistribution of iron during directional solidification of metallurgical-grade silicon (MG-Si) was conducted at low growth rate. Concentrations of iron were examined by ICP-MS and figured in solid and liquid phases, at grain boundary and in growth direction. Concentrations are significantly different between solid and liquid phases. The thickness of the solute boundary layer is about 4 mm verified by mass balance law, and the effective distribution coefficient is $2.98\times10^{-4}$. Iron element easily segregates at grain boundary at low growth rate. In growth direction, concentrations are almost constant until 86% ingot height, and they do not meet the Scheil equation completely, which is caused by the low growth rate. The effect of convection on the redistribution of iron was discussed in detail. Especially, the "dead zone" of convection plays an important role in the iron redistribution.

**Key words:** directional solidification; metallurgical-grade silicon; redistribution; iron; grain boundary

## 1 Introduction

In order to meet the remarkable development of photovoltaic industry, cost-effective ways to manufacture multi-crystalline silicon must be applied. Because of the high purification requirement of solar cells, silicon refining is meaningful and important [1]. Nowadays, besides the chemical method, series of metallurgical techniques are applied. Directional solidification and zone melting are effective to remove metallic impurities [2,3]; slag refining and alloy solvent refining are effective to separate boron from silicon [4,5]; vacuum melting and electron beam melting do good jobs in removing phosphorus, aluminum and calcium [6,7]; nonmetals can also be removed by oxidation or electro-refining [8,9]. Whereas, some methods for purifying silicon are high cost.

Metallic impurities, especially transition metals, are detrimental to solar cells for they act as recombination center of the minority carrier [10]. What is worse, solar cells with the same total impurity contents can have widely different minority lifetime based on the impurities distribution [11]. Many literatures reported the redistribution of metallic impurities during directional solidification of MG-Si. YUGE et al [12] removed metallic impurities from molten silicon with electron beam heating, and the feedstock was supplied continuously at a constant mass to water cooled copper mold and solidified gradually in a directional manner. MARTORANO et al [2] studied the influence of solidification velocity on impurities segregation in directionally solidified silicon with vertical Bridgman furnace. TAN et al [13] researched the removal of aluminum and calcium in multi-crystalline silicon by vacuum induction melting and directional solidification, considering the influence of evaporation and segregation on impurities removal. AUTRUFFE et al [14] investigated the impact of growth rate on impurities segregation at grain boundaries. The results showed, for fast diffusion element, that the concentration difference of impurity between grain and grain boundary is obvious.

Iron is a representative impurity in multi-crystalline silicon, which is difficult to be removed. However, most

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of literatures only discussed the redistribution of average concentration along the growth direction. In the present work, we comprehensively investigate the redistribution of iron. Not only concentrations along growth directional are discussed, but also concentration difference between solid and liquid is compared. What is more, concentrations at grain boundary are investigated in detail by a relatively convenient method. The thickness of effective solute boundary layer is estimated, and the effect of natural convection on the iron redistribution is discussed.

## 2 Experimental

The configuration of a multi-heater directional solidification furnace (JS-450) is shown in Fig. 1. Quartz crucible was painted by $Si_3N_4$ coatings to prevent impurities from the crucible, with the outer sizes of 830 mm × 830 mm × 450 mm and the wall thickness of 20 mm. The crucible was supported by graphite blocks. At the top of crucible, a carbon fiber plate was fixed to protect silicon from contaminating by the thermal decomposition of graphite resistance heaters. Argon gas was imported through a graphite tube into the furnace to protect the silicon from being oxidized at high temperature. Thermocouple 1 (TC1) was installed near the surface of top heaters to measure the furnace chamber temperature, and thermocouple 2 (TC2) was installed through the directional solidification block to measure the temperature at the crucible bottom. A quartz rod was inserted from the furnace top into the crucible to detect the crystal growth rate during solidification. The furnace chamber pressure was maintained at about $6\times10^4$ Pa by adjusting the import and export of argon flow. The furnace wall was cooled by water and it was considered as a constant temperature boundary. Thermal field was controlled by two ways: 1) controlling the power of graphite resistance heaters; 2) adjusting the insulation cage upward or downward.

