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Density Measurement of Molten Silicon by a Pycnometric Method

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The density of molten silicon was measured using a newly developed pycnometer made of boron nitride. The present method has many advantages for measuring the density of molten silicon, which has a high temperature and can be easily oxidized. The pycnometer was precisely machined, and its volume at high temperatures was acculately determined. The procedure to overflow the excess melt was carried out in a closed apparatus under a helium atmosphere. A special procedure was introduced to avoid the error generated by the volume expansion of silicon when it solidified. The total uncertainty of the measurement was estimated to be within 0.5%. The measured density showed a linear relationship with respect to temperature and agreed well with literature values. The expansion coefficient of molten silicon was similar to those of typical molten metals in spite of the low expansion coefficient of solid silicon. This suggested that the structural change of molten silicon was similar to those of typical metals.

KEY WORDS: density; molten state; pycnometer; semiconductor; silicon.

1. INTRODUCTION

Although the semiconductor silicon is the most important material in the electronic industry and in information technology, measurements of the physicochemical properties of silicon in the molten state are relatively rare or inaccurate. The density and thermal expansion coefficient are the two most basic and important parameters not only in industrial processes but also for the determination of other physical properties such as viscosity, surface tension, etc. The densities of molten silicon reported in the literature [1–8] show a larger scatter compared with those of conventional

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molten metals, probably because handling molten silicon is difficult due to its high reactivity with the atmosphere and many refractory materials. In this work, precise measurement of molten silicon was attempted to obtain a reliable density. In this experiment, a new pycnometric method was developed, taking reduced reactivity and increased reliability into consideration.

2. EXPERIMENTAL

Molten silicon has properties similar to those of molten metals. However, it has a high melting temperature and is easily oxidized. Furthermore, the oxide film is very tough and is troublesome for measurement. The pycnometric method has many advantages for high-temperature melts, although it is a classical method and is popular near room temperature. It is relatively simple and has fewer sources of systematic errors such as the effect of the gas flow rising around the suspension wire up to the weighing balance in the case of the Archimedean method. Strict control of the atmosphere to prevent the oxidation of the melts is easy because the pycnometer can be operated in a closed apparatus. On the other hand, in general, it is very difficult to make a dimensionally precise pycnometer with refractory materials and the measurement is relatively inefficient because one measurement gives, in general, only one density at a given temperature. However, the authors considered that the advantages outweighed the disadvantages in the case of high-temperature molten silicon.

The pycnometers previously reported were made of graphite for tin and lead [9], alumina for iron [10], tantalum for plutonium and rare earth metals [11, 12], etc. The materials were chosen on the basis of machinability and stability against the molten metals. However, molten silicon is very reactive with most materials due to its active property and considerably high temperature. Therefore, the authors chose boron nitride, which is inert to most molten metals including silicon at high temperatures. In addition, hot-pressed boron nitride is easily machinable. The basic design of the pycnometer was to determine the volume as accurately as possible by making the shape simpler. Figure 1 shows the typical pycnometer, which was used in this work, made of hot-pressed boron nitride of a high purity. The inner diameter of the lower part of the pycnometer is 12 mm, and the lower part has a screw under the bottom to connect with a support rod. The shape of the upper part is relatively complicated. A fine bore of 0.8 mm was drilled through the inverse funnel-type bottom to the sharpened top and had a brim 2 mm larger than the outer diameter. They were machined precisely so that the upper part can be inserted tightly into the lower part. The volume that can be produced by both parts was about 1.8 cm^3. The pycnometers were preheated to about 1880 K in helium prior

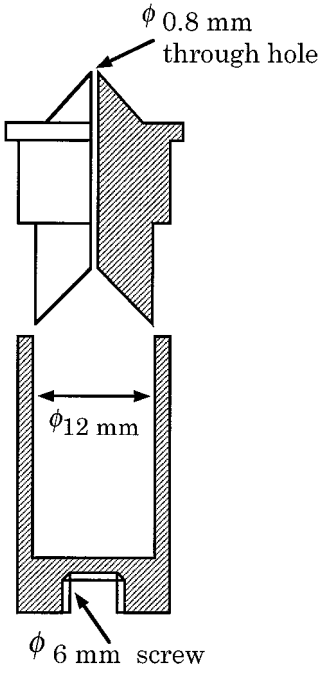

Fig. 1. Schematic diagram of the boron nitride pycnometer.

to calibration. The volume was calibrated using mercury at room temperature. The mercury temperature was controlled within 0.2 K, and the volume was calibrated with a precision of 3×10^{-4} cm^3.

