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Effect of calcium-oxide on the removal of calcium during industrial directional solidification of upgraded metallurgical-grade silicon

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ABSTRACT

Directional solidification is often used to remove metallic impurity in the photovoltaic industry for the low equilibrium distribution coefficient between solid and melt. However, in our present experiments, compared with other impurities, the removal of calcium is variable at the low height of ingot, which is caused by the existence of insoluble CaO particle. CaO exists as insoluble particle in the feedstock. During directional solidification stage, CaO motions with the melt convection, and it is likely to envelop in solid. Consequently, the content of calcium is relatively high if many CaO particles are just contained, which is verified by the analysis of SEM-EDS. In a word, the removal efficiency depends upon the chemical state of calcium. The reason why CaO exists is studied, and the envelopment of the particle is mainly discussed by means of thermodynamics, especially on gravitational force, repulsive force, and drag force.

1. Introduction

Use of coal, oil and natural gas induces pollution in the environment. It is necessary to dig new friendly resources. Solar cells are one of the most promising energy sources [1,2]. The majority of solar cells are made of crystalline silicon. Multicrystalline silicon is an important material with the advantages of low production cost and relatively high conversion efficiency, while it needs high purity [3,4]. There is still no general agreement about the maximum impurity content in solar grade silicon. However, investigators agree that most of the metallic impurities can form defects and enhance the formation of dislocations, which act as recombination centers of photo-carriers and give rise to the decrease of conversion efficiency of solar cells [5]. Thus, removal of impurity to acceptable levels for solar cells is of great importance. Nowadays, chemical method can produce qualified products, however, it is costly and environment polluted. What is worse, the manufacturing route is dangerous. Physical method (metallurgy method) is considered relatively cost-effective, environment friendly and relatively safe [3]. Among the metallurgy methods, directional solidification method is quite effective to remove metallic impurity which has a small equilibrium distribution coefficient between solid and melt silicon (far less than 1) [6,7]. After directional solidification, many impurities, especially, the metallic impurities, are segregated to melt, and purer solid is achieved. As a result, the former part of the ingot to solidify is much purer than the part that solidified later. Moreover, if solidification velocity is much low, for example, less than 5 μm/s, the impurities removal ratio of the former part could be constant.

Many studies have shown the removal of transition metals by directional solidification method or modified methods [8–11]. However, in terms of calcium, it is sparsely investigated and has not been well understood yet. Some investigators claimed that the tolerance of calcium in crystalline silicon solar cells is 40 ppmw [12]. It may be reasonable for considering the sole calcium element. But in multicrystalline silicon of solar cells, calcium impurity may interact with other impurities, and even form precipitates or refractory compound, doing harm to solar cells performance [13]. Therefore, it is better to remove calcium as possible as we can. As we all know, calcium can be removed by oxygen blowing or slag refining for it easily reacts with oxygen. Calcium is also removed by vacuum melting or electron beam melting method for its high saturated vapor pressure [14]. But in our co-workers' experiments, calcium is not always removed efficiently by electron beam melting or slag refining method, especially, removal ratio is not constant. So, calcium is a stubborn element in the silicon. Calcium has small equilibrium distribution coefficient, about 1.6×10^{-3} [15], therefore, we can try to remove it by directional solidification method. Here, one important thing should not be neglected is the

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route of feedstock, that is to say, how the feedstock has been handled and what condition the feedstock has experienced play an important role in the following impurity removal stage. The chemical state of impurity in the feedstock has heavy influence on its removal. If the impurity exists stably as insoluble compound, for example, CaO, it will give rise to negative effect on the removal.

In the present paper, under the given experiment condition, we remove calcium by industrial directional solidification, investigating the redistribution of calcium along the crystal growth direction. Compared with other impurities, like aluminum, copper and boron, calcium has significant feature, namely, its removal ratio is variable. We discussed the causing, influence factors and mechanism in detail.

2. Experiments

The configuration of multi-heaters directional solidification furnace (Jingsheng-450) is shown in Fig. 1. Quartz crucible is supported by graphite susceptors, and the inner side of the square crucible is $830 \times 830 \times 450$ mm^3. Silicon nitride painted on the crucible is used as anti-wetting layer and facilitate the ingot demoulding after solidification. In case of silicon which is contaminated by the thermal decomposition of graphite resistance heaters, the crucible is covered with a carbon fiber plate. A cutout is set in the plate center as passageway of argon. Thermocouple 1 (TC1) is installed near the surface of top heaters to measure and control the furnace chamber temperature, and thermocouple 2 (TC2) is installed through the directional solidification block to measure the temperature at the crucible bottom. A quartz rod is inserted from the furnace top into the crucible to detect the crystal growth rate. The furnace chamber pressure is kept at 600 mbar (6×10^4 Pa) by adjusting the argon flow. The furnace wall is cooled by water. Thus, it is considered as a constant temperature boundary. Thermal field is controlled by two ways: (1) controlling the power of graphite resistance heaters; (2) closing or pulling the insulation cage upward.

