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Development of grain structures of multi-crystalline silicon from randomly orientated seeds in directional solidification

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ABSTRACT

Development of grain structures of multi-crystalline silicon from small spherical seeds with random orientations in directional solidification was investigated. The electron backscattered diffraction (EBSD) analyses of the grains at different pulling rates, i.e., 1, 5, and 20 cm/h, were carried out. It was found that {112}/{111} orientations were dominant at the low crucible pulling speed, while {111} at the high pulling speeds. The percentage of {100} grains was found very low near the top of the ingots. The percentage of non-Σ grain boundaries was around 70% at the beginning and decreased with the solidification distance, while Σ3 grain boundaries or twins increased indicating the importance of twin formation during the development of grain structures. The mechanisms for grain competition and selection were further discussed.

1. Introduction

Multi-crystalline silicon (mc-Si) grown by directional solidification has attracted much attention in photovoltaic industry because of its low production cost and high throughput. However, the crystal quality deteriorates as the ingot grows taller due to the accumulation of impurities and the generation (multiplication) of dislocations. Because these defects, as well as crystal properties, are affected by grain morphologies and lattice orientations, the control of grain structures is important during crystal growth [1–5]. One of the approaches is the so-called dendrite casting method [1,2], which controls the initial undercooling to induce [110]/[112] dendrites and Σ3 grain boundaries. However, the control of undercooling is not so easy in a commercial growth station due to the large thermal resistance from the thick bottom of the quartz crucible and the imperfect nitride coating [3,4]. This thus limits the applications of the method for mass production. The simplest way to control crystal structure is to use seeds with given orientations, and the use of mono-crystalline seeds has become popular in recent years for the production of the so-called mono-like or quasi-mono ingots [6,7]. Unfortunately, the grain competition and new grain formation may spoil the structures and reduce the production yield. Therefore, it is believed that using a preferred growth orientation for directional solidification could increase the structure yield and reduce defect density [3,7]. Trempa et al. [7] have discussed this issue based on the twin formation mechanisms, and concluded that {100} orientation turned out to be the most difficult one to the growth of mono-like ingots. Nevertheless, the growth habit of mc-Si in directional solidification has not yet been investigated extensively [8,9]. The grain selection and nucleation, as well as the development of grain boundaries, during crystal growth remain unclear. Their relationship with defect generation is not known as well.

To understand the development of grain structures, Voigt et al. [8] investigated the grain orientations from cast mc-Si wafers. Relative orientations between pairs of grains, as well as grain boundaries, were clarified. They found that the grains seemed to be oriented randomly, but the relative grain orientation could be described mostly by special coincidence orientations. This indicated that the grain structure developed from far fewer independent nuclei that were decided at the initial stage of nucleation and crystal growth, as discussed previously [1,2]. For germanium, Azuma et al. [9] used multiple seed crystals with random orientations for a directional solidification and found that {110} was the preferred orientation. They further used a {110} seed for the growth of SiGe crystals, and the polycrystallization was effectively restrained. Fujiwara et al. [10] also observed that the preferred growth orientation of SiGe changed from {111} to {110} with the increasing Ge composition; they believed that {111} was the preferred growth orientation for silicon due to the smaller interfacial energy. Fujiwara et al. [11–13] further studied the melt growth behavior of mc-Si using an in situ monitoring system during a thin-film directional solidification. They observed that different growth behaviors of oriented grains appear in different cooling conditions. {100} and {110} poly-silicon grains were favored at a high cooling rate,

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e.g., 30 K/min, as a result of kinetic control; the growth velocity of $<100>$ was 40.8 cm/h at 30 K/min. On the contrary, at a low cooling rate, e.g., 1 K/min, {111} grains were dominant due to thermodynamic control that favors the orientation with the lowest interfacial energy [13]. By using phase field modeling, Chen et al. [14] also illustrated similar developments. They further used the force balance at the tri-junction to explain the dominance of {111} grains at the low growth rate. The critical velocity for facet formation, as a result of morphological instability, was estimated around 12 cm/h [12]. However, the growth velocity for {100} dominated growth was unknown [13]. Therefore, for the grain competition in a normal speed at about 1 cm/h in commercial mc-Si production, {111} grains should be dominant. However, no experiments have been performed to verify this because the initial nucleation and growth from the quartz crucible are predetermined by the initial undercooling. Moreover, the grain competition in silicon is far more complicated than that discussed by Fujiwara et al. [11–13] due to twin formation. Duffar and Nadri [15] discussed the twin formation in the growth of mc-Si, and then they came out an interesting two-dimensional computer model [16] to describe the development of grain structures, and tried to verify them by in situ X-ray observation [17], based on twining mechanisms [18,19]. According to their model, the nucleation of twins from undercooled {111} facets plays a crucial role on the grain structures. On the other hand, the grain competition of the columnar grains with rough surfaces follows pretty much the traditional rule that the less disoriented grains survive. With twin formation through {111} facets, highly disoriented grains can still survive till the top of the ingot.

