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Removal of aluminum and calcium in multicrystalline silicon by vacuum induction melting and directional solidification

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ABSTRACT

A multicrystalline silicon ingot was obtained from metallurgical-grade silicon by vacuum induction melting and directional solidification. Based on the concentration distributions of aluminum and calcium along the growth direction, the removal mechanism of such impurities with both high saturated vapor pressures and low segregation coefficients is investigated. The results show that the removal of this type of impurities only depends on evaporation during vacuum induction melting process, thus their contents decrease significantly due to the strongly evaporation under the high temperature and high vacuum conditions. During subsequent directional solidification process, a model including both segregation and evaporation is used to simulate the concentration distribution. The results show that the impurity distribution is controlled by both two mechanisms in the initial stage of solidification and is mainly determined by segregation in the end stage due to the decrease of the diffusibility and evaporability of the impurity atoms.

1. Introduction

As the raw material of solar cells, the demand for solar grade silicon (SoG-Si) has been drastically increasing year by year with the rapid development of photovoltaic industry [1,2]. SoG-Si, prepared directly from metallurgical-grade silicon (MG-Si) by metallurgical route, attracts more and more attention due to its characteristics of low cost, low energy consumption and environmentally friendly [3,4]. Metallurgical route consists of several procedures to remove impurities from silicon according to the difference of physical properties. As two of the critical processes of metallurgical route, vacuum induction melting is an effective method to remove volatile impurities [5] and directional solidification is widely used to remove impurities with a low segregation coefficient [6].

As the major impurities in silicon, aluminum (Al) and calcium (Ca) deteriorate the electrical properties of silicon materials, such as electrical resistivity and minority carrier lifetime, so they need to be removed to a fairly low level to meet the performance requirement of solar cells [7]. The segregation coefficients of Al and Ca in silicon are 2.0×10^{-3} and 8.0×10^{-3}, respectively [8], which is insufficiently small, thus their contents cannot satisfy the purity requirement after primary directional solidification [9,10]. As a consequence, multiple directional solidification is used for further removal of them, leading to high cost and energy consumption. However, the saturated vapor pressures of Al and Ca are far larger than that of silicon, so they can be also removed from the melt free surface to the gashouse phase under a high temperature and high vacuum environment by vacuum refining [11,12]. As a consequence, the evaporation of Al and Ca is considered to have an important effect on their distributions during directional solidification, which may show a different removal mechanism.

In our previous work, the removal of Al and Ca from silicon melt during electron beam melting was investigated [10,13]. However, only the melting process was focused and the effect of evaporation on impurities' segregation during solidification process was not considered due to a very short solidification time. In this paper, based on the distributions of Al and Ca in silicon ingot after vacuum induction melting and directional solidification are obtained, the removal mechanisms of these impurities in different steps are discussed. A new theoretical model including both segregation mechanism and evaporation mechanism is developed to clarify the

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influence of the two removal mechanisms on the distributions of this kind of impurities.

2. Experimental

Experiment was conducted in a vacuum induction melting furnace. Fig. 1 shows the schematic diagram of the experimental apparatus. It consists of vacuum system, melting system, insulation system, pulling system and cooling system. The insulation system is used to prevent the heat flowing across the crucible wall, eliminate the radial temperature gradient. During the directional solidification process, the quartz crucible moves downwards with the heat sink while the heating power remains stationary. Then the heat in molten silicon flows only along axial direction and is taken by the cooling system so that the silicon crystal grows from the bottom to the top.

As the raw material, MG-Si with an initial purity of 99.8% was used in this experiment; the initial contents of Al and Ca were 3.40×10^{-2} wt.% and 1.91×10^{-2} wt.%, respectively. Prior to processing by vacuum induction melting and directional solidification, 6 kg MG-Si was washed sufficiently with alcohol to remove possible solid residues and extraneous impurities from the surface. Subsequently, it was placed in a quartz crucible with an inner diameter of 19 cm and a purity of 99.9%, and then the chamber was evacuated to a pressure less than 0.1 Pa. Three thermocouples were placed beside the crucible along the vertical direction with an interval of 5 cm. After melted completely, the molten silicon was kept at 1723 K for 1.5 h. Then the crucible was pulled downward out of the induction heating zone with a speed of 1.97×10^{-6} m/s. After the molten silicon solidified completely, the temperature was gradually lowered to 1273 K, and then the power was shut off.

