

Effect of Alloying Elements on Carbon Solubility in Liquid Silicon Equilibrated with Silicon Carbide

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Carbon solubilities in liquid Si-X alloys (where X represents the alloying elements) that have been equilibrated with silicon carbide were determined in the temperature range between 1723 and 1873 K. The Si-X alloy was melted in a silicon carbide crucible under Ar-CO mixture gas flowing. After the equilibrium between the liquid silicon and silicon carbide was established, the carbon content and alloying element (X) content of the quenched sample were measured. The carbon solubility increased as B, Al, P and Ca contents increased in the liquid silicon, but decreased as Ti, V, Cr, Mn, Fe, Co, Ni and Cu contents increased. The effect of the alloying elements on the carbon solubility was discussed thermodynamically.

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I. Introduction

Carbon impurities in silicon affect the properties of silicon as a semiconductor⁽¹⁾⁻⁽⁴⁾ and in solar cell use⁽⁵⁾. Since the carbon impurities are introduced into a silicon single crystal or into solar-grade (SOG) silicon through a liquid silicon occurring either during crystal growth or refining, it is important to understand the behavior of carbon in a liquid silicon. Understanding the interaction between carbon and other impurities, such as P, B or Fe, in the liquid silicon is essential if improvements in the processes of silicon single crystal growth and SOG silicon production are to be achieved. To date, however, no analyses of the interaction between carbon and other elements in the liquid silicon have been undertaken.

The present authors have investigated the solubility of carbon in pure liquid silicon equilibrated with silicon carbide in the temperature range between 1723 and 1873 K⁽⁶⁾. In the present work, the solubilities of carbon in liquid Si-X alloys (where X represents the alloying elements) equilibrated with silicon carbide were determined, and the effect of X on carbon solubility was discussed thermodynamically.

II. Experimental

The Si-X alloy (X=B, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni and Cu) was melted in a silicon carbide crucible that had been synthesized by pressureless sintering (CER-ASIC-B, Toshiba Ceramics Co., Ltd.). The melting was performed with an Ar-CO mixture gas flowing in order

to produce a stable silicon carbide film on the liquid silicon and to establish equilibrium between the liquid silicon and silicon carbide. The details of the melting procedure have been reported elsewhere⁽⁶⁾. The melting experiment was done in the temperature range between 1723 and 1873 K in Si-Fe, Si-P and Si-B systems, and at 1823 K in the other systems. The vapor pressures of phosphorus and calcium are so high that Si-P and Si-Ca alloys were prepared before melting, then charged in a silicon carbide crucible with the desired amount of pure polycrystalline silicon (11 N, Wacker-Chemitronic) for melting. In other systems involving elements with relatively low vapor pressures, polycrystalline silicon with the pure element was charged in a silicon carbide crucible and melted. It was confirmed in an Si-P system that the content of an alloying element did not change during melting after the stable silicon carbide film was formed on the liquid silicon. After the equilibrium between the liquid silicon and silicon carbide was established, the liquid silicon with the silicon carbide crucible was quenched. More than 10 samples were obtained from each quenched silicon for chemical analysis. The carbon content and alloying element content in the sample were determined, respectively, by the combustion-IR absorption method (IR212, LECO) and ICP atomic emission spectroscopy (SPS1200A, Seiko Instruments Inc.).

III. Results and Discussion

1. Carbon solubility in liquid silicon alloys

The relationship between the analytical values of carbon and of the alloying elements in the Si-Fe, Si-P and Si-B systems are demonstrated in Figs. 