The complete apparatus is shown in Fig. 2. The heating element of the furnace was a spiral $MoSi_2$, which was used to obtain good temperature uniformity at very high temperatures. Additionally, several molybdenum plates were located above and below the pycnometer to improve the temperature profile. The atmosphere inside the apparatus was dry helium, and a zirconium sponge located near the pycnometer was used to remove the oxygen. The pycnometer containing cylindrical solid silicon was supported by a graphite rod and was installed at the appropriate position in a 99.5% Al_2O_3 support tube. At this stage, the upper part had been partially inserted into the lower part. After the silicon melted, the apparatus was temporarily evacuated to remove the bubbles that might appear in the pycnometer. After the temperature became stable, the 99.5% Al_2O_3 push tube was lowered slowly to overflow the excess volume of molten silicon by pushing the upper part of the pycnometer. However, there is a danger of losing

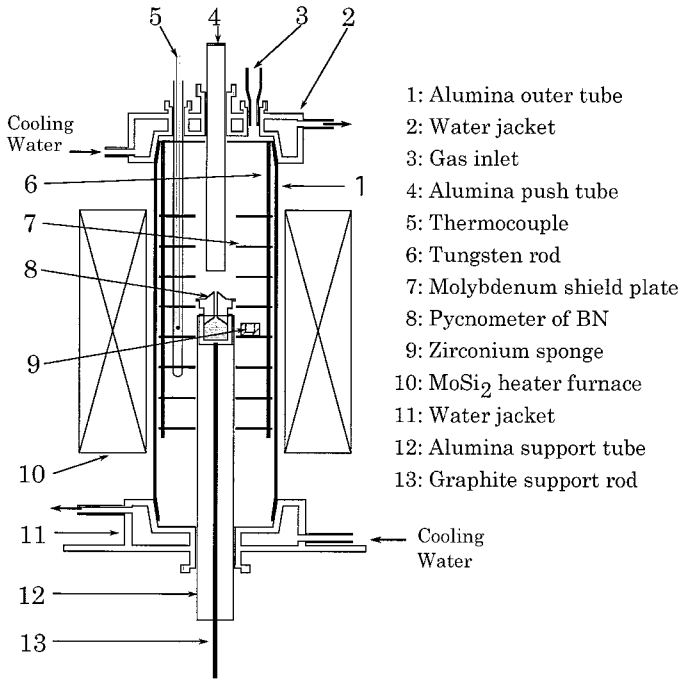

Fig. 2. Schematic diagram of the apparatus.

molten silicon if we let it solidify under this condition since the silicon volume expands as much as 10% as it solidifies. An unknown amount of molten silicon may be lost from the pycnometer during solidification, which would contribute to the measurement error. Therefore, an additional consideration was required to avoid the problem. Figure 3 shows the procedure. First, the upper part was inserted into the lower part to fix the volume of molten silicon. The next step was to pull the pycnometer down by pulling the support rod down. In this procedure, only the upper part is stopped at the end of the support Al_2O_3 tube by the brim of the upper part. Consequently, the volume in the pycnometer was enlarged to receive the expanded silicon as shown in Fig. 3. The pycnometer was cooled after operation, and the solidified silicon was weighed to calculate the density. In most cases, the pycnometer was used only once due to breakage during the silicon solidification.

Silicon samples used for measurement were quarried from an ingot of single-crystal semiconductor of 8N purity and were ground to a cylindrical shape with a diameter slightly less than the inner diameter of the pycnometer.

