Analysis of grain growth behavior of multicrystalline Mg2Si

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15 mm is attractive as an environmentally friendly semiconductor. Mg2Si is an n-type compound semiconductor with high Clark numbers (Mg:8th, Si:2nd). In addition, Mg2Si is non-toxic and low-cost, and shows electrical conductivity and good thermoelectric properties in a temperature range of 300 °C to 600 °C.2–6

In recent years, export restrictions on rare elements by resource-rich countries and environmental regulations on materials have been tightened, and the development of devices using materials that take resource and environmental risks into consideration has become one of the most important issues. From this background, magnesium silicide (Mg2Si) is attracting attention as an environmentally friendly semiconductor. Mg2Si is an n-type compound semiconductor with anti-fluorite type structure2 and consists of elements with high Clark numbers (Mg:8th, Si:2nd). In addition, Mg2Si is non-toxic and low-cost, and shows electrical conductivity and good thermoelectric properties in a temperature range of 300 °C–600 °C.2–6

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1. Introduction

In recent years, export restrictions on rare elements by resource-rich countries and environmental regulations on materials have been tightened, and the development of devices using materials that take resource and environmental risks into consideration has become one of the most important issues. From this background, magnesium silicide (Mg2Si) is attracting attention as an environmentally friendly semiconductor. Mg2Si is an n-type compound semiconductor with anti-fluorite type structure2 and consists of elements with high Clark numbers (Mg:8th, Si:2nd). In addition, Mg2Si is non-toxic and low-cost, and shows electrical conductivity and good thermoelectric properties in a temperature range of 300 °C–600 °C.2–6

Moreover, Mg2Si’s indirect bandgap energy of 0.61 eV at room temperature corresponds to the cut-off wavelength of about 2 μm.3–11

From these properties, Mg2Si is suitable to mass consumption and expected to be an alternative material for infrared (IR) detectors and thermoelectric generators (TEG), which conventionally had to contain rare and toxic elements such as As, Bs, and Te to achieve high performance.5–18

IR detectors enable automatic nighttime monitoring and operation of vehicles. TEG can convert waste heat into electricity. Both are essential for the coming Internet of Things society where everything is connected to the internet, and machines automatically acquire data for analysis by artificial intelligence. Each device has a suitable structure, such as a single crystal for IR detectors and a multicrystal for TEG. Hence, for the improvement of device performance, improvement of crystal quality is essential. Although crystalline structures such as the distribution of grain sizes, crystal orientations, and grain boundary arrangement affect crystal quality significantly, it is difficult to control them. The challenge we face is to make it possible to control crystalline structures. For this purpose, we need to clarify the growth mechanism of the crystalline structure.

In this paper, we report on our attempt to clarify the growth mechanism of multicrystalline structure by three-dimensionally analyzing the growth behavior of the multicrystalline Mg2Si grown by the vertical Bridgman (VB) method. The growth behavior is discussed in terms of the measured crystal orientations and growth rate estimated by crystal growth simulation.

2. Experimental methods

Mg2Si crystal was grown by the VB method for IR detectors. Details of the crystal growth condition are found elsewhere.11,13,14

The source materials of Mg (4 N-grade purity) shots and Si grains (10 N-grade purity), the total weight of which was about 11 g, were used. The temperature gradient was applied from 1090 °C in the melting zone to 1000 °C in the lower part of the furnace. After melting the source materials for 2 h in the melting zone, the crystal was grown by pulling up the heater at 10 mm h−1. Figure 1(a) shows an image of a typical Mg2Si crystal grown by the VB method using the boron nitride (BN)-coated pBN crucible. The diameter and length of the crystal were 15 mm and about 27 mm, respectively. The grown crystal was sliced into 13 consecutive wafers of 15 mm × 1.0 mm at a pitch of 1.5 mm as shown in Fig. 1(b). Optical images of both sides of all the 13 wafers were taken with a house-made apparatus consisting of a camera, a rotating collimate light for illumination, and a stage.19 As the light rotates around the sample, optical images were taken within every 10 degrees of rotation. We integrate 36 images (which is a full rotation around the wafer) into a 36-dimensional intensity vector which we call the “intensity profile.” The intensity profile in each pixel depending on the position of the light source is regarded as a vector to reflect the crystal orientation to permit grain segmentation by mean shift clustering. Mean shift clustering is a method to find the maximum point of the probability density function when a point group xi is distributed in a d-dimensional space, and to divide the point

