

Solubility of Carbon in Liquid Silicon Equilibrated with Silicon Carbide

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The solubility of carbon in liquid silicon equilibrated with silicon carbide was determined in the temperature range from 1723 to 1873 K. Silicon was melted in a silicon carbide crucible with an Ar-CO mixture gas flowing. Carbon in silicon was analyzed by the combustion-IR absorption method. The temperature dependence of the carbon solubility in liquid silicon can be represented by the following equation:

$$\log(C_c/\text{mass}\%) = 3.63 - 9660/T (\pm 0.02) \quad (T: 1723-1873 \text{ K})$$

The carbon solubility at the melting point of silicon was calculated to be 79 ppm (9.1×10^{18} atoms·cm⁻³). The level of oxygen impurities in the melt was much lower than that of liquid silicon equilibrated with solid silica. The standard Gibbs free energy change for carbon dissolution in liquid silicon can be represented as:

$$C(s) = \underline{C}(1 \text{ mass}\%, \text{ in liquid silicon})$$
$$\Delta G^\circ = 7.20 \times 10^4 - 11.4T \log T + 6.20T \quad (\text{J})$$

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I. Introduction

Silicon has been widely used for semiconductors and solar cell devices due to its excellent electronic properties. Because light elements in silicon such as hydrogen, carbon, nitrogen, or oxygen affect the performance of the devices⁽¹⁾, it is important to control the contents and distribution of the light elements in the silicon crystal.

Carbon impurities in the silicon crystal produced by the Czochralski (CZ) method are introduced by carbon heaters or holders during CZ crystal growth via the silicon melts. The carbon impurities in the silicon crystal affect both oxygen precipitation and oxygen donor formation⁽²⁾⁻⁽⁵⁾. The reduction of highly-pure silica by carbon has been noted for the production of solar-grade (SOG) silicon in recent years because the process is a low-cost method of mass production. Carbon, which affects the cell efficiency⁽⁶⁾, may be incorporated into silicon up to the solubility value during the reduction process. The carbon impurities in the SOG silicon must be less than 5 ppm. The decarburization from liquid silicon has been investigated with electron beam remelting⁽⁷⁾, filtration and oxidation⁽⁸⁾⁽⁹⁾, and argon blowing⁽¹⁰⁾. The thermodynamics of carbon in liquid silicon are significant for the

refining process of silicon.

The solubility of carbon in liquid silicon equilibrated with silicon carbide has been studied by several researchers⁽¹¹⁾⁻⁽¹⁶⁾. However, carbon analysis and the thermodynamics of carbon in liquid silicon have not yet been investigated thoroughly. The present authors have determined the oxygen and nitrogen solubilities for liquid silicon equilibrated with solid silica and silicon nitride, respectively⁽¹⁷⁾⁽¹⁸⁾. In the present work, we have determined the carbon solubility for liquid silicon equilibrated with silicon carbide in the temperature range between 1723 and 1873 K. We also will discuss in this paper the dissolution of carbon in liquid silicon in thermodynamic terms.

II. Experimental

A schematic diagram of the experimental assembly for the melting of silicon is shown in Fig. 1. The melt temperature was maintained within ± 1 K of the specified value with a PID controller in the temperature range between 1723 and 1873 K, monitored with a Pt/Pt13Rh thermocouple. Highly-pure polycrystalline silicon (Wacker-Chemitronic, 11N) was used as the starting material. The initial carbon and oxygen contents of the silicon were approximately 20 and 5 ppm, respectively. A silicon carbide crucible synthesized by pressureless sintering (CERASIC-B, Toshiba Ceramics Co., Ltd.) was employed for the melting of silicon after treatment in an HF-HNO₃-H₂O solution and drying. The surface of the silicon melt must be covered with a silicon carbide film to establish the Si/SiC equilibrium, and an ambient oxygen

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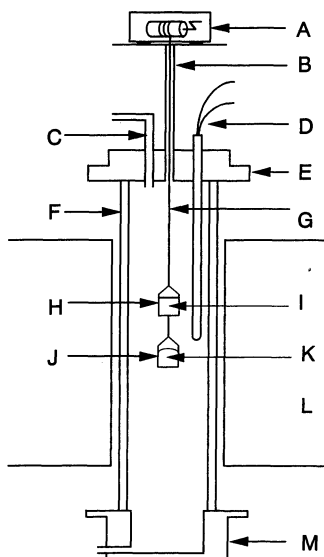