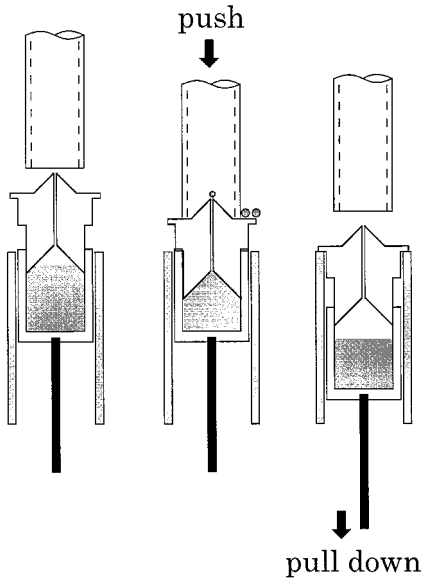

Fig. 3. Operation of the pycnometer.

3. RESULTS AND DISCUSSION

In the pycnometric method, the expansion coefficient of the pycnometer is very important since the measurement is carried out at high temperatures. Figure 4 shows the results of measurements of the change in length of the pieces of boron nitride, which were quarried out horizontally and vertically from the pycnometer used. The dilatometer used for the measurement was Model DL-9600 (Shinku-Riko Inc., Japan). Figure 4 shows that the expansion coefficient of hot-pressed boron nitride was very small, although anisotropic expansion was observed. As the measurement of expansion was limited to 1773 K, the volume at temperatures higher than 1773 K was corrected by assuming the same values as at 1773 K. The error caused by the expansion of the pycnometer was estimated to be less than 0.2%. Around the pycnometer, temperature uniformity of better than 0.3 K was achieved over 40 mm along the vertical direction, although the uncertainty of the absolute temperature was within 1 K. The uncertainty of fixing the volume by inserting the upper part was less than 0.3% at the calibration point. Therefore, the estimated uncertainty of the measurement is less than 0.5%.

Densities obtained in this work are shown in Table I and also in Fig. 5, along with several literature values. In previous reports, many methods

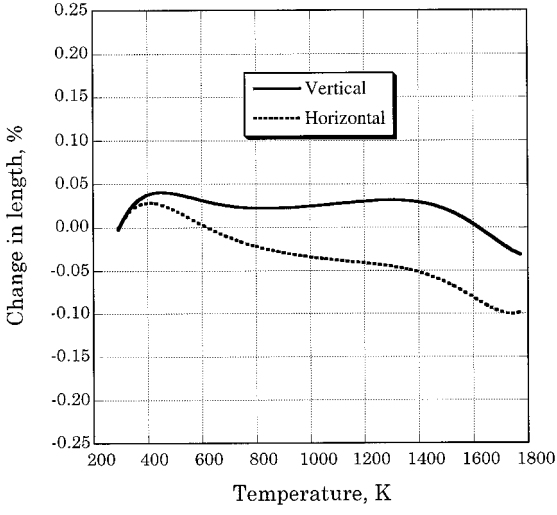

Fig. 4. Results for thermal expansion of boron nitride used for the pycnometer.

were used for measuring the density of molten silicon such as the Archimedean method by Glazov et al. [1] and Sasaki et al. [2, 3], the improved sessile drop method by Mukai et al. [4, 5], the levitation method by Rhim et al. [6], the maximum bubble-pressure method by Lucas [7] and the γ-ray transmission method by Taran-Zhovnir et al. [8]. From Rhim et al. [6] and Sasaki et al. [2, 3], only those data points between the melting temperature and 1823 K are shown in Fig. 5, although Rhim et al.'s measurement was carried out almost 300 K below the melting temperature. Sasaki et al. [3] reported less reliability of their data at temperatures higher than 1823 K. The variety of methods used probably indicates the difficulty of the measurement. The differences between the reported values are as large as 5%. The present results show intermediate values and agree well with Rhim et al.'s results [6], although the temperature dependence is somewhat different. Sasaki et al. [2, 3] reported an anomaly of the density near the melting temperature, and the results depended upon whether silicon carbide or quartz was used as the container material. It was very difficult to check the anomaly in this work because all of the density values were obtained in separate experiments. However, the anomaly is questionable because no other studies, including the present work, have observed similar behavior. Furthermore, the smooth density–temperature curve measured down to a temperature well into the supercooled region by Rhim et al. [6] did not support this anomalous result.

