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Removal of aluminum from silicon by electron beam melting with exponential decreasing power

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ABSTRACT

Aluminum is one of the main impurities in silicon, which can be separated and eliminated by electron beam melting. However, high removal efficiency can be obtained only by increasing melt temperature or extending refining time, resulting in high energy consumption. In this work, the directional solidification of silicon was achieved by electron beam with exponential decreasing power, considering that aluminum has both characteristics of segregation and evaporation. The distributions of aluminum show increasing trend from the bottom to the top of the electron beam melted silicon ingot, which is the same as that after traditional directional solidification. The removal efficiency is improved by the coupling of segregation and evaporation. Compared with traditional electron beam melting, the loss of silicon reduced by more than 52% and the energy consumption reduced by more than 54%. This method is more effective to remove aluminum from silicon with low energy consumption.

1. Introduction

In recent years, the photovoltaic industry is developing rapidly due to the energy shortage, increasing by over 30% per year [1]. As a key raw material for solar cells, crystalline silicon occupies more than 90% of the global photovoltaic market [2,3]. As a consequence of the dramatic increasing requirement for silicon materials, the current focus is to improve the efficiency of solar cells while still using cost-effective, high-throughput, and large-scale processes. The metallurgical route is a promising way for the purification of metallurgical-grade silicon (MG-Si) to solar-grade silicon (SoG-Si) [4,5]. Based on the difference of physical properties between silicon and impurities, several refining steps are used to remove different impurities in turn on the premise that silicon do not participate in chemical reactions.

Electron beam melting is one of the key procedures in metallurgical route, which has been proved to be an effective method to remove volatile impurities from silicon [6,7], especially for phosphorus [8–10]. Under a high temperature and high vacuum condition provided by electron beam equipment, impurity elements with high saturated vapor pressure can be evaporated from molten silicon to gaseous phase, and then removed by the vacuum system.

As a major impurity in silicon, aluminum deteriorates the electrical properties, such as electrical resistivity, minority carrier lifetime and then photoelectric conversion efficiency [11,12], so it must be removed to a fairly low level to meet the performance requirement of solar cells. However, the removal efficiency depends upon the temperature and refining time [13], so it requires to raise the temperature or extend the refining time to obtain higher removal efficiency, resulting in a large energy consumption.

In this paper, the directional solidification of silicon was achieved by electron beam with exponential decreasing power. Based on the distribution of aluminum in silicon ingot, the removal efficiency and mechanism were discussed. Meanwhile, the evaporation loss of silicon and the energy consumption during the whole process were also evaluated by comparing with the traditional electron beam melting process.

2. Directional solidification of silicon induced by electron beam

In our previous work [14], the directional solidification of silicon induced by electron beam has been achieved by controlling the decreasing rate of beam power, and the simulation results

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show that the solidification rate is uniform with an exponential decreasing rate. Fig. 1 shows the schematic diagram of directional solidification of silicon induced by electron beam. A unidirectional temperature gradient always exists in the molten pool, because the surface of the molten pool is heated by electron beam and the bottom contacts directly with the water-cooled copper crucible, so that the melt solidifies from the bottom to the top. The segregation coefficient of aluminum is smaller than 1, so the removal efficiency of aluminum is considered to be improved with the action of segregation behavior.

3. Experimental

3.1. Experimental apparatus

Experiments were conducted in an SEBM-30A-type electron beam melting furnace. It consists of a chamber with the volume of 1 m^3, an electron beam gun with an accelerating voltage of 30 kV and a maximum power of 30 kW, a water-cooled copper crucible, a circulation water cooling system and two independent vacuum systems. The crucible has a button shape and a maximum of 2 kg silicon can be melted in it.

3.2. Materials and pretreatment

MG-Si with an initial purity of 99.8 wt.% was used as the raw material, in which the initial content of aluminum was 1.71×10^{-1} wt.%. Prior to the processing by electron beam melting, it was washed sufficiently in alcohol by a supersonic wave cleaner to remove oil, organic compounds and possible extraneous impurities adhered to the surfaces. After that, it was put in a drying oven for 2 h.

