Interpretation of the Asymmetric Color and Shape of Brownish Ring in Quartz Crucible

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ABSTRACT

Brownish rings (BRs) with white interiors are formed during the manufacture of silicon ingots in quartz glass crucibles. These BRs inhibit the yield of silicon ingots. However, the composition and mechanism of the formation of these BRs remain unclear thus far. Therefore, in this study, we analyzed the color and shape of these BRs. Raman analysis revealed that the brown and white colors appear owing to oxygen deficiency rather than crystallization from excess oxygen supply as previously assumed. Moreover, the dark shade of the brown areas depends on the degree of oxygen deficiency and the asymmetrical width of the brown areas is attributed to the direction of the molten silicon flow, which is influenced by the rotation and heat of the ingot crucible.

Key Words : Quartz glass crucible, Brownish ring, Crystallization, Oxygen deficiency, Coloring of cristobalite, Czochralski

1. Introduction

Silicon ingots are typically manufactured at high temperatures (≥1400 °C), following which a brownish ring (BR) is observed on the surface of the quartz glass crucible [1-3]. We previously reported that this BR is an asymmetric brown ring with a white colored interior; it has a high density and the larger curved surfaces receive the greatest amount of heat. In terms of the microstructure, several pinholes were observed in the brown areas of these rings [1]. The peeling observed along the cracks on the circumference of these BRs intermingle with the molten silicon and reduce the yield of the silicon ingots [4,5].

Hiroshi et al. have previously reported that BR is a crystallization phenomenon owing to an excess supply of oxygen during single silicon crystal production and that the white part at the center of the BRs were a result of silicon monoxide dissolution [6]. However, this theory of the origin of BR is unconvincing because Hiroshi et al. did not consider the color and symmetry of the BRs [1] In this study, we investigated the Raman spectra of the brown and white areas of BRs and elucidated the mechanism of BR formation during the formation of silicon ingots.

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2. Experimental

For the sample, we selected fragments of a quartz glass crucible in which large numbers of BRs were formed after the generation of a single-crystal silicon ingot. The edge of BR was designated as the brown part and the interior as the white part. A stereomicroscope (SMZ18, Nikon, Japan) was used to examine the BRs, and Raman spectroscopy (Invia, Renishaw, Japan) in the range 100–1000 cm^{-1} was used to analyze the crystal structure of BR.

3. Results & Discussion

Fig. 1 shows the shape of BR within the crucible, as observed by the stereomicroscope. BR is composed of a brown ring with a white interior. In particular, the brown colored area is asymmetrical with varying width along the circumference of the ring; some surface peeling is also observed.

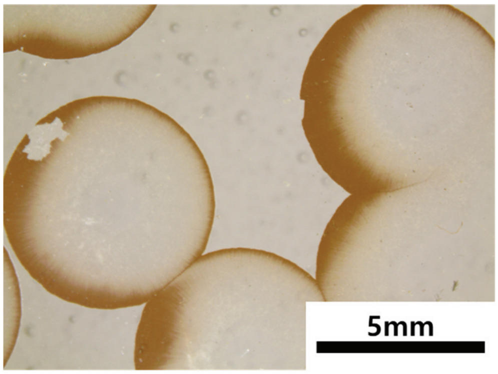

Fig. 1. Typical brownish rings with spalling observed via stereomicroscope.

Fig. 2 shows the Raman spectra of the brown and white areas of the BR and the glass crucible. The Raman spectrum of the brown part is consistent with that of silicon, whereas that of the white part is in good agreement with those of cristobalite and silicon.

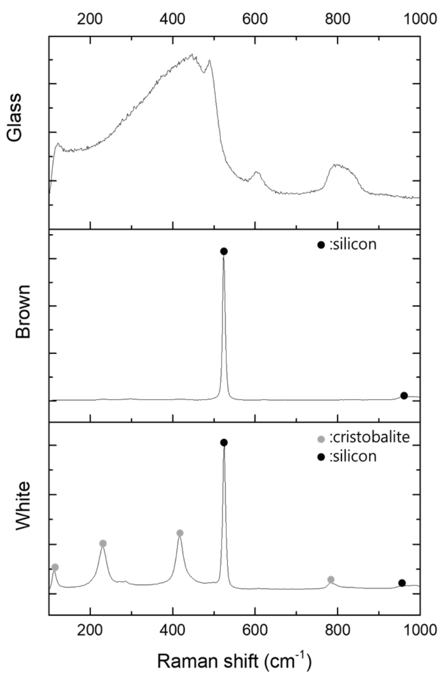

Fig. 2. Raman spectra of the brown and white areas of the brownish ring and the as-received quartz glass specimen that was not reacted with molten silicon [1].

