Liquinert quartz crucible for the growth of multicrystalline Si ingots

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Abstract
The growth of a multicrystalline silicon (mc-Si) ingot for solar cell applications was attempted using a Liquinert quartz crucible. A mc-Si ingot was also grown in a quartz crucible coated with Si₃N₄ powder for comparison with that from the Liquinert quartz crucible. The mc-Si ingot grown in the Liquinert quartz crucible had a shinier surface which has few impurity particles and higher minority carrier lifetime than the mc-Si ingot grown in a quartz crucible coated with Si₃N₄ powder. These results indicate that contamination with impurities was reduced with the Liquinert quartz crucible; therefore, this crucible has the potential to be a powerful tool for the production of high-quality mc-Si ingots for solar cell applications.

Introduction
Multicrystalline Si (mc-Si) ingots for solar cell applications are produced by casting based on unidirectional solidification. It has been demanded to reduce the defects, such as impurities, dislocations, sub-grain boundaries, and grain boundaries, to improve the efficiency of mc-Si solar cells. Quartz crucibles are typically used in the casting process and are coated with silicon nitride (Si₃N₄) powder, which serves as a mold release agent to inhibit adherence of the mc-Si ingot to the crucible. However, it is difficult to avoid contamination of the mc-Si ingot with impurities during the melting/solidification process, where impurities included in the Si₃N₄ powder are dissolved into the Si melt or where Si₃N₄ powder is detached from the crucible and dissolved into the Si melt. Such impurities act as lifetime killer and can be the origin of dislocations, which degrades the quality of mc-Si ingots. Therefore, other materials have been considered as substitutes for the Si₃N₄ powder coating layer or for the crucible itself [1–8].

In this study, the use of a Liquinert quartz crucible was attempted for the growth of a mc-Si ingot. The concept of Liquinert, the name of which comes from “liquid is in an inert state,” was proposed by Sakuragi [9, 10], whereby a liquid is in a state that is non-wetting and non-reactive with a crucible at high temperature. There are three requirements so as to realize the liquinert state; (1) high-purity raw material, (2) high-purity atmosphere, and (3) less-reactive crucible. When all of them are satisfied, mol-
ten raw material becomes round shape without wetting with crucible wall. In this situation, we can take out a crystal from a crucible without sticking after crystal growth. For example, in the crystal growth of NaI(Tl) scintillation material which has strong hygroscopic nature, a tiny amount of residual water in raw materials or in atmosphere becomes the cause of wetting and sticking even after dehydration procedure by vacuum pumping at high temperature. Therefore, we had to remove residual water perfectly from raw materials/atmosphere to realize a liquinert state for producing a high quality crystal [10]. Union Materials Inc. (UM) have developed this technology and have produced a variety of shaped crystals, such as needle-shaped BiSbTe single crystals, sheet-shaped mc-Si, and window-shaped CaF₂ single crystals [9]. In a growth of a mc-Si ingot, the required essentials of above (1) and (2) are generally satisfied because we can use high-purity Si raw materials (the purity is 11N) and a high-purity Argon gas (G1 grade, the purity is 99.9999%). Therefore, if we could use a suitable crucible and/or coating layer materials, it would be possible to realize the liquinert state even for silicon. If a mc-Si ingot could be grown in the liquinert condition, the problem of impurity contamination into the melt/crystal during the growth processes would be solved. Recently, according to this concept, FTB Research Institute, Co., Ltd., and Sakuragi have developed a Liquinert quartz crucible for the growth of single crystal Si by the Czochralski method [11]. If this crucible is available for the growth of a mc-Si ingot by casting, then the quality of a mc-Si ingot could be significantly improved, which would lead to an improvement in the energy conversion efficiency of solar cells.

In this study, we report on the growth of a mc-Si ingot by casting with a Liquinert quartz crucible to determine whether this crucible has the potentiality for the production of high-quality mc-Si ingot or not.

**Si Crystal Grown Under Nonwetting and Nonreacting Conditions**

Before the development of the Liquinert quartz crucible for the growth of a mc-Si ingot, preliminary experiments were conducted using a small amount of Si raw materials. Si melt typically reacts with SiO₂, so that Si crystals adhere to a silica container. Sakuragi et al. showed that the chemical reaction between a Si melt and a crucible at a high temperature was triggered by a minute amount of residual water in the atmosphere [10]; therefore, the liquinert condition, which is in a nonwetting and nonreacting condition, would be obtained if a water-free atmosphere could be achieved.

