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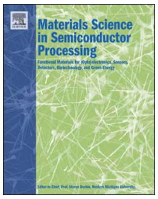

Effect of temperature gradient on the diffusion layer thickness of impurities during directional solidification process

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ABSTRACT

The diffusion layer thickness of impurity during directional solidification process was evaluated under different temperature gradient conditions. The thickness of Fe, Cu, Ni and Ti in silicon ingot under 9.74 K/m were 6.19 mm, 4.92 mm, 4.61 mm and 8.70 mm, respectively; The thickness of Fe, Cu, Ni and Ti in silicon ingot under 28.49 K/m were reduced to 3.35 mm, 1.21 mm, 1.85 mm and 5.81, respectively. The diffusion layer thickness was reduced by the large temperature gradient to lead a low effective segregation coefficient. As a result, the impurity concentration of silicon ingot under 28.49 K/m was reduced to 0.94 ppmw. The strong vortex in the solid-liquid boundary interface was enhanced by the large temperature gradient, as the main transport mechanism to accelerate the diffuse of impurity atom in the diffusion layer , which effectively reduced the thickness of diffusion layer.

1. Introduction

The rapid expansion of crystalline silicon solar cells industry demands a mass of solar grade silicon (SoG-Si) [1,2]. A low content of impurities in SoG-Si especially the deep energy level impurities is necessary to ensure the electrical resistivity, minority carrier lifetime and photoelectric conversion efficiency of solar cells [3–5]. SoG-Si prepared from metallurgical grade silicon (MG-Si) by metallurgical route has attracted more and more attentions [6,7], because of the low cost, low energy consumption , and environmentally friendly [8], which includes silicon refining by vacuum and direction solidification [9]. A large number of metal impurities are usually removed by directional solidification , due to their low segregation coefficient [10].

The concentration of impurities is affected by the effective segregation coefficient, which depends on the equilibrium segregation coefficient, the speed of crystal growth and diffusion layer thickness of impurity [10,11]. Tan et al. [12,13] have controlled of crystal growth speed by pulling rate, which removes the molten silicon from heater to control the removal of metal impurity in the silicon ingot. Yuge et al. [14] have proved that the slow speed of crystal growth can reduce the concentration of metal impurity in the solid without considering the diffusion layer thickness change. The diffusion layer thickness of impurity as a certain value are calculated in this paper, which is a very common way of calculation. In the most papers, the diffusion layer of impurity is only used to calculate the impurity concentration as a certain parameter. The diffusion layer thickness of Cu and Mn are used as 3 mm and 6 mm under low vacuum condition [15]. The diffusion layer thickness of impurity is used as 0.3 mm under high vacuum condition [16]. However, the diffusion layer thickness for different impurities with different solidification conditions should not be the same during directional solidification. The change of diffusion layer for different types of impurities under the different conditions should be further studied.

The diffusion layer thickness of impurity can be changed by flow of molten silicon, which can be introduced by certain technology, such as alternating magnetic field [17,18]. The effect of temperature field on flow of molten silicon during directional solidification has been revealed. In this paper, different temperature gradients in molten silicon were obtained to control diffusion layer thickness of metal impurities during the directional solidification. The diffusion layer thickness of Fe, Cu, Ni and Ti under different speeds of crystal growth conditions are studied. The transport mechanisms of the impurities in diffusion layer thickness under different temperature gradient conditions are also discussed.

2. Experimental

Fig. 1 shows the directional solidification furnace consisted of vacuum plant, heating unit, thermal insulation system, heat changed block and so on. Thermal insulation system, which was used to move up

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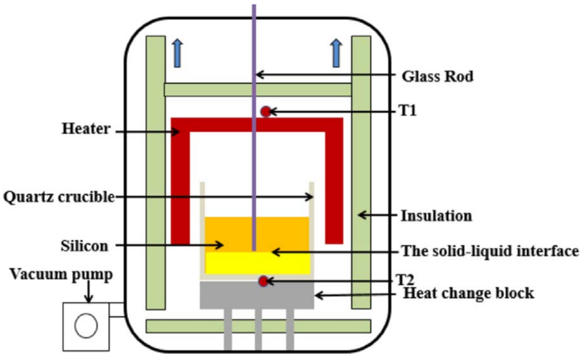

Fig. 1. Schematic diagram of the experimental apparatus.

to control the loss of heat. The heater temperature (T1) and heat changed block were used to control the temperature gradient and the crystal growth speed. The heater temperature (T1) and the heat exchange block (T2) can control the temperature gradient of environment with the crystal growth.

More than 300 kg MG-Si was placed in Si_3N_4 coated quartz crucible, of which the inner dimensions were 800 × 800 × 540 mm. The sum concentration of metal impurities in MG-Si for the three silicon ingots used in this experiment was up to about 867.15 ppmw. The main metal impurity is Fe, which is 659.4 ppmw. The impurity concentration in MG-Si is more than that of SoG-Si, which need be removed by directional solidification in the quartz crucible and the furnace. Production process including heating, melting of feedstock, crystal growth, ingot annealing and ingot cooling, which is the same with technological standards.