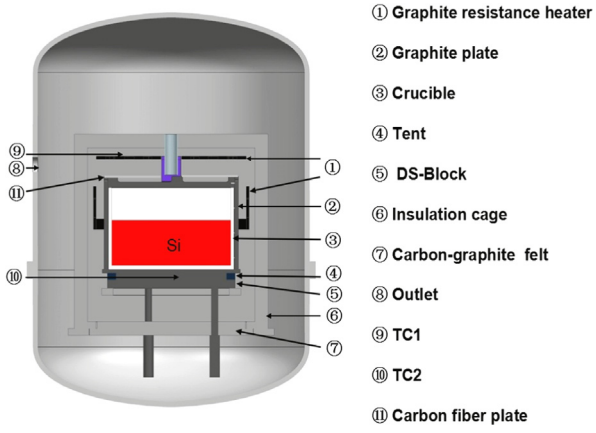

Fig. 1. Schematic configuration of directional solidification furnace.

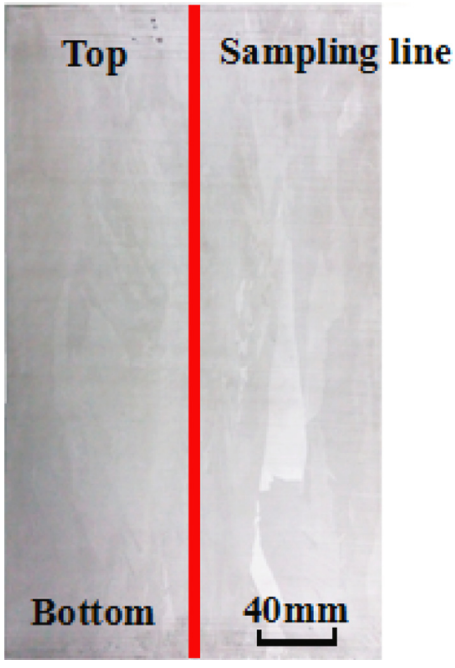

Fig. 2. Sampling brick ($156 \times 156 \times 270$ mm^3) was cut from the central ingot, and the detected samples were took brokenly along the sampling line.

Two group experiments (grouped 1, 2) were conducted. 435 kg upgraded metallurgical-grade silicon feedstock (about 4 N purity) was used to study for the two groups, respectively. Feedstock was loaded into the crucible and melted. During the melting step, the insulation cage was closed entirely. Furnace chamber was about 1823 K at 415 min, then, the temperature decreased gradually to 1698 K. After this step, the furnace chamber temperature was controlled appropriately by the combination of resistance heaters and insulation cage, and solidification began. Finally, the temperature at the furnace chamber top and bottom was about 1690 K, 1267 K, respectively. At the same time, solidification came to an end. After annealing, furnace cooling to ambient temperature directly.

The parameters in two groups were set in common, average crystallization rate was about 1.62 μm/s for each group, and the ingots were both $830 \times 830 \times 270$ mm^3. $156 \times 156 \times 270$ mm^3 brick was cut from the central ingot for further investigation, as showed in Fig. 2. Samples were took brokenly along the sampling line, and the impurity content was detected by the Inductively Couple Plasma Mass Spectrometry (ICP-MS, Thermo Fisher, ICAP QC).

3. Results

The content of impurities was analyzed by taking samples brokenly along the sampling line shown in Fig. 2. Boron (B), aluminum (Al), copper (Cu) and calcium (Ca), these four elements are chose to discuss. Fig. 3(a) shows the content of B, Al, Cu and Ca along the ingot height in group 1. There is a clear trend that all content profiles show an accumulation of impurities at the top of the ingot, which is the last part to solidify. What is more, the contents of all impurities except Ca are almost constant along approximately 70% (0.7) or more of the ingot. In fact, at the lower solidification rate, the content of all impurities should have been removed as constant at the lower height of ingot. Considering the content of Ca, it increases along the height, but discontinuously. At the low height of ingot, some points are obviously higher than that of the others, with the content differences of orders of magnitude.

In order to verify this phenomenon is not occasional, we conducted the other experiment with setting the same parameters, namely, group 2. We took samples as group 1, but 12 samples. The result is shown in Fig. 3(b). It shows similar content profiles of impurities as Fig. 3(a), and the Ca is still discontinuously, with the content differences of orders of magnitude.

4. Discussions

4.1. Causing of the discontinuous content of calcium

The basic mechanisms of segregation has been reported clearly [9,11]. The pressure is 600 mbar (6×10^4 Pa) in the present experiment, thus, not much lower than ambient pressure. As a result, the