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Multicrystalline Mg2Si crystal with a diameter of 15 mm was grown via vertical Bridgman method. To clarify the growth mechanism of the multicrystalline structure, the grain growth behavior of the crystal was analyzed. This was carried out through segmenting grains by mean shift clustering using the light intensity profile obtained from multiple optical reflection images of the wafers and stacking the segmented images through the growth direction. Further crystal orientation measurement revealed that a grain with a higher surface energy competitively expanded to the lateral direction during crystal growth. We speculated that the growth behavior occurred because the supercooling was high enough to show difference in each grain’s growth rate. This idea was supported by crystal growth simulation to show a tendency for the crystallization rate to increase toward the latter half growth stage, which is consistent with the assumption for crystal growth with high supercooling.

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groups near the maximum point into clusters.\textsuperscript{20} It is noted that a three-dimensional multicrystalline structure is obtained by stacking consecutive segmented images in the ingot growth direction.\textsuperscript{21–24} For a part of the samples, we measured crystal orientations by the electron backscatter diffraction (EBSD). Moreover, crystal growth analysis software (STR CGSim) was used for thermo-fluid simulation.\textsuperscript{25}

3. Results and discussion

3.1. Results

Figure 2 shows a typical optical image of the wafer 1\textsubscript{bottom}. It is seen that the wafer contains four crystal grains. All the other wafers also contained four crystal grains, which confirms that the number of grains stayed the same through crystal growth. The color of each crystal grain is different because the different surface textures of each crystal grain affect reflectivity for visible light. The appearance of the surface textures originates from microscopic cleavage at the surface during polishing, depending on the crystal orientation. Figure 3 shows the result of grain segmentation by mean shift clustering for every wafer side. We successfully divided all the wafers into four grains using the intensity profile obtained by the home-made apparatus. Figure 4(a) shows the reconstructed multicrystalline structure of the crystal. It is noted that reconstruction of the multicrystalline structure permits the observation of any virtual cross-section of the crystal. Figure 4(b) shows an example of the vertical cross-section. It appears that grain\textsubscript{3} consistently extended in the direction of grain\textsubscript{2}, and this trend seemed to become stronger toward the latter half of crystal growth. Figure 5 shows the proportion of the area of crystal grain\textsubscript{3} in the cross-section of Fig. 4(b) plotted against the ingot height. We can see that the degree of the increase in area proportion of grain\textsubscript{3} increases in latter half of crystal growth. Figure 6 shows the relationship between grain area and crystal height. We can see that the proportions of the four-grain area changed through crystal growth. Grain\textsubscript{1} showed a tendency to grow slightly, but then shifted to a sharp tendency to get smaller in the latter growth stage. Grain\textsubscript{2} showed the tendency to get smaller and converged in the latter growth stage. Grain\textsubscript{3} showed a consistent trend to get larger through the crystal growth. Grain\textsubscript{4} was the only grain to show little change in grain area.

