MEASUREMENT OF HIGH TEMPERATURE HEAT CONTENT OF SILICON BY DROP CALORIMETRY

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Abstract

Heat content of silicon has been measured in a temperature range of 700–1820 K using a drop calorimeter. Boron nitride was used as a sample crucible. The enthalpy of fusion and the melting point of silicon determined from the heat content-temperature plots are 48.31 ± 0.18 kJ mol^{-1} and 1687 ± 5 K, respectively. The heat content and heat capacity equations were derived using the Shomate function for the solid region and the least square method for the liquid region, respectively, and compared with the literature values.

Keywords: drop calorimeter, enthalpy of fusion, heat capacity, heat content, high temperature, melting point, silicon

Introduction

Single crystals of silicon are important materials used in electronic device applications. The solid and liquid phases coexist at the quasi-equilibrium state in conventional processes to fabricate the single crystal of silicon. Therefore, knowledge of the thermochemical data such as heat capacity, melting point and enthalpy of fusion is important for the analysis of fabricating processes. Furthermore, production of a single crystal of silicon having the higher quality and a larger diameter is required for the Czochralski (Cz) technique of single crystal growth. In order to achieve this demand, mathematical simulations of the transport phenomena prevailing in the Cz single crystal growth have been carried out based on the thermochemical data. On the other hand, anomalous behavior for liquid silicon has been reported by viscosity [1, 2], density [3] and sound velocity [4] measurements. A careful investigation of thermochemical properties is thought to be of interest. Nevertheless, only few data are reported on the heat content measurements of silicon. By means of drop calorimetry, Magnus [5], Serebrennikov and Gel'd [6], Olette [7] and Kantor *et al.* [8] measured the heat content of silicon, that had 99.2, 99.3, 99.99 mass% purity prepared by

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the zone melting method and specific resistance of 100 Ω cm corresponded to 8–9 N, in the temperature ranges of 372–1175, 297–1556, 1467–1826 and 1698–1915 K, respectively. These data were determined using a SiO_2 sample crucible except for Magnus [5]. There is a remarkable disagreement between the previous reports on the heat capacity determined from the heat content data at high temperature above 900 K.

Hence, this work has been made aiming at obtaining accurate values of these thermochemical properties. Boron nitride (BN) was used as a sample crucible, and the heat content of silicon was determined in a temperature range 700 to 1820 K using a drop calorimeter. The heat content and heat capacity equations were derived using the Shomate function [9] for the solid region.

Experimental apparatus and procedures

A high temperature drop calorimeter, based on the experience with a related drop calorimeter used to determine the heat contents at temperature up to 1500 K [10], was developed and improved for the heat content measurements up to 1850 K with significant modifications to a heating furnace, a calorimeter and a sample assembly. The construction of the calorimeter designed in the present work is schematically shown in Fig. 1. It consists of a heating furnace, a device of dropping a sample and a calorimeter assembly. The improved furnace has a heating element made of molybdenum silicide ($MoSi_2$). A uniform temperature zone was a length of 25 mm within ±1 K in a temperature range of 700–1800 K. The calorimeter assembly was also improved for
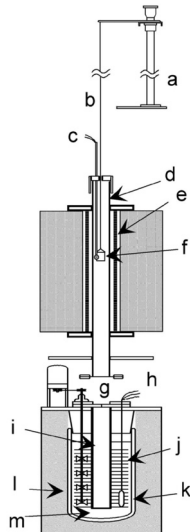