Fig. 1 Schematic diagram of the experimental assembly. A: Winch, B: Glass tube, C: Gas inlet glass tube, D: Thermocouple, E: Water cooled brass cap, F: Alumina reaction tube, G: Mo wire, H: Graphite crucible, I: Granular carbon, J: Silicon carbide crucible, K: Silicon Melts, L: Mo resistance furnace, M: Water cooled brass cap.

partial pressure below 10^{-13} Pa⁽¹⁹⁾ is required to prevent the melt surface from silica formation at 1873 K. Therefore, silicon was melted in an Ar-CO atmosphere (Ar:CO = 19:1, total pressure = 0.1 MPa). The mixture gas was introduced into the top of the alumina reaction tube after purification and was exhausted from the bottom. The total gas flow rate was maintained at 2.5×10^{-6} m³·s⁻¹ (STP). A carbon crucible filled with granular carbon was placed above the silicon melt in the reaction tube for removal of oxidant impurities in the mixture gas.

After the furnace temperature was held at the specified value, a silicon carbide crucible containing the polycrystalline silicon (10–15 g) was lowered to a hot zone (50 mm within ± 1 K) of the reaction tube. After the Si/SiC equilibrium was established, the silicon melt with the silicon carbide crucible was quenched by lowering it into a water-cooled brass cap.

The carbon content of silicon was analyzed by the combustion-IR absorption method (IR212, LECO) and by a combustion-coulometric titration (VK-1C, Kokusai Electric Co., Ltd.).

III. Results and Discussion

1. Analysis of carbon in silicon

The metal-bath method is useful for carbon analysis in silicon using the combustion method. In the present work, iron, copper, tin, and tungsten were considered as materials for the metal bath, and it was found that iron (502-231, LECO) and copper (Kojundo Chem. Lab. Co., Ltd., >99.8%) were suitable for use in the combustion method. Iron (2 g) and copper (1 g) were used for each carbon analysis (with approximately 0.2 g of quenched

silicon). Before the carbon analysis, the metal-bath materials and a crucible were heat-treated in air at 873 and 1273 K, respectively.

The calculated and analytical values for the carbon content in standard samples, as determined by the combustion-coulometric titration and combustion-IR absorption methods are shown in Figs. 2 and 3, respectively. Fe standard samples (Fe-std in the figures, JSS200-10, JSS201-11, JSS023-1, LECO501-102, LECO501-674 and LECO501-148) and Si-SiC mixtures (Si-SiC in the figures) were used as the standard samples. It was confirmed that the recovery of carbon was 100% in both of the analytical methods, and there was no significant

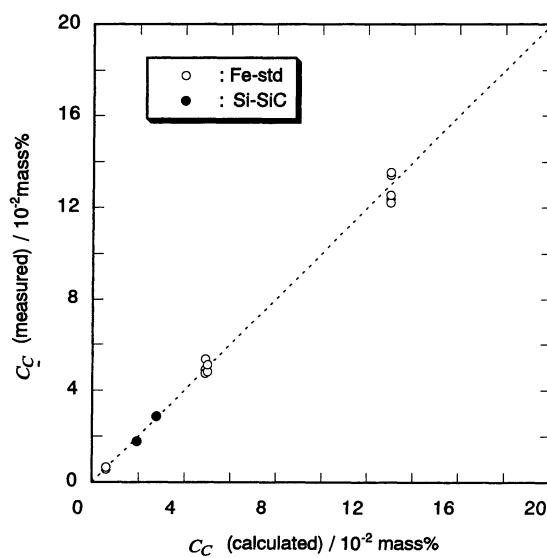


Fig. 2 Comparison of calculated and analytical values of the carbon content in Si-SiC mixtures and Fe standard samples by the combustion-coulometric titration.

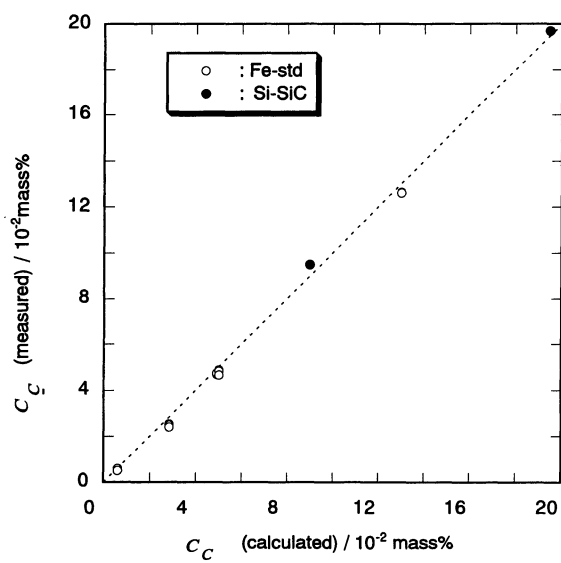


Fig. 3 Comparison of calculated and analytical values of the carbon content in Si-SiC mixtures and Fe standard samples by the combustion-IR absorption method.

