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Evolution of grain structures during directional solidification of silicon wafers

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ABSTRACT

The evolution of grain structures, especially the types of grain boundaries (GBs), during directional solidification is crucial to the electrical properties of multicrystalline silicon used for solar cells. To study this, the electric molten zone crystallization (EMZC) of silicon wafers at different drift speeds from 2 to 6 mm/min was considered. It was found that < 111 > orientation was dominant at the lower drift velocity, while < 112 > orientation at the higher drift velocity. Most of the non-∑GBs tended to align with the thermal gradient, but some tilted toward the unfavorable grains having higher interfacial energies. On the other hand, the tilted ∑3GBs tended to decrease during grain competition, except at the higher speed, where the twin nucleation became frequent. The competition of grains separated by ∑GBs could be viewed as the interactions of GBs that two coherent $\sum 3^n$ GBs turned into one $\sum 3^n$GB following certain relations as reported before. On the other hand, when ∑ GBs met non-∑ GBs, the non-∑ GBs remained which explained the decrease of ∑ GBs at the lower speed.

1. Introduction

Multi-crystalline silicon (mc-Si), grown by directional solidification, is an important material for solar cells. Nowadays, around 70% of solar cells are made from mc-Si [1]. However, due to the high cost of Si feedstock and wafer slicing, the kerf-free growth, such as the string ribbon growth (SRG) and the edge-defined film-fed growth (EFG) [2,3], remain promising for further cost reduction. To improve the wafer quality for solar cells, the control of GBs during solidification is particularly important. However, the evolution of grain structures, especially the GBs, during silicon solidification has not yet been well understood.

A few studies have been devoted to grain competition, faceted dendrite and twin nucleation. Fujiwara et al. [4] suggested that undercooling was a key parameter for grain competition that decides the tilting of the GB between two grains. The competition was found to be dominated by the interfacial energy at the lower growth rate, e.g., 2 mm/min, and the kinetics at the higher growth rate. Atwater et al. [5] also indicated that the direction of GBs was caused by the growth rate difference between two grains. Moreover, based on their approach, Duffar and Nadri [6] proposed three types of GB grooves that determined the direction of GBs observing from the experiments [7]. In addition, Duffar and Nadri [8] further proposed a model to describe the twinning mechanism for the nucleation of new grains where the nucleation of twins on the {111} facet having the highest undercooling played a crucial role. Fujiwara et al. [9] also studied the growth mechanism of faceted dendrite by using an in situ observation and further proposed a nucleation mechanism on the re-entrant corner binding by two {111} facets. They also proposed the so-called dendrite casting method using initial undercooling process to induce < 110 > and < 112 > dendrites at the crucible bottom and to generate more electrically inactive ∑3 GBs [10]. It reported that < 110 > and < 112 > dendrites could be induced at the crucible bottom and more electrically inactive ∑3 GBs could also be generated by the method proposed by them, dendrite casting method using initial undercooling.

Recently, a new casting technology by using small randomly oriented seeds was proposed for the so-called high-performance mc-Si (HPMC) [11]. The main characteristics of HPMC were the uniform small grains and the high portion of random GBs, which could be more than 70%. These non-coherent random GBs turned out to be effective in suppressing the multiplication of dislocations [12] either by blocking the propagation of dislocation clusters or relaxing the thermal stress, or both [11,13]. However, more ∑ GBs generated during grain growth, and to a certain degree, the ingot quality started to degrade due to the spreading of dislocation clusters. The evolution of the grain orientations and grain boundaries was first investigated by Wong et al. [14] using small spherical Si beads, having random orientations, as the seeds for directional solidification. The twin nucleation found at the tri-junctions was the major source of ∑3 GBs and hence the ∑3 GBs increased while the random GBs decreased

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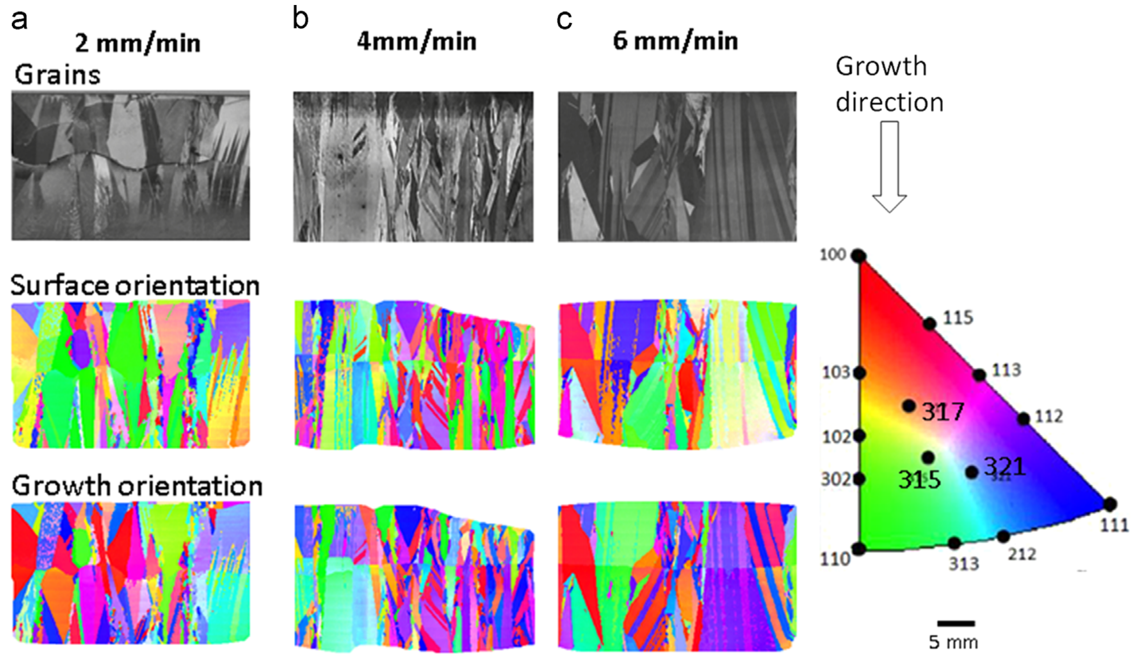