Figure 1 shows tiny Si crystals grown in a small SiC crucible coated with Si₃N₄ powder under flowing high-purity Ar gas containing SiCl₄ as a liquinert condition. Spherical Si crystals were obtained without adherence of the Si to the above crucible. The surfaces of the crystals grown with the liquinert condition were shiny, as shown in Figure 1. To create a liquinert condition in a casting furnace, a quartz crucible must be coated with a material that is less reactive with the Si melt, because it is not practical to enclose SiCl₄ gas in a casting furnace, and a SiC crucible for much larger amount of Si raw materials is also not practical. Therefore, FTB Research Institute, Co., Ltd., and UM have been developing the Liquinert quartz crucible for larger size of Si ingots.

**Growth of mc-Si Ingot in a Liquinert Quartz Crucible**

The Liquinert quartz crucible used in this study was produced by FTB Research Institute, Co., Ltd., and consists of a quartz crucible with the coating layer. We expected to form a barium oxide (BaO) as a coating layer because it is stable at high temperature (the melting temperature of BaO is 2013°C [12]). Furthermore, a quartz crucible coated by BaO is often used to reduce the pollution from the crucible wall for the growth of single crystal Si by the Czochralski method [13]. Therefore, in this study, barium hydroxide was spread all over the inner surface of a...
quartz crucible (GE214), and then it was heated to form a coating layer, as shown in Figure 2. The size of the crucible used in this study was $186 \times 186 \times 250 \text{ mm}^3$. For comparison, a similar quartz crucible (GE214) coated with Si$_3$N$_4$ powder (purity $>98\%$) was also used. Many mc-Si ingots were grown in both crucibles under the same growth conditions to evaluate the effectiveness of the Liquinert quartz crucible for improvement in the quality of mc-Si.

For the growth experiments, 3.8 kg of high-purity raw Si materials (11N) and 5.25 g of B-doped Si wafer ($0.016 \Omega \text{ cm}$) were mixed in a crucible, and the crucible was set in a furnace. The temperature of the furnace was elevated to $1430^\circ\text{C}$ to melt the materials in the crucible. When the materials were completely melted, the unidirectional growth process was started to grow a mc-Si ingot. The mc-Si ingot was grown by the dendritic casting method, in which dendrite growth is promoted along the bottom wall of the crucible during the earlier stage of growth [14, 15]. In this method, the bottom of the crucible was quickly cooled at the earlier stage of growth to promote dendrite growth. Then, the mc-Si ingot was grown at a constant rate of 0.4 mm/sec until the melt was completely solidified. All mc-Si ingots were grown under similar conditions with the same procedure. During the heating and the crystal growth processes, a high-purity Ar gas (6N) was flowing inside of the furnace.

Figure 3 shows the top surfaces of as-grown mc-Si ingots grown in Liquinert and Si$_3$N$_4$-coated quartz crucibles. The difference in the shininess of both ingot surfaces was evident. The surface of the ingot grown in the Liquinert quartz crucible was much shinier owing to the disuse of Si$_3$N$_4$ powder for the coating. According to this result, it is expected that contamination with impurities is restrained with the Liquinert quartz crucible. Figure 4 shows the side and bottom surfaces of both as-grown mc-Si ingots. The surfaces of the ingot grown in the Liquinert quartz crucible were very smooth and shiny, so that the grain structures were not visible (Fig. 4A), while the surfaces of the ingot grown in the Si$_3$N$_4$-coated quartz crucible were rough and the grain structures were visible (Fig. 4B). From those results, we can conclude that wetting and reaction between the Si melt and crucible were restrained in the Liquinert quartz crucible.

Wafers with a size of $125 \times 125 \times 0.2 \text{ mm}^3$ were cut from the middle part of both ingots, and the resistivity and minority carrier lifetime were measured. The average values of resistivity and minority carrier lifetime for each wafer are presented in Table 1. The resistivity of the wafer taken from the ingot grown in the Si$_3$N$_4$-coated quartz crucible was lower than that of the wafer taken from the ingot grown in the Liquinert quartz crucible, although the growth conditions for both ingots and the portions of the ingot from which the wafers were cut were similar. This suggests that impurities were dissolved into the Si melt/ingot from Si$_3$N$_4$ powder. The higher resistivity and minority carrier lifetime shown for the wafer taken from the ingot grown in the Liquinert quartz crucible confirm that the impurity contamination was reduced by using the Liquinert quartz crucible.

This was the first step to develop the Liquinert quartz crucible for the growth of mc-Si ingots, and we obtained positive results. Therefore, we will continue to develop...
this technology for the improvement of the quality of mc-Si ingots.

Summary

An attempt was made to use a Liquinert quartz crucible for the growth of mc-Si ingot for solar cell applications. It was shown that contamination with impurities from the crucible/coating layer was reduced with the Liquinert quartz crucible and a shiny ingot was successfully grown. The minority carrier lifetime was improved compared to that of a mc-Si ingot grown in a Si₃N₄-coated quartz crucible. These results indicate that the Liquinert quartz crucible has the potential to be a powerful tool in the near future for the production of high quality mc-Si ingots for solar cell applications.

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Conflict of Interest

None declared.

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