difference between the extraction of carbon in Fe standard samples and Si-SiC mixtures. In the present work, the carbon in the quenched silicon was determined by the combustion-IR absorption method with Fe standard samples.

2. Holding time

The relationship between the holding time and the carbon content in liquid silicon at 1773 K is shown in Fig. 4. A constant carbon content was obtained and the surface of the melt was fully covered with a silicon carbide film after 10 ks. Therefore, it was suggested that a holding time of 15 ks was enough to establish the equilibrium between liquid silicon and silicon carbide.

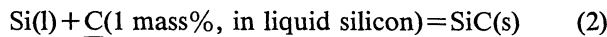
3. Solubility of carbon

The analytical values for the carbon content in liquid silicon equilibrated with silicon carbide are summarized in Table 1. The \bar{C}_{ave} value represents the mean value of several analyses for one experimental run. Figure 5 demonstrates the relationship between $\log(\bar{C}_C (= \bar{C}_{ave}) / \text{mass}\%)$ and $1/T$. The temperature dependence of the carbon solubility in liquid silicon equilibrated with silicon carbide can be represented by eq. (1).

$$\log(\bar{C}_C / \text{mass}\%) = 3.63 - 9660/T (\pm 0.02) \quad (1)$$

$(T: 1723\text{--}1873 \text{ K})$

The carbon solubility at the melting point of silicon (1685 K) was calculated to be 79 ppm ($9.1 \times 10^{18} \text{ atoms} \cdot \text{cm}^{-3}$). The equilibrium reaction between liquid silicon and silicon carbide can be expressed by eq. (2).



The equilibrium constant (K_2) for eq. (2) can be written by eq. (3).

$$K_2 = a_{\text{SiC}} / a_{\text{C}} \cdot a_{\text{Si}} \quad (3)$$

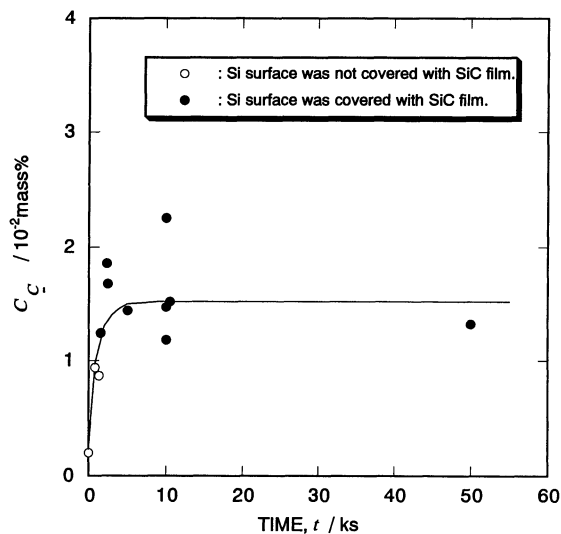


Fig. 4 Change in carbon content in liquid silicon over time at 1773 K.

Table 1 Analytical values for carbon and oxygen in liquid silicon equilibrated with silicon carbide.

Sample No.	Temperature, T/K	\bar{C}_{ave}/ppm	\bar{O}_{ave}/ppm
C-1	1723	114	
C-2	1723	102	
C-3	1723	113	
C-4	1723	109	
C-5	1723	112	23
C-6	1723	110	37
C-7	1773	148	7
C-8	1773	136	31
C-9	1773	140	21
C-10	1773	151	
C-11	1773	154	
C-12	1823	223	11
C-13	1823	219	
C-14	1823	198	
C-15	1823	205	26
C-16	1823	204	15
C-17	1873	315	
C-18	1873	322	6
C-19	1873	297	
C-20	1873	314	13
C-21	1873	303	15