Fig. 1 Construction of the drop calorimeter; a – Dropping mechanism; b – Pt-Rh wire; c – Pt/Pt-Ph thermocouple; d – Alumina tube; e – Molybdenum silicide heater; f – Pt crucible; g – Shutter; h – Pt resistance thermometer; i – Copper tube; j – Copper fins; k – Dewar vessel; l – Insulating material; m – Distilled water

the measurements of high temperature heat content. The calorimeter, which consists of a Dewar vessel with an inner diameter of 150 mm and a depth of 330 mm and a copper tube with 27 copper fins, contains 3.4 kg distilled water. The temperature change of the calorimeter water is measured up to 0.001 K with a platinum resistance thermometer. The water equivalent of the calorimeter was 17.70 ± 0.22 J K^{-1} determined in the preliminary experiments using sapphire as a standard material and is about 1.6 times larger than that of the earlier design [10]; the quoted limit of error is the standard deviation from the calculated mean. A sample assembly used in this work is shown in Fig. 2. It consists of a boron nitride (BN) crucible with an inner diameter of 14 mm, a height of 15 mm and a mass of 1.10 g and a BN disk with a diameter of 14 mm, a thickness of 2 mm and a mass of 0.26 g, which was vacuum-sealed into a fused quartz cell with an outer diameter of 18 mm, a height of 20 mm, a thickness of 2 mm and a mass of 7.8 g to avoid oxidation of the sample. The cell is supported in a platinum sample holder with an outer diameter of 20 mm, a height of 22 mm and a mass of 11.1 g. The BN disk over the crucible in the cell, as shown in Fig. 2, was employed in order to prevent breakdown of the quartz cell due to the softening at high temperature, thus the sample assembly could be used up to 1850 K. The sample holder is suspended in the furnace by the dropping device through a Pt–10 mass% Rh alloy wire of a diameter of 2 mm. The thermocouple was calibrated against the melting points of pure zinc, gold and palladium. The sample assembly could be repeatedly used owing to the protection function of the dropping device. The temperature of the sample in the furnace was measured with a Pt/Pt–13% Rh thermocouple situated just beside the platinum holder.
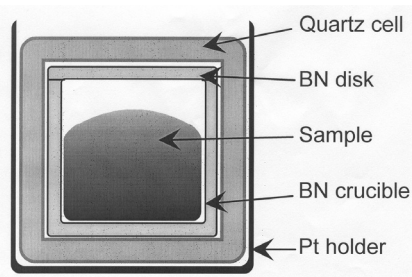

Fig. 2 Schematic diagram of sample assembly

A single crystal of silicon used in the present work has purity 11 N produced by the floating zone melting method (FZ). The sample of 1.9988 g was vacuum-sealed into the sample cell as shown in Fig. 2. The sample was set in a uniform temperature zone of the furnace. After thermal equilibrium was attained, the sample holder was dropped into the calorimeter. Contribution of the sample assembly to the heat effect was also determined in the preliminary experiments, and the heat content of the specimen was obtained by reducing these proportions from the total heat. The heat loss to the surrounding during dropping the specimen from the furnace to the calorimeter was compensated by conducting the experiments with the same sample holder and under the same dropping condition as in the preliminary experiments.
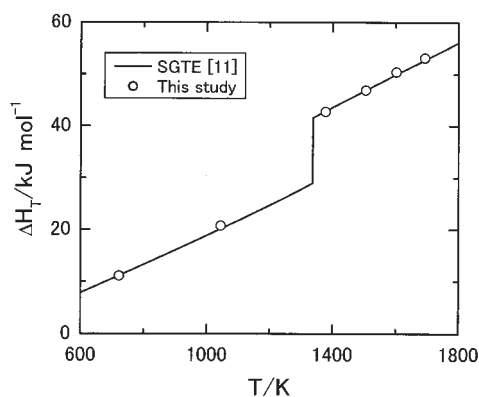
Fig. 3 Heat content of gold

As an example, the heat content measurements for gold of 13 g in a temperature range from 700 to 1700 K and compared with the literature values [11]. The results are shown in Fig. 3 and agree within ±2% with SGTE data [11].

