



## Short communication

## Growth control and enrichment of Si crystals from Si-Sn melt by directional solidification

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## ABSTRACT

The growth control and enrichment of Si crystals using Si-50 at.% Sn melts *via* upwards and downwards directional solidification at various moving rates was investigated. As expected, a large area of quasi-bulk Si (98.6% enrichment percentage) was successfully obtained at the 0.01 mm/min upwards moving rate. Moreover, after HCl leaching, the residual at.% of Sn in the enriched Si area was easily reduced to the 0.00132–0.00163 range, which was almost the same as that for the solid solubility of Sn in Si. Furthermore, a model was established to explain the crystal growth process and enrichment mechanism during directional solidification. In conclusion, we chose the upwards moving direction for the follow-up experiments, which solved the most critical first step of using Si-based alloy solvent refining to produce solar grade Si.

Considering the continuous depletion of traditional fossil fuels, solar energy has been rapidly developing in the last decades as green renewable energy [1]. Si is the main feedstock for the photovoltaic (PV) industry. Conventionally, solar grade silicon (SOG-Si) has been produced using off-spec electrical grade Si (SEG-Si) with low yield rate. Currently, the improved Siemens and fluidized bed methods serve as mainstream techniques to produce SOG-Si. Nevertheless, these methods are energy-intensive and costly [2].

The metallurgical refining process enables the purification of metallurgical grade Si (MG-Si) as a sustainable process [3], and it has advantages of mass productivity and relatively low cost. Extensive research has been conducted using metallurgical refining processes such as acid leaching [4], vacuum melting [5], oxidation treatment [6], slag refining [7], directional solidification [8,9], and electron beam melting [10].

Recently, a novel metallurgical method concept named ‘solvent refining’ was proposed by our group [2], which significantly reduced the melting temperature, thus further reducing the producing costs of Si in the PV industry. Previous investigations on Si-Al [11–14], Si-Fe [15], and Si-Cu [16] solvent systems were conducted. Moreover, other Si-based solvents such as Si-Na [17,18], Si-Ca [19,20], Si-Ga [21], Si-Ni [22], Si-Al-Zn [23], and Si-Al-Sn [24], as well as their combinations were studied. The research proved that crystal growth, enrichment, separation, and purification of primary Si greatly affected the efficiency of such refining processes.

Various technologies have been applied for the enrichment and

separation of solidified Si from the Si-Al melt, such as electromagnetic fields [25–27], supergravity fields [28,29], and powder metallurgy techniques [30], based on the comparable density between solidified Si and liquid Si-Al ( $\rho_{\text{Si}(300\text{K})} = 2.33\text{ g/cm}^3$  [31],  $\rho_{\text{Al}(1173\text{K})} = 2.33\text{ g/cm}^3$  [32]). However, the application of these techniques was limited owing to the high associated costs. Meanwhile, the growth rate of bulk Si in the Si-Al system is still low [33]. Fe was selected as a solvent by ESFAHANI S et al. [34,35] because of the density difference between Fe and Si. This method can make the residual Si-Fe alloy circulate but with a poor separation effect, coupled with the high cost of heavy media, which also increased the cost. Cu was used as a solvent by MITRAŠINOVIĆ et al. [36] because of the low solid solubility of Cu in Si and a great density difference between Cu and Si, the separation of purified Si and Si-Cu alloy can be achieved. But in the process of melting, Cu and Si form intermediate compounds, which makes it difficult to separate Cu from Si after purification. Therefore, effective solvent favouring both the growth rate, enrichment and purification of Si is highly needed.

Growth control and enrichment of Si crystals from the Si-Sn melt have not been studied systematically although this system has many outstanding advantages: (i) the Si-Sn system has a moderate liquidus slope [37], which indicates a large amount of precipitated Si at equilibrium [38]; (ii) the precipitated primary Si can grow and float easily due to the buoyancy caused by the significant density difference between primary Si and liquid Si-Sn ( $\rho_{\text{Si}(300\text{K})} = 2.33\text{ g/cm}^3$ ,  $\rho_{\text{Sn}(1555\text{K})} = 6.32\text{ g/cm}^3$  [39]); (iii) the activity coefficient of B in the