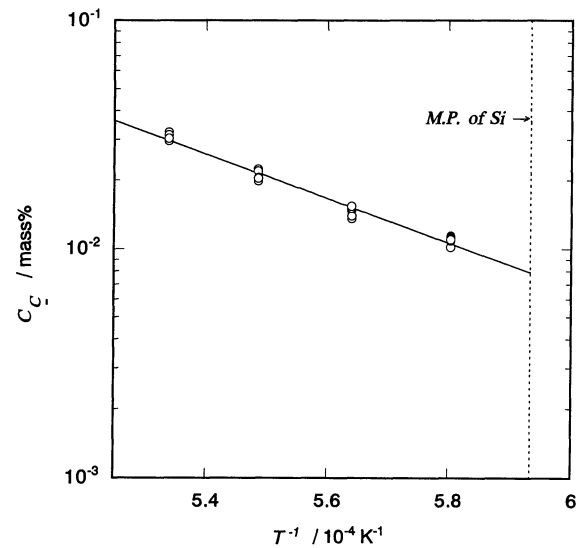


Fig. 5 Temperature dependence of carbon solubility in liquid silicon equilibrated with silicon carbide.

where a_{SiC} and a_{Si} are the activities of SiC and Si, respectively, and are equal to unity because the purity of the silicon carbide crucible is greater than 97 mass% and the carbon solubility in liquid silicon is lower than 400 ppm. a_{C} is the carbon activity in liquid silicon and its standard state is taken as 1 mass% in liquid silicon. Then, eq. (3) can be rewritten as eq. (4).

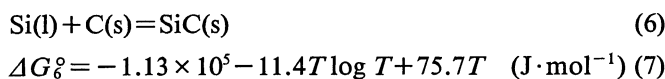
$$K_2 = 1/a_{\text{C}} = 1/(f_{\text{C}} \cdot [C_{\text{C}} / \text{mass}\%]) \quad (4)$$

where f_{C} is an activity coefficient of carbon in liquid silicon. It could be assumed that carbon in liquid silicon obeys Henry's law ($f_{\text{C}} = 1$) because the carbon content in

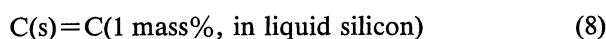
the present work was lower than 400 ppm. Therefore, the standard Gibbs free energy change of eq. (2), ΔG_2° , can be expressed by eq. (5) using eqs. (1) and (4).

$$\begin{aligned}\Delta G_2^\circ &= -RT \ln (K_2) \\ &= -1.85 \times 10^5 + 69.5T \quad (\text{J})\end{aligned}\quad (5)$$

where R is the gas constant. The standard Gibbs free energy of formation for silicon carbide (eq. (6)) can be expressed by eq. (7)⁽¹⁹⁾.



Using eqs. (2), (5), (6) and (7), the standard Gibbs free energy change of the carbon dissolution reaction (eq. (8)) can be given as eq. (9).



$$\Delta G_8^\circ = 7.20 \times 10^4 - 11.4T \log T + 6.20T \quad (\text{J}) \quad (9)$$

where the reference state was taken as an infinite dilute solution.

Previously reported values for carbon solubility in liquid silicon equilibrated with silicon carbide are summarized in Table 2 and compared with the present data in Fig. 6. Hall⁽¹⁴⁾, and Scace and Slack⁽¹⁵⁾ have determined carbon content by a gravimetric method. It has been assumed that no dissolved carbon precipitates as SiC during the cooling process⁽¹⁴⁾, or that all of the dissolved carbon precipitates⁽¹⁵⁾. Sahara *et al.*⁽¹¹⁾ and Ottem *et al.*⁽¹⁶⁾, who have determined carbon content by the combustion-

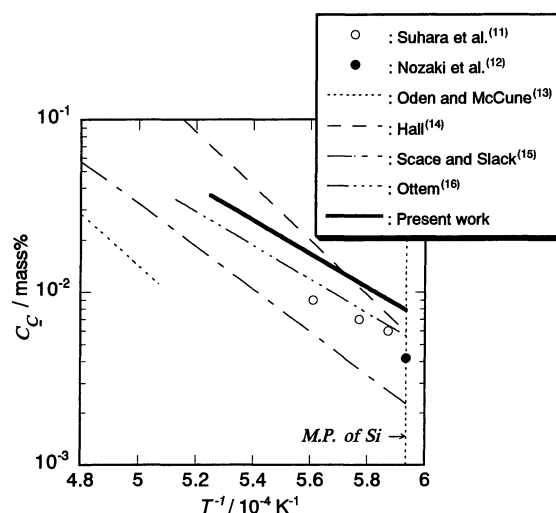


Fig. 6 Comparison of the reported and present carbon solubilities in liquid silicon equilibrated with silicon carbide.