Results and discussion

Heat content

The heat content, $\Delta H_T = H_T - H_{298.15}$, measured in a temperature range of 700–1820 K is plotted in Fig. 4. Table 1 shows the relations between the heat content and temperature which were determined using the Shomate function, as will be discussed later. Probable errors were calculated numerically from the experimental data around the heat content curve in Fig. 4. The final thermal equilibrium temperature of the sample in the calorimeter was in a temperature range of 295–300 K, and the heat content of the sample was compensated to the standard thermodynamic temperature of 298.15 K based on the specific heat capacity of solid silicon [11]. As shown in Fig. 4, the heat content of silicon increases with the increasing temperature in the solid region, and
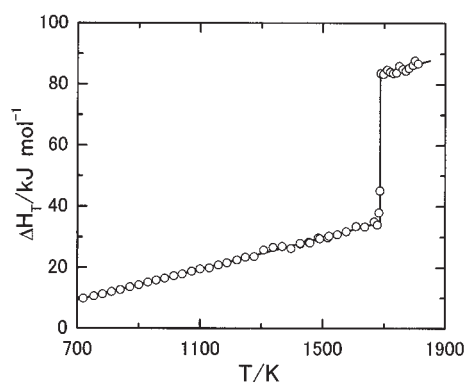

Fig. 4 Heat content of silicon

represents deflection point at a melting point temperature of 1687 K while the heat content in the liquid region again increases linearly within the limit of experimental accuracy. If the anomalous behavior attributed to the structure changes exists in the liquid, the measured heat content in the liquid region would be curve due to the change in the heat capacity. Therefore, the anomalies seem unlikely as far as the temperature dependence of the heat content is concerned. Sato *et al.* also reported no anomaly in the liquid silicon by a viscosity measurement in recent years [12].

Table 1 Heat content of silicon

	$\Delta H_T = AT + BT^2 + CT^{-1} + I$					
Substance	$\Delta H_T / \text{J mol}^{-1}$					Temp. range/K
	A	$B \cdot 10^3$	$C \cdot 10^{-5}$	$I \cdot 10^{-4}$	Probable error	
Si(s)	24.5	0.75	4.37	−0.89	±40	700–1687
Si(l)	28.7	–	–	3.47	±140	1687–1820

As listed in Table 2, the enthalpy of fusion and the melting point of silicon are 48.31 ± 0.18 kJ mol^{-1} and 1687 ± 5 K, respectively. Within the limit of experimental accuracy, the melting point of silicon agrees well with the literature values [7, 8, 11, 13–17]. The enthalpy of fusion determined in this study is about 2 kJ mol^{-1} lower than the data reported by Olette [7] and Kantor *et al.* [8]. The heat content of the solid silicon agrees with the previous data [5, 6] at low temperature, but diverges at higher temperature, being about 1 kJ mol^{-1} lower than the reported values. For the liquid region, the heat content in the present work is about 3 kJ mol^{-1} lower than the data of Olette [7] and Kantor *et al.* [8]. At high temperature, the result determined in the present work is lower than the previous data, which may be due to the difference in the purity of samples and the crucible materials.

Table 2 Melting point, enthalpy and entropy of fusion for silicon

Melting point/K	Enthalpy of fusion/kJ mol^{-1}	Entropy of fusion/ J mol^{-1} K^{-1}	References
1685±2	50.61±0.42	–	Olette [7]
1690±4	50.00±0.75	–	Kantor *et al.* [8]
1683±5	–	–	Hansen *et al.* [13]
1683±1	–	–	Lucas and Urbain [14]
1688±2	–	–	Gayler [15]
1683±2	–	–	Hoffmann and Schulze [16]
1687	–	–	Massalski *et al.* [17]
1687	50.2	29.8	SGTE [11]
1687±5	48.31±0.18	28.6±0.2	this study

Heat capacity

Based on the experimental result of heat content, the temperature dependence of heat capacity was determined using the Shomate function [9]. Shomate developed a useful thermodynamic function which permits fitting heat content data with algebraic equations, accurate smoothing of heat content data, correlation of low temperature heat capacity data with high temperature heat content data, accurate evaluation of heat transition at high temperature, and accurate calculation of heat capacities from heat content data. The method is briefly described as follows.