The furnace was filed with flowing argon. Its pressure was about 6×10^4 Pa. After melted completely, the crystal of three silicon ingots grew by different temperature gradients, which were obtained by choosing appropriate movement speed of insulation system, heat changed block and the heater temperature (T1). The three silicon ingots were named ingot 1, ingot 2 and ingot 3. In this experiment, the temperature of T1 in ingot 2 and ingot 3 decreased, while the temperature of T1 in ingot 1 firstly increased and then decreased during the directional solidification, as shown in Fig. 2(a). The temperature gradient between T1 and T2 were different for the three silicon ingots, as shown in Fig. 2(b). The temperature gradient between T1 and T2 of ingot 2 was largest in the three silicon ingot. The temperature of molten silicon surface near the heater usually was slightly lower than temperature of T1 by simulation calculation. The difference value is within 3 °C [19].

The height of crystal growth was measured for period of time intervals by a glass rod. The glass rod was put into molten silicon. When the end of glass rod touched the solid-liquid interface, the position of the other end of glass rod was measured. Then, the glass rod was pulled out molten silicon. After a while, the glass rod was put into liquid again, the position of the other end of glass rod was once again measured. The difference value of position is the height of crystal growth. The space height from the position of the T1 to the bottom of crucible was 706 mm. The distance from the position of T1 to the solid-liquid boundary interface equals that space height minus height of crystal growth.

At the beginning of solidification, the solid silicon (under 80% height) can be seen as pure silicon because of the low impurity concentration, as shown in Table 1 . The columnar crystal continuously grow as the solidification. There is barely nucleation process in the solid-liquid boundary with crystal growth, which doesn't need supercooling to supply nucleation energy. As a result, the influence of supercooling on solidification is not need considered. Assuming that the temperature of the solid-liquid boundary interface is 1414 °C (melting point), corresponding temperature difference equals that the temperature of T1 minus the melting point. So the corresponding temperature gradient could be obtained by the temperature difference divided by the distance.

A longitudinal section of silicon is from the center of ingot. Two silicon bars which were paralleled along the direction of crystal growth were cut in center and edge region of the longitudinal section, as shown in Fig. 3. The center silicon bar is in the center of the silicon ingot. The edge silicon bar is in 10 cm of the crucible. Some samples of every silicon bars in different location of solidification fraction were chosen to detection, respectively. The metal impurities in each sample were measured by Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The transition metal impurities of Fe, Cu, Ni and Ti which belong to the deep energy level impurities were measured.

3. Result

3.1. Temperature gradient and speed of crystal growth

Three different temperature gradients of molten silicon are shown in Fig. 4(a). The temperature gradient of molten silicon the three silicon ingots was about 9.74 K/m, 12.66 K/m, and 28.49 K/m, respectively.

The temperature gradient for solid silicon is between the solid-liquid interface and the T2, as shown in Fig. 4(b). The heat exchange block was adjustable to control the temperature of T2. So the temperature gradient of solid silicon under 9.74 K/m was the least in the three silicon ingots. The temperature gradient of molten silicon and solid silicon can impact the speed of crystal growth.

The speed of crystal growth is calculated, which equals that the height of silicon ingot is divided by a period time of crystal growth, as shown in Fig. 5(a). The crystal for the three silicon ingots grows with

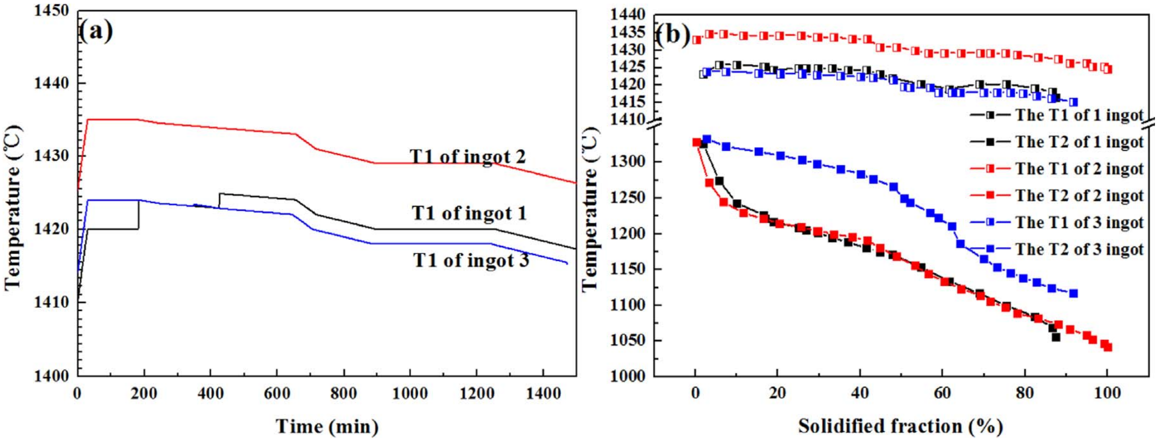

Fig. 2. (a) Setting temperature of T1 (b) measured temperature of T1 and T2 for the three silicon ingots.