IR absorption method have reported lower solubility values than those listed in the present work. Figure 7 shows the contents of oxygen impurities in liquid silicon which have been analyzed by the inert-gas-fusion IR absorption method. The oxygen content is much lower than the oxygen solubility in liquid silicon equilibrated with solid silica⁽¹⁷⁾, as shown by the straight line in Fig. 7. The carbon content in liquid silicon may be reduced by the reaction with dissolved oxygen, i.e., the formation of CO gas in the melts. The oxygen impurities in the melt may

Table 2 Experimental and calculated values of carbon solubility in liquid silicon equilibrated with silicon carbide.

Investigators (Ref. No.)	Silicon Melting	Carbon analysis	Temperature /K	Carbon solubility /mass ppm	Remarks
Suhara <i>et al.</i> (11)	Graphite crucible Ar gas flowing	Combustion-IR absorption	1708–1788	1703 K:60 1733 K:70 1783 K:90	
Nozaki <i>et al.</i> (12)	FZ with carbon pained on the surface	Charged particle activation analysis	1685	42	Calculated with carbon solubility in solid silicon and equilibrium distribution coefficient
Oden and McCune (13)	Graphite crucible Vacuum or Ar(135 kPa)	Combustion-IR absorption(?)	1973–2423	$4.217 \times 10^9 \exp(-34409/T)$	
Hall (14)	Silica crucible Ar gas flowing	Gravimetry	1793–1998	$1.307 \times 10^{11} \exp(-36258/T)$	
Scace and Slack (15)	Graphite or alumina crucible Ar(3.5 MPa)	Gravimetry	1833–2500	$4.756 \times 10^8 \exp(-28400/T)$	Assuming the dissolved carbon crystallizes as SiC upon cooling.
Ottem (16)	Graphite or silica crucible Ar gas flowing	Combustion-IR absorption	1720–1950	$3.359 \times 10^7 \exp(-22417/T)$	
Present work	Silicon carbide crucible Ar + CO(5%) gas flowing	Combustion-IR absorption Combustion- coulometric titration	1723–1873	$4.266 \times 10^7 \exp(-22240/T)$	

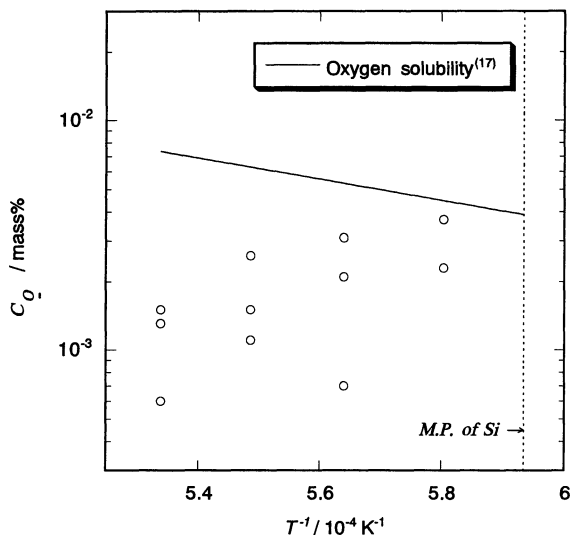


Fig. 7 Oxygen content in liquid silicon.

disturb the Si/SiC equilibrium due to the formation of SiO₂ at the Si/SiC interface. The previous investigations of carbon solubility have not examined the effect of the dissolved oxygen. In the present work, the dissolved oxygen content was suppressed to be at a much lower level than that allowed by the solubility values. Therefore, the effect of the dissolved oxygen on carbon solubility appears to be negligible.

IV. Conclusions

The solubility of carbon in liquid silicon equilibrated with silicon carbide was determined in the temperature range between 1723 and 1873 K. The temperature dependence of the carbon solubility was expressed as:

$$\log(C_C/\text{mass}\%) = 3.63 - 9660/T (\pm 0.02) \quad (T: 1723\text{--}1873 \text{ K})$$

Because the level of oxygen impurities in silicon was much lower than that allowed by the solubility values, the effect of oxygen impurities on carbon solubility appears to be negligibly small. The standard Gibbs free energy change for carbon dissolution in liquid silicon can be represented as:

$$C(s) = \underline{C}(1 \text{ mass}\%, \text{ in liquid silicon})$$

$$\Delta G^\circ = 7.20 \times 10^4 - 11.4T \log T + 6.20T \quad (\text{J})$$

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