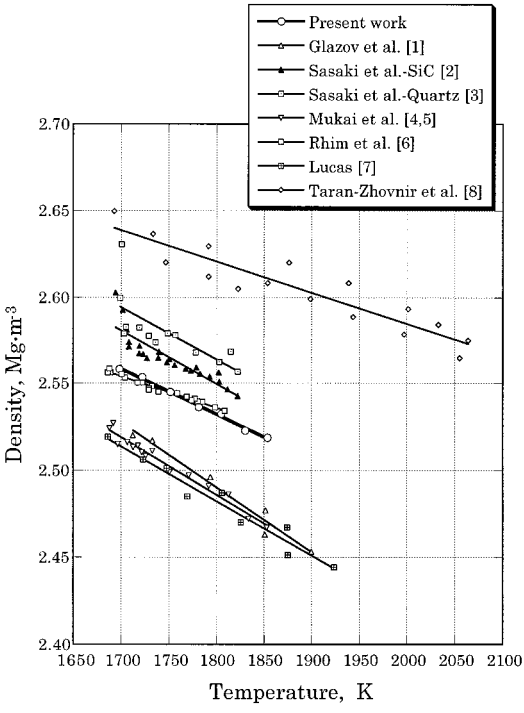

Fig. 5. Comparison of densities of molten silicon with literature values.

Table I. Density of Molten Silicon and an Equation for the Density as a Function of Temperature

Temp. (K)	Density ($mg \cdot m^{-3}$)
1698.6	2.558
1722.2	2.554
1751.8	2.545
1781.7	2.536
1805.1	2.532
1830.2	2.523
1853.7	2.519

$$\rho = 3.005 - 2.629 \times 10^{-4} T \ (T \text{ in K})$$

The thermal expansion coefficient near the melting temperature obtained in this work was $1.03 \times 10^{-4}\,K^{-1}$. The values from the literature in Fig. 5 range from 0.7 to $1.4 \times 10^{-4}\,K$ except for the anomalous behavior reported by Sasaki et al. [2, 3]. The range of scatter is relatively wide since the determination of the expansion coefficient is considerably more difficult than that of the absolute density. This also supports the difficulty of the measurement on molten silicon. The authors consider that the density in this work is reliable based on the consideration of errors in the present measurement and also based on the fact that both the absolute density and the expansion coefficient take intermediate values among the literature results. The calculated values based on the Lucas compilation [13] indicate that the expansion coefficients are about $1 \times 10^{-4}\,K^{-1}$ for most molten metals except for low-temperature alkali metals (greater than $2 \times 10^{-4}\,K^{-1}$ except for Li). In the solid state, silicon shows almost the smallest expansion coefficients among the pure metals and semimetals [14]. This reflects the differences in bonding between silicon and other metals, since solid silicon has a diamond-type structure as is well known and has a stronger covalent bond than the metallic bond. However, the expansion coefficient of molten silicon shows a value similar to that for conventional molten metals as shown above. This suggests that silicon in the molten state is a metallic liquid rather than a covalent-bond liquid as had been speculated.

4. CONCLUSION

The density of molten silicon was measured accurately using a newly developed pycnometer made of boron nitride. The error of the measurement was estimated to be within 0.5%. The density and the thermal expansion coefficient obtained were well within the range of previously reported values, and they might be considered to be the most reliable data since all sources of error involved in the measurement were taken into consideration. Silicon in its molten state was considered to be a metallic liquid based on its expansion coefficient.

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