3.2. Discussion

We will discuss the growth behavior by focusing on Grain\textsubscript{2} and Grain\textsubscript{3} to show a drastic change in the grain area. It is reported that crystal orientation and the growth direction of the grain boundary are highly correlated.\textsuperscript{24,26–31} For example, in situ observation of Si melt growth revealed two types of grain growth behaviors during directional growth depending on the growth rate.\textsuperscript{26–29} Fujiwara et al. observed that when the crystal is grown at a high growth rate with large supercooling, Si\{100\} tends to extend to the lateral direction as shown in Fig. 7(a). On the other hand, when the crystal is grown at a low growth rate with small supercooling, Si\{111\} with low surface energy tends to extend to the lateral direction as shown in Fig. 7(b). Since Si has a diamond structure, a plane with a low atomic density such as Si\{100\} is referred to as a rough plane with high surface energy, and a plane with a high atomic density such as Si\{111\} is referred to as a smooth plane with low surface energy. These observations were explained in terms of the minimization of the total free energy. When the supercooling is high, the volume of the crystal controls the total free energy and the rough plane with a higher growth rate tends to extend. On the other hand, when the supercooling is low, the area of the melt/crystal interface controls the total free energy and the smooth plane with low surface energy tends to extend. Therefore, we can speculate that grain orientation is the key to explaining the growth behavior of multicrystalline Mg\textsubscript{2}Si. Figure 8 shows the crystal orientation in the growth direction of the sample 13\textsubscript{top} measured by EBSD. Since Mg\textsubscript{2}Si has an anti-fluorite structure, the \{111\} plane has the highest atomic density and \{001\} has the lower atomic density. Considering that the orientation of Grain\textsubscript{3} is closer to \{001\} than that of Grain\textsubscript{2}, Grain\textsubscript{3} has higher surface energy compared to Grain\textsubscript{2}.
Therefore, it can be defined that Grain2 to be a stable grain and Grain3 to be the rough grain which means that the rough grain extended toward the lateral direction as shown in Fig. 9.

This indicates that the crystal might have grown with high supercooling. To validate this discussion, we performed the crystal growth simulation, and the schematic of the simulation is as shown in Fig. 10. Figure 11 shows the crystallization rate obtained from the crystal growth simulation, which is calculated as.

\[ v = \frac{1}{S} \int_{S} u_{v} dS, \]  

where \( v \) is the averaged crystallization rate, \( u_{v} \) is the vertical component of the crystallization rate normal to the melt/crystal interface and \( S \) is the melt/crystal interface area. It can be said that the crystallization rate is high at the latter growth stage. This is due to the change in the temperature.
distribution inside the furnace as crystal growth proceeds, which is caused by the effect of moving the crucible position. As a consequence, the melting point position moves during the crystal growth, which leads to a change in the growth rate. In fact, the simulation results showed that the melting point position moved upward, leading to an increase in the growth rate, especially in the latter growth stage. This result matches with the result that the growth rate of crystal Grain3 increased toward the latter growth stage as shown in Fig. 5. In other words, we can imply that the rise of the degree of supercooling at the latter growth stage, resulted in the increase of the growth rate of crystal Grain3. Based on these results, we will discuss the behavior of Grain1 and Grain4. As shown in Figs. 4(b) and 6 Grain1 exhibits a shift from an increasing to a decreasing trend at the latter growth stage. It can be expected that three factors affected the behavior of Grain1: the limited area of horizontal cross-section, the increase in the growth rate of Grain3 at the latter stage, and the convergence of the Grain2. Due to these factors, Grain3 which has a very large growth rate at the latter growth stage pushed Grain1 strongly with the momentum of pushing Grain2. Grain4 has little change in area, but as can be seen by comparing 1_bottom and 13_top in Fig. 3, it is observed...
that its movement position changes as it is pushed by Grain3. Hence, the growth behavior of Grain1 and 4 against Grain3 also suggests that Grain3 was dominant in the growth competition.

4. Conclusions

We investigated the grain growth behaviors of bulk multicrystalline Mg2Si by reconstructing its structure. The grain growth behavior showed that Grain3 with a rough plane was dominant in the grain growth competition, which suggests that the crystal grew with large supercooling. This assumption was consistent with the result of the crystal growth simulation that the crystallization rate was high at the latter growth stage. These results show that we can control the dominant crystal grain by controlling the magnitude of supercooling, leading to the control in crystalline structures.

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