In this study, we used spherical silicon beads as the seeds for directional solidification of mc-Si. Because these beads were sufficiently small and randomly oriented, the development of grain structures, as well as the grain size, should be interesting and useful to better understand the growth behaviors of mc-Si. The bias from the initial undercooling could be minimized. In the following section, the experimental setup and procedure are described briefly. Section 3 is devoted to results and discussion, followed by conclusion in Section 4.

2. Experimental

Mc-Si ingots (70 mm in diameter) were grown by directional solidification. The directional solidification setup using induction heating is shown in Fig. 1(a), where the crucible was insulated by alumina felt to better control the solidification front. Spherical silicon beads (0.92 mm in diameter from CV 21, Japan) were used as the seed layer (about 20 mm in height), as shown in Fig. 1(b), before silicon small ships were placed in the nitride-coated quartz crucible. The resistivity was controlled by boron doping in the range of 1–2 Ω-cm.

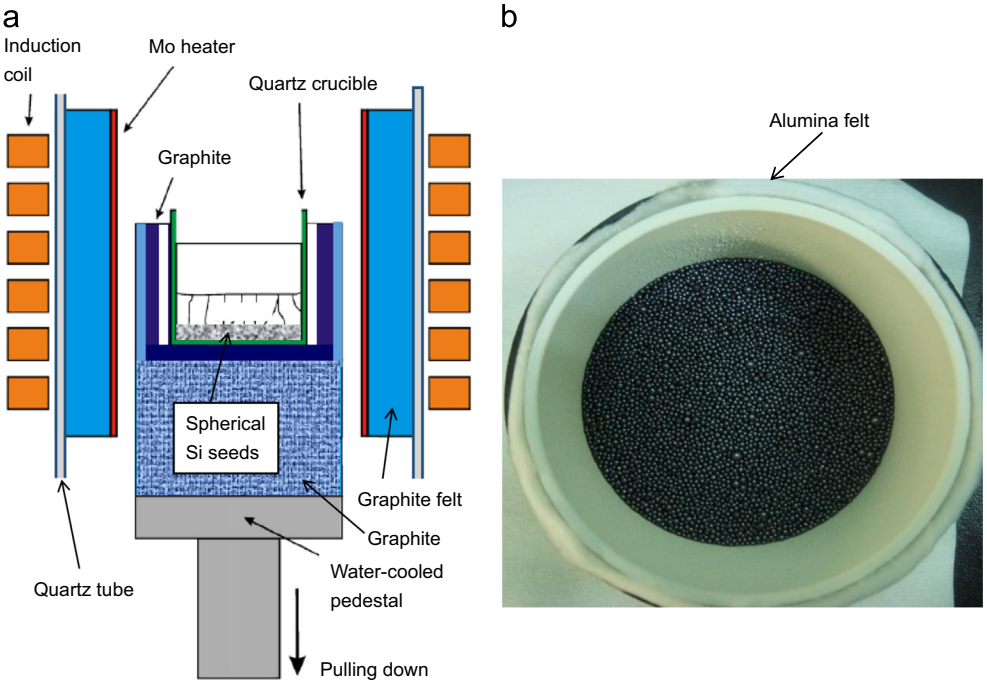

Fig. 1. (a) Schematic illustration of the experimental setup; (c) silicon beads in the nitride-coated quartz crucible.

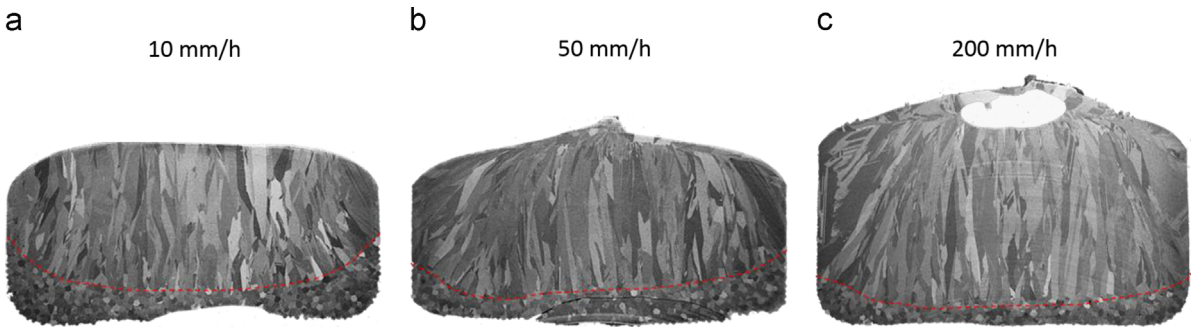

Fig. 2. Longitudinal cross section of ingots at different pulling speeds: (a) 10 mm/h; (b) 50 mm/h; (c) 200 mm/h; the dashed line indicates the initial melt/solid interface.