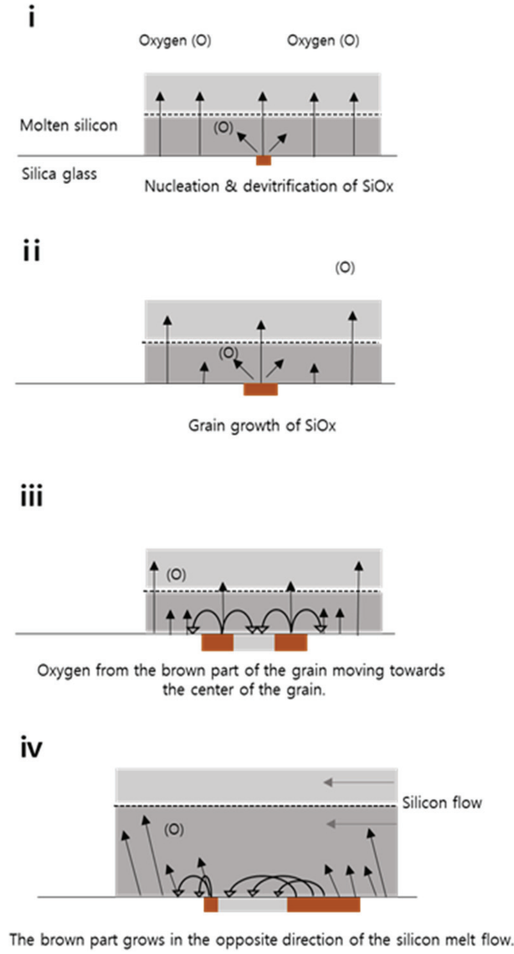

Fig. 3. Schematic of the formation of the brownish ring in molten silicon. (i) Nucleation and devitrification of SiOx clusters in molten silicon. (ii) Grain growth of SiOx. As the circumference of the brownish ring becomes oxygen deficient, i.e., where x of the SiOx decreases, the brownish grain develops. (iii) Oxygen from the brown part of the grain moving towards the center of the grain where the x of SiOx increases. The center of the grain, cristobalite, becomes white in color. (iv) Brown part grows in the opposite direction of the silicon melt flow.

Hiroshi et al. reported that BR originates from an excess oxygen supply during silicon ingot production and that the shape of the brown ring is produced owing to the dissolution of silicon monoxide in the crucible [6]. However, this explanation does not account for the Raman spectra, which indicate that the brown areas are oxygen deficient. Kim et al.

synthesized quartz powder under ambient conditions and observed that the quartz powder turned brown in a reducing atmosphere via X-ray photoelectron spectroscopy, which is consistent with the results of our study [7]. The asymmetric shape of the brown colored area in BR may be attributed to the flow of the silicon fluid controlled by the crucible rotation during the silicon ingot production process.

Fig. 3 shows the proposed mechanism for BR formation based on our microscopic and Raman spectral analyses. The diffusion of the oxygen towards the molten silicon occurs owing to the difference in the oxygen concentration at the interface between the crucible and the molten silicon. A crystalline nucleus of SiO_{2-X} forms on the crucible surface at areas with oxygen deficiency. The crystalline nucleus also becomes a diffusion pathway for oxygen and leads to the formation of an oxygen-rich layer at the interface with the crucible. These crystalline nuclei grow in the process of producing high-temperature ingots owing to this oxygen deficiency. The oxygen atoms that initially diffused into the oxygen-rich layer of silicon through the brown part then diffuse into the center of the oxygen-deficient crystal phase to form a cristobalite phase. Hence, the center of the crystal phase where oxygen atoms stabilize becomes white in color.

As shown in Fig. 3(iv), when the convection of the molten silicon occurs during the process of forging the silicon ingots, the oxygen diffusion is biased in one direction because the oxygen supply is biased to one side. The brown part caused by oxygen deficiency continues to grow without direction, whereas cristobalite, which is the white part, is formed where oxygen supply is the highest in the grain. Hence, the width of the brown portion of the BR is asymmetrical.

Therefore, the BRs are not formed owing to oxygen supply but because of oxygen deficiency and molten silicon flow.

4. Conclusion

In this study, we analyzed the brownish rings with a white interior that are formed during the production of silicon ingots. The Raman spectra of the brown and white parts are consistent with those of silicon and silicon-cristobalite, respectively. This indicates the presence of oxygen deficiency at the brown areas of the ring. In particular, the asymmetrical width of the brown areas is attributed to the convection of molten silicon influenced by the rotation and heat of the ingot crucible.

Therefore, asymmetric SiO_{2-X} crystallization (silicon-like & cristobalite) may have occurred in the quartz glass crucible in response to oxygen deficiency and molten silicon flow owing to the reduction reaction of SiO_2 the main component of the quartz crucible on the surface of the crucible.

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References

1. Y.S. Jung, J.H. Choi, K.W. Min, Y.M. Byun, W.B Im, S.-H. Noh, N.-H. Kang and H.-J. Kim, “A study on the brownish ring of quartz glass crucible for silicon single crystal ingot”, J. of The Korean Crystal Growth and Crystal Technology, Vol. 32, pp. 115-120, 2022.
2. K. Watanabe, K. Tanaka and M. Hasebe, “The ESR investigation of brownish ring at the surface of quartz crucible used for Cz-Si crystal growth”, Chemistry Letters, Vol. 25, pp. 627-628, 1996.
3. K. Yamahara, X. Huang, S. Sakai, A. Utsunomiya, Y. Tsurita and K. Hoshikawa. “Surface of silica glass reacting with silicon melt: effect of raw materials for silica crucibles”, Japanese J. of Applied Physics, Vol. 40, pp. 1178-1182, 2001.
4. S. Noh, N. Kang, H. Yun and H-J. Kim, “Status of quartz glass crucible”, Ceramist, Vol. 22, pp. 452-463, 2019.
5. S. M Schnurre and R Schmid-Fetzer, “Reactions at the liquid silicon/silica glass interface”, J. of Crystal Growth, Vol. 250, pp. 370-381, 2003.
6. H. Imai and H. Hirashima, “Evolution of cristobalite clusters on silica glass surfaces in molten silicon”, J. of The Electrochemistry Society, Vol. 147, pp. 1182-1185, 2000.
7. M.K. Kim, B.Y. Jang, J.S. Lee, J.S. Kim and S. Nahm, “Microstructures and electrochemical performances of nano-sized SiOx (1.18 ≤ x ≤ 1.83) as an anode material for a lithium (Li)-ion battery”, J. of Power Sources, Vol. 244, pp. 115-121, 2013.

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