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Crystallization kinetics in Si-1 at%Sn during rapid solidification in undercooled melt

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ABSTRACT

In order to elucidate the cause of the morphological transition of crystals growing in an undercooled melt of semiconducting materials, we carried out the containerless solidification of undoped Si and Si-1 at%Sn using a CO_2 laser-equipped electromagnetic levitator (EML). The crystallization of these materials was successfully achieved under controlled undercooling. The relation between the shape of growing crystals and the degree of undercooling in Si-1 at%Sn was similar to that in undoped Si; that is, plate-like needle crystals were observed at low undercooling, whereas at medium and high undercooling the shape of growing crystals changed to massive dendrites. The grain-size of as-solidified samples of Si-1 at%Sn was remarkably small compared with that of undoped Si. The surface morphologies of samples solidified by dropping the melt onto a chill plate of mirror-polished silicon consisted of typical twin-related $<110>$ dendrites. On the other hand, samples that were dropped from the undercooled state consisted of twin-free $<100>$ dendrites. The nucleation rate of two-dimensional nuclei calculated on the basis of two mechanisms, which are the twin-plane re-entrant edge mechanism and the twin-free mechanism, suggested that the morphological transition to twin-free $<100>$ dendrites from twin-related $<110>$ dendrites occurs when the degree of undercooling becomes larger than the critical value. These results indicate that the cause of the morphological transition of Si growing in the undercooled melt is not the roughening transition of the crystal–melt interface but the transition of the nucleation kinetics to the twin-free mechanism from the twin-related mechanism.

1. Introduction

For resource-poor Japan, the use of natural energy is a major political, economic and scientific issue. In particular, there is a pressing requirement for establishing solar power generation technology to achieve high efficiency and low cost by using natural energy. To meet both requirements, attempts to manufacture spherical Si crystals for use in solar cells have been developed over several decades by applying the levitation techniques [1,2]. Furthermore, spherical Si are attracting attention not only as an alternative technology for solar energy utilization, but also as a technology in non-energy fields, such as usage in small three-dimensional sensors [3]. In the mass production of spherical crystals, drop-tube processing is commonly employed. In this method, melt is ejected into a drop tube where the melt breaks up into droplets that solidify during free fall. The principle of the drop-tube processing is simple and straightforward. However, the disadvantage of this process is attributed to the fact that the nucleation and growth of crystals during free fall cannot be monitored. Therefore, various apparatuses were used to simulate the crystallization process of Si during free fall in a drop tube [4,5].

Aoyama et al. [6] used an electromagnetic levitation furnace equipped with a high-speed video-camera (HSV) to measure the mutual relationship between undercooling ΔT, growth velocity V, and the morphologies of growing crystals. As a result, they determined that the relation between ΔT and V can be classified into three regions: at Region I ($\Delta T < 100$ K), needle-like crystals appear; at Region II ($100\ \text{K} < \Delta T < 200\ \text{K}$), massive dendrites appear; and at Region III ($\Delta T > 200$ K), refined massive dendrites appear. In addition, they analyzed the relation between ΔT and V based on the dendrite growth model [7] that assumed interface attachment kinetics, and reported 0.4 m/K s as a kinetics coefficient μ. Their analysis was the first of this kind in the way of experimental data on the relationship between V and ΔT in Si. However, the application of the single model remains a problem, because interface morphology at low undercooling is significantly different from those at medium and high undercooling. In relation to this point, Nagashio et al. [8], observing the facet dendrite of the

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sample that solidified from undercooled state, revealed that twin-free < 100 > dendrites are formed at high undercooling, whereas only twin-related < 110 > dendrites are formed at low undercooling. Their result suggests that the needle-like crystal and the massive dendrite are twin-related < 110 > dendrites and twin-free < 110 > dendrites, respectively. In light of their result, Watanabe et al. [9] incorporated two types of rate-controlling process: two-dimensional (2D) nucleation at the re-entrant corner formed on the edge of a twin plane at low undercooling, and 2D nucleation on the twin-free facet plane at high undercooling. On the other hand, the pioneering work on Ge by Devaud and Turnbull [10] induced several related works [11–15]. In particular, Battersby et al. [16] reported that the melt which solidifies taking a form of lateral growth at low undercooling solidifies with a form of continuous growth, suggesting roughening transition at high undercooling. Furthermore, they reported that a small amount of impurities reduces the level of undercooling required for interfacial roughening and therefore enhances growth velocities. If their result may be applied to Si, adding impurities to Si is expected to decrease the level of undercooling which is required for Region II. As a result, growth velocities will be expected to increase.

In the present investigation, in order to confirm whether this expectation is valid, we carried out an experiment using Si-1 at%Sn as a testing material.

2. Experimental procedure

Samples of Si-1 at%Sn were prepared by three steps with a non-consumable arc-melting furnace. First, master alloys, the chemical composition of which is Si-20 at%Sn, were pelletized by melting both semiconductor-grade undoped Si and high purity (6N) Sn. Next, this master alloy was diluted to the chemical composition of Si-5 at%Sn and then re-diluted to make the final chemical composition Si-1 at%Sn. At each step, pellets were turned over and re-melted several times to homogenize the chemical composition.