The temperature dependence of the high temperature heat contents can be expressed generally by Eq. (1), while Eq. (2) where $E=0$ in Eq. (1) or Eq. (3) where $C=0$ and $E=0$ in Eq. (1) is also used widely.

$$H_T - H_{298.15} = AT + BT^2 + CT^3 + DT^{-1} + ET^{1/2} + I \tag{1}$$

$$H_T - H_{298.15} = AT + BT^2 + CT^3 + DT^{-1} + I \tag{2}$$

$$H_T - H_{298.15} = AT + BT^2 + DT^{-1} + I \tag{3}$$

The heat capacity can be obtained by differentiating the heat content equation, and in its differentiated form, the following equation is obtained from Eq. (3).

$$C_p = A + 2BT - DT^{-2} = a + bT + dT^{-2} \tag{4}$$

The Shomate function is defined as:

$$\text{Shomate function} \equiv T[(H_T - H_{298.15}) - C_{p,298.15}(T - 298.15)]/(T - 298.15)^2 \tag{5}$$

Here, $C_{P,298.15}$ is heat capacity at 298.15 K. When the heat content is given by Eq. (3), the Shomate function can be expressed as:

$$\text{Shomate function} \equiv BT + D/(298.15)^2 \tag{6}$$

On the basis of Eq. (6), the coefficients B and C in Eq. (3) can be determined from the Shomate function–temperature plots, and A and I are evaluated from the boundary conditions of $H_T - H_{298.15} = 0$ at 298.15 K and $C_p = C_{p,298.15}$ at 298.15 K.
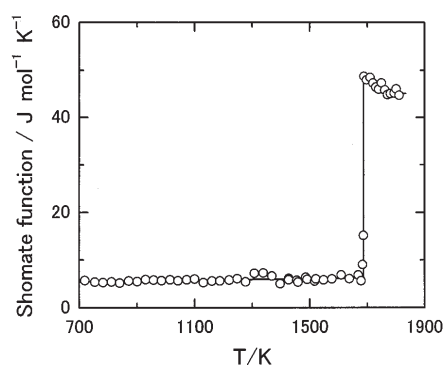

Fig. 5 Temperature dependence of Shomate function for silicon

The Shomate function of silicon calculated using the heat content value and the literature data of $C_{P,298.15}$=20.00 J mol^{-1} K^{-1} [11] is shown in Fig. 5. Above 700 K and below melting point, the Shomate function exhibits a linear equation against temperature as given below:

$$\text{Shomate function}=4.92+7.51\cdot10^{-4}T \tag{7}$$

Table 3 Heat capacity of silicon

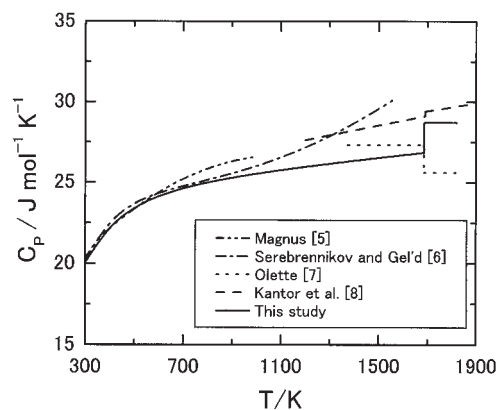|	$C_p=A+BT+CT^{-2}$			
Substance	C_p/J mol^{-1} K^{-1}			Temp. range/K
	A	$B\cdot10^3$	$C\cdot10^{-5}$	
Si(s)	24.5	1.5	–4.37	700–1687
Si(l)	28.7	–	–	1687–1820

Fig. 6 Heat capacity of silicon

Hence, the heat content and heat capacity of the solid in a high temperature region can be expressed by Eqs (3) and (4). The heat capacity in the solid determined by the Shomate function and that in the liquid calculated by the least square method are listed in Table 3, and the heat capacity is shown in Fig. 6 with the literature data. Above 1100 K and below the melting point, the heat capacity of solid silicon is about 1–2.5 J mol^{-1} K^{-1} lower than the previous data [5– 8]. The heat capacity for the liquid region is about 1 J mol^{-1} K^{-1} lower and 3 J mol^{-1} K^{-1} higher than the literature values of Olette [7] and Kantor *et al.* [8], respectively.

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