Fig. 1. Grain structures and corresponding crystallographic orientations in the surface plane and the growth direction: (a) 2 mm/min, (b) 4 mm/min, and (c) 6 mm/min.

during grain coarsening. By using a similar experiment, Prakash et al. [15] further studied the interactions of GBs from the longitudinal cut of the cast sample. The generation, annihilation and the evolution of some specific GBs were discussed. Unfortunately, because of the grain growth was not perfectly vertical; the interactions of GBs in some cases could be misleading. To study the evolution of GBs, the ribbon growth could be a better candidate. A few studies were reported for the dominant growth orientations and grain boundaries [16,17]. The narrow grains with {110} direction at the surface were found at high pulling rates, e.g., 30 mm/min [16]. Stockmeier et al. [17] also observed that the typically elongated grains had $<211>$ orientation parallel to the growth direction having {110} surface orientation at the pulling rate of 10–30 mm/min. They also proposed a simple model based on the minimization of GB energy to explain the twin formation. However, the grain competition and the interactions of GBs during ribbon growth were not investigated.

In this paper, we used the EMZC method as a tool to study the evolution of grain structures, especially the evolutions and the interactions of GBs, during directional solidification of silicon sheets at different speeds. The results might be useful to better understand and control the grain growth of mc-Si during directional solidification. In the next section, the experimental setup and characterization methods are described briefly. Section 3 is devoted to result and discussion followed by conclusions in Section 4.

2. Experimental

The experimental setup for EMZC of silicon sheets was similar to that reported by Costa et al. [18], and one could find the details elsewhere [19]. In short, the silicon wafer, $120 \times 50\ \text{mm}^2$ in size and 200 μm in thickness, was placed between two water-cooled electrodes. A 1-kW linear halogen lamp focused by a linear elliptic mirror was used as a heat source for electric current concentration. As the current passed through the heated zone up to 22.5 A, which was controlled by a power supply (Sorensen DC 55 V 55 A 3 kW), at the lamp power of 900 W, a stable molten zone about 600 μm in width was obtained. The lamp was then moved downward at a given speed for solidification. Three speeds 2, 4, and 6 mm/min were considered, and the actual solidification speed was also monitored by a microscope; the actual speed (1.8, 3.7, and 5.5 mm/min) was slightly lower than the lamp speed but the difference was not too much. Temperature distribution was also measured by a mono-color pyrometer with a spot size of 0.3 mm (Sensortherm Gmbh Metis MS 90). The thermal gradient near the solidification front was about 180 K/mm. Commercial wafers (A4+ wafers from Sino-American Silicon Products Inc.) with smaller grains were picked for the experiments.

After the solidification experiments, the wafers were chemically etched (HNO_3:HF=6:1) for subsequent characterizations. The grain orientations and the types of GBs were examined by electron back scattered diffraction (EBSD) (Horiba Nordlys F+) with a step size of 10 μm, which was installed in an SEM (Hitachi S3400). All the statistics were also carried out the build-in software, which calculated the area or distance, as well as the ratio. If the grains were smaller than the step size, they would be ignored.

3. Results and discussion

3.1. Grain structure

For the recrystallized wafers, we focus on the regions near the middle are focused for the subsequent discussion. Fig. 1 shows the typical grain structures from EMZC for different lamp speeds, i.e., 2, 4, and 6 mm/min; the direction is indicated by a narrow. The first wafer shown in Fig. 1(a) was broken accidentally after zone crystallization during handling. Due to the high thermal gradients and thus the high thermal stress, the recrystallized wafers were severely buckled and could be broken easily. As shown in Fig. 1, the GBs might not be parallel to the growth direction. In particular, for the cases at 2 mm/min as shown in Fig. 1(a), some GBs, mainly the twin boundaries, were tilted from the growth direction. The tilted GBs tended to reduce as the growth progressed. For the cases in Fig. 1(b) and (c), the GBs were also more or less parallel to the growth direction, except some tilted twin boundaries; however, some twin boundaries were generated during crystal growth. There were other tilted GBs near the edges, but they were due to the convex growth front.