3.3. Experimental procedure

600 g silicon was placed inside the water-cooled crucible, thereafter the chamber was evacuated to a pressure less than 5×10^{-2} Pa and the gun chamber was evacuated to a pressure less than 5×10^{-3} Pa. The electron beam was then irradiated on the surface of the silicon with a circular scanning pattern to ensure it was heated homogeneously and steadily. As shown in Fig. 2, the beam power increased gradually to 9 kW so that the silicon could be melted completely. The refining time was started once silicon was melted completely in the crucible. The melt was then maintained for 900 s with the beam power of 18 kW. After that, the power was stopped instantaneously or reduced exponentially. The experimental parameters are given in Table 1.

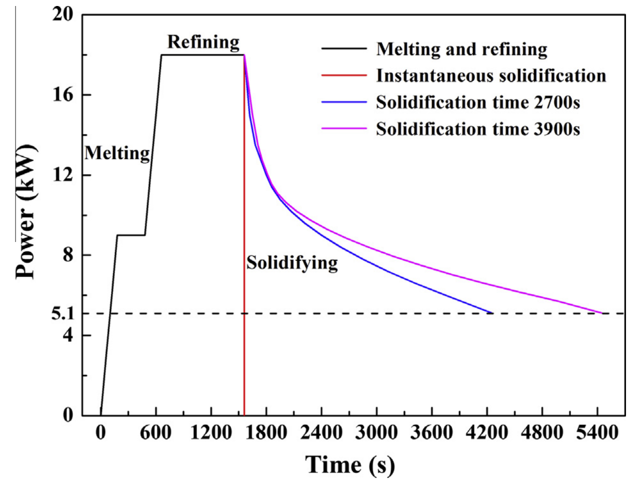

Fig. 2. Power changes with time during the whole electron beam melting process.

Table 1
Melting conditions in electron beam melting experiment.

	Sample 1	Sample 2	Sample 3
Melting power (kW)	18	18	18
Refining time (s)	900	900	900
Solidification time (s)	Instantaneous	2700	3900
Pressure (Pa)	5×10^{-2}–5×10^{-3}	5×10^{-2}–5×10^{-3}	5×10^{-2}–5×10^{-3}
Scanning pattern	Circle	Circle	Circle

3.4. Testing and characterization

The obtained silicon ingots were cut along the vertical cross section. It was polished and etched with 20% NaOH solution for 20 min so that the morphologies of the crystal can be observed clearly. The resistivity distribution on the cross section was measured by KDY-1 four-point probe resistivity tester. Five samples were chosen in the central region at 0%, 25%, 50%, 75%, and 100% of the ingot height for chemical analysis. As for each sample, the aluminum concentration was determined by inductively coupled plasma optical emission spectroscopy (ICP-MS).

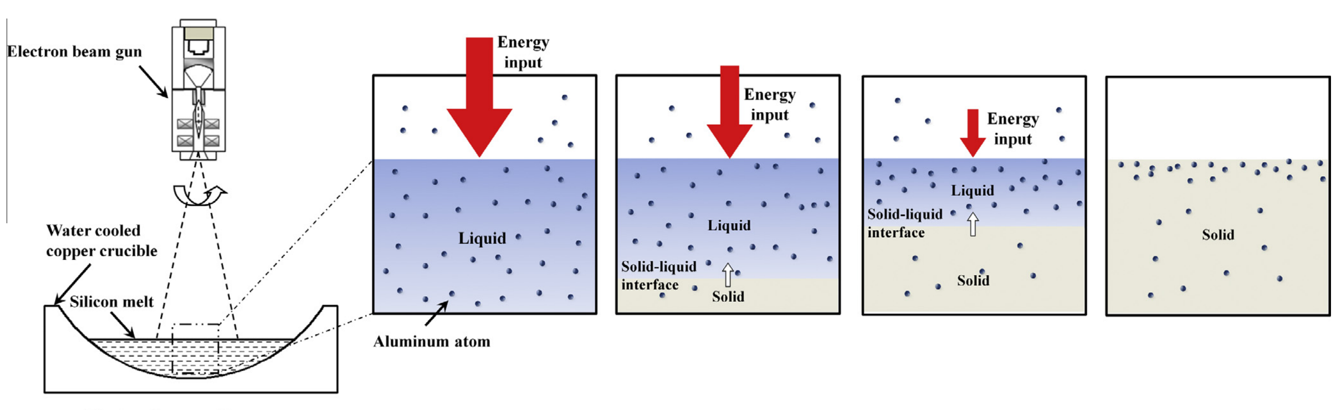

Fig. 1. Schematic diagram of directional solidification of silicon induced by electron beam.