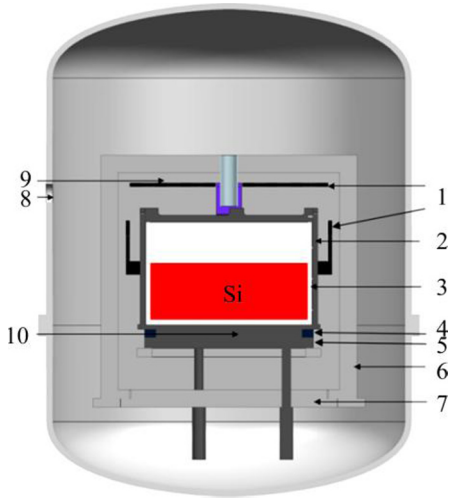


**Fig. 1** Schematic configuration of directional solidification furnace (1—Graphite resistance heater; 2—Graphite plate; 3—Crucible; 4—Tent; 5—DS-black; 6—Heat insulation cage; 7—Carbon-graphite felt; 8—Outlet; 9—TC1; 10—TC2)

410 kg MG-Si was used to be conducted. Original average concentration of iron in feedstock was $657.94\times10^{-6}$. The feedstock was loaded into the crucible and melted. During melting, insulation cage was closed entirely. The furnace chamber temperature was about 1823 K after 415 min. Temperature then decreased gradually to 1698 K. After this step, the furnace chamber temperature was controlled appropriately by a combination of resistance heaters and the insulation cage, and solidification was initiated. Finally, the temperatures at the top and bottom of the furnace chamber were about 1690 and 1267 K, respectively. Meanwhile, solidification ended. After annealing, the furnace was directly cooled to ambient temperature.

The growth rate was 2.67 μm/s. The ingot was cut into two halves symmetrically along the growth direction. The sketch map is shown in Fig. 2(a). Samples were taken out along red sample lines to be examined. Sample taken from sample line 2 represents concentration profile in the center of ingot, while sample taken from sample line 1 represents concentration profile away from the center. Near the sample line 2, a block was taken out as shown in Fig. 2(b). At 24% ingot height, a cubic sample, 1 $cm^3$, was selected as shown in Fig. 2(c). This sample represents average concentration including inner-grain and grain boundary; near the cubic sample, the block was crashed and grain boundary was exposed in laminate or powder. Concentration in the laminate or powder sample closes to that at grain boundary. Then, the laminate or powder was taken out as shown in Fig. 2(d). All samples were detected by inductively couple plasma mass spectrometry (ICP-MS, Thermo Fisher, ICAP QC).

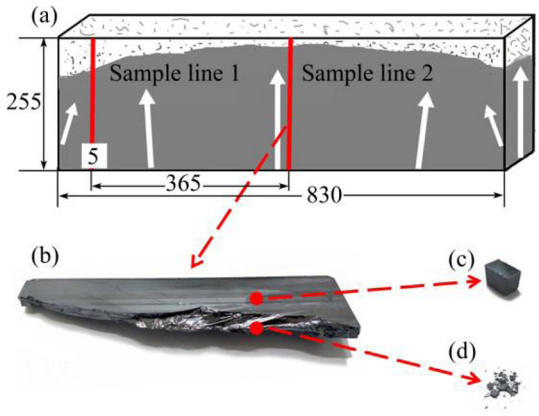


**Fig. 2** Sketch map of ingot (Crystal growth directions are marked with white arrows and sample lines are marked by red lines) (a), block of ingot taken out (b), cubic sample taken out at 24% height of block (c) and laminate or powder taken out near cubic sample (d)