Containerless crystallization experiments on Si and Si-1 at%Sn samples were carried out by using a CO_2 laser-equipped electromagnetic levitator (EML), shown schematically in Fig. 1. Blocks of Si and Si-1 at%Sn of approximately 2 g were melted by a CO_2 laser and levitated in 5N Ar gas atmosphere. The samples, after being heated to approximately 1800 K, were cooled to predetermined temperatures by blowing 5N He gas over them. Except for several samples that spontaneously nucleated, nucleation of crystals was forced by touching them with a molybdenum needle at the predetermined undercooling. The growth velocity was measured by using a colored high-speed video camera (HSV) with a maximum sampling rate of 640,000 frames/s. The temperature of the levitated samples was measured with a monochromatic pyrometer. Since the emissivity of the solid phase of Si greatly differs from that of the liquid phase, the emissivity was

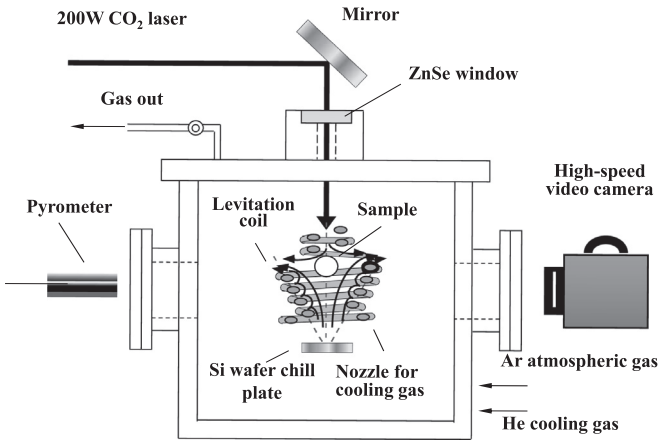

Fig. 1. Schematic illustration of the electromagnetic levitator used in the investigation.

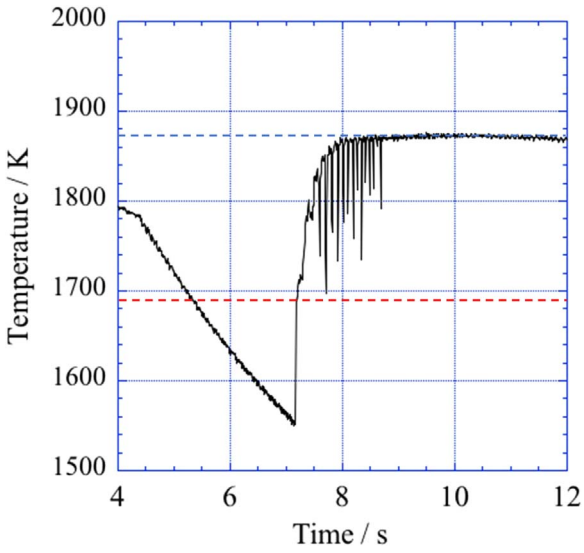

Fig. 2. Typical profile of temperature *vs.* time measured with a pyrometer. The temperature of a sample was determined by adjusting the emissivity so that the temperature of the liquid phase (red line) just after the recalescence was the equilibrium melting temperature of Si. The temperature at post-recalescence plateau stage (blue line) looks higher than the melting temperature because the emissivity of the solid phase of Si is approximately more than two times larger than that of the liquid phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

adjusted to make the temperature of the liquid phase after the recalescence indicate the equilibrium melting temperature (Fig. 2). To elucidate the relationship between the microstructure and the rate-controlling process, the melt was dropped onto an optically polished silicon plate and solidified under controlled temperature conditions. The surface morphologies of as-solidified samples were analyzed by a laser scanning microscope (LSM). The microstructural-crystallographic characterization of as-solidified samples was carried out using electron backscatter diffraction (SEM-EBSD) apparatus.

3. Experimental results

Fig. 3 shows typical HSV images taken successively during recales-

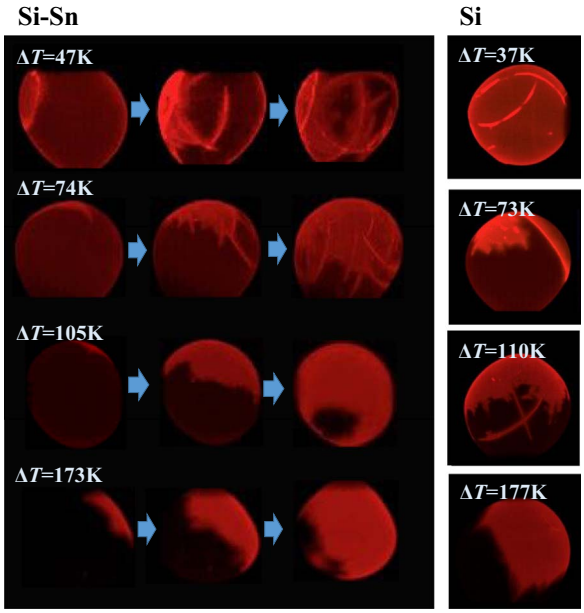

Fig. 3. HSV images of samples taken during recalescence. The dark and bright areas show the undercooled melt and the solidified region, respectively.