The silicon ingot was cut vertically along the growth direction and six samples were chosen in the central region from the bottom to the top. As for each sample, the respective impurity contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

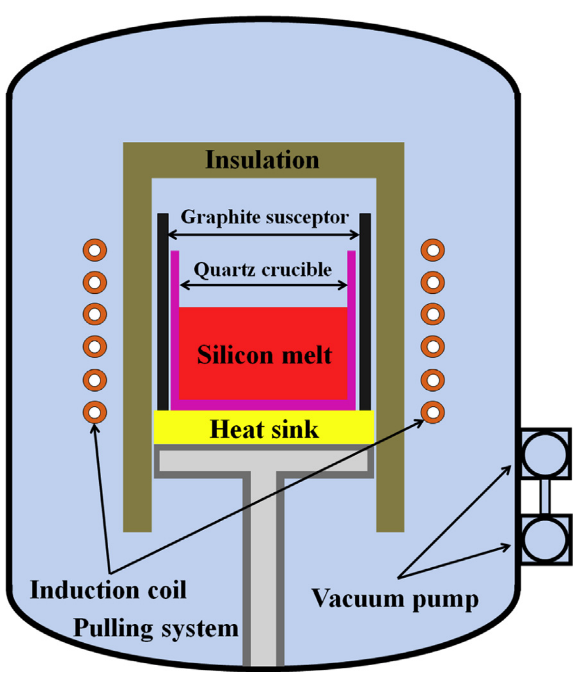

Fig. 1. Schematic diagram of the experimental apparatus.

3. Results and discussion

3.1. Distribution of Al and Ca in silicon ingot

The obtained silicon ingot is with a diameter of 19 cm and a height of about 11.5 cm. The macro morphology of the vertical section is shown in Fig. 2. A crystal broken area can be obviously observed at about 80% of the ingot height between the columnar grain area and the isometric crystal area. During directional solidification, most of the grains nucleate at the bottom and grow to the top. When the columnar grains grow to about 80% of the ingot height, it is interrupted due to the constitutional supercooling at the solid–liquid interface front. The top layer of the ingots contains more impurities than the other area, which must be cut off.

Six samples were chosen along the axial direction for chemical analysis. The measured impurity contents in different positions are shown in Fig. 3, as well as the initial content. Compared with that in the raw material, most of the impurities are removed, especially in the bottom part of the ingot. The impurity contents shows an obvious increasing trend from bottom to top, which stems from the impurities concentrating in the liquid phase during solidification process.

3.2. Evaporation of impurities

From a thermodynamics point of view, the difference between the vapor pressures of liquid silicon and the dissolved impurities is the basic principle for the removal of impurities from silicon by vacuum induction melting. The saturated vapor pressure of pure element i is only a function of temperature, which can be shown as Van Laar's equation [14]:

$$\log P_i^0(Pa) = AT^{-1} + B\log T + CT + D, \quad (1)$$

where A, B, C and D are constants given in Table 1 for Al, Ca and Si, T (K) is the absolute temperature.

During a melting process, the impurity element may be removed from the melt or enriched in the melt, which depends on the evaporation rates of the impurity element and matrix material. A very useful kinetic criterion to evaluate the feasibility of removing impurity element from molten silicon is defined as volatility coefficient, β, which can be described as [15]:

$$\beta = \sqrt{\frac{M_{Si}}{M_i}}\frac{\gamma_i^0 P_i^0}{P_{Si}^0}, \quad (2)$$

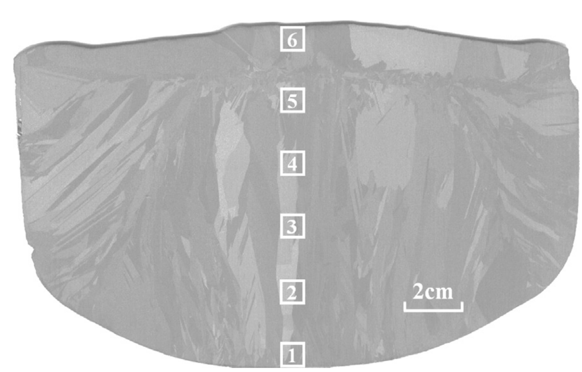

Fig. 2. Macro morphology of the vertical section. The silicon ingot was cut parallel to the growth direction and a crystal broken area can be obviously observed at about 80% of the ingot height. Six samples were chosen in the central part from the bottom to top for chemical analysis.