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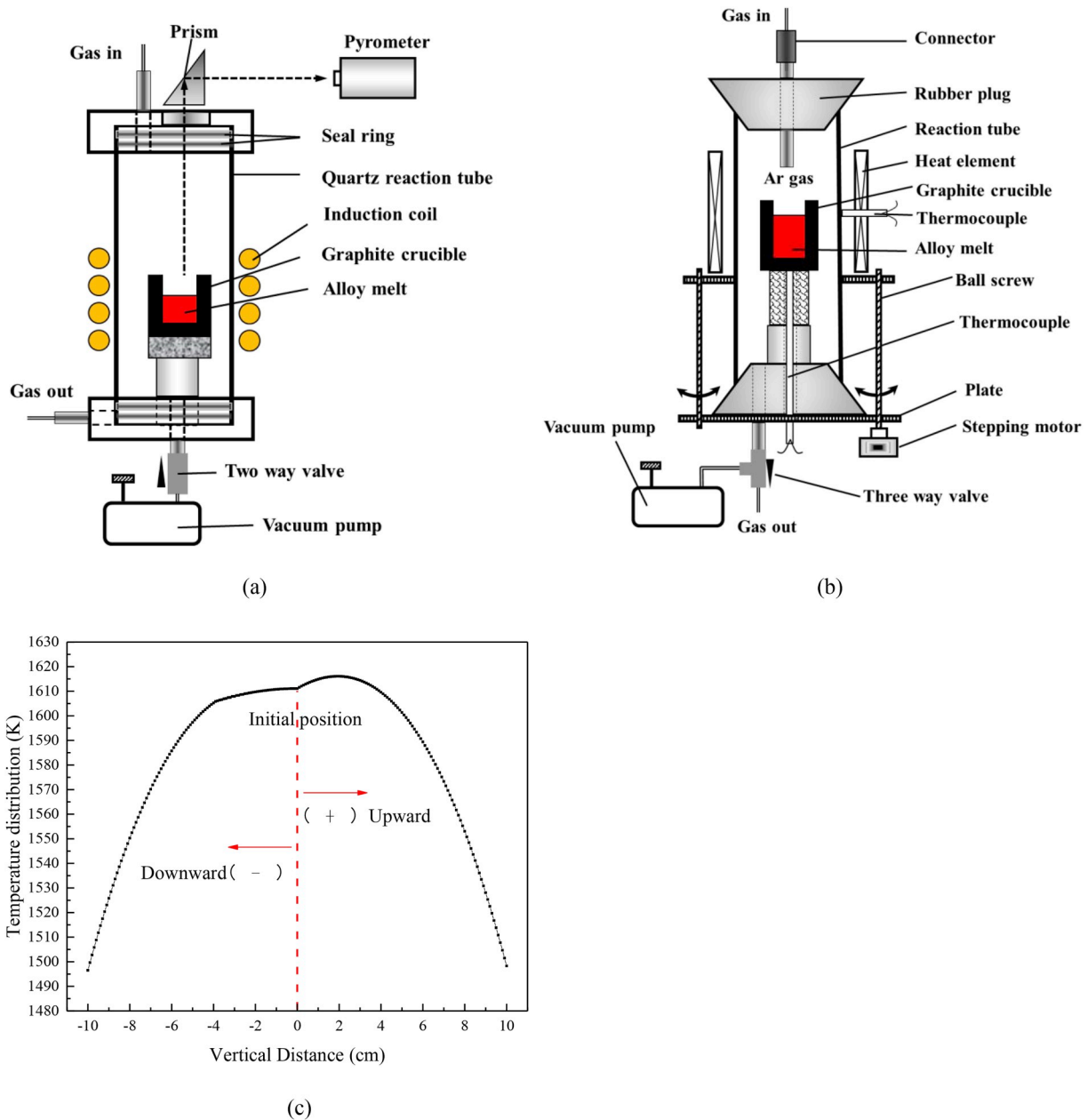


Fig. 1. Schematic diagrams of the equipment (a) induction furnace, (b) directional solidification furnace, and (c) temperature distribution along the vertical direction.

Sn-rich side is three orders of magnitude larger than that in the Si-rich side, so B becomes thermodynamically more unstable in the Si-Sn alloy melts [40]. Therefore, additives (such as Zr, Ti, and Hf) which have strong affinity for B can be used to enhance the B removal fraction during the solidification refining process; (iv) Sn is an electrical inactivity element in solar cells [41] which means that it can tolerate relative high content of Sn in refined Si; and (v) Sn has a higher vapour pressure than Si that means the remaining Sn in Si can be removed by vacuum melting.

The current study was aimed at clarifying the growth control and enrichment of Si crystals from the Si-Sn melt under different moving directions and at different rates. The optimal conditions for crystal growth and enrichment were determined. Moreover, a model was established encompassing the crystal growth process and enrichment mechanism of the Si-Sn melt during directional solidification.

A high frequency induction furnace (50 kHz) was employed to conduct the pre-melting experiments. The schematic of this apparatus is

shown in Fig. 1(a). In total, 30 g of bulk Si (99.9999%) and Sn grains (99.9%) were placed in a high-purity dense graphite crucible (20 mm outer diameter (O.D.), 14 mm inner diameter (I.D.), 70 mm length) to prepare the Si-Sn alloys. To prevent the oxidation of the melt, the quartz chamber (60 mm O.D., 54 mm I.D., 400 mm length) was first evacuated using a vacuum pump (ultimate pressure < 6 Pa). The chamber was then filled with Ar gas (99.99%) at a flow rate of 200 mL/min. The surface temperature of the Si-Sn melt was monitored through a prism, using a dual-wavelength infrared pyrometer.

Subsequently, directional solidification experiments were conducted as follows. First, the pre-melted alloys were placed into the alumina reaction tube (30 mm O.D., 24 mm I.D., 1000 mm length) of a SiC electric resistance furnace combined with a vertical motion system controlled by a stepping motor, which was used to carry out the directional solidification experiments, as shown in Fig. 1(b). The moisture, CO<sub>2</sub>, and O<sub>2</sub> in the Ar gas were removed by passing the gas successively through soda lime, silica gel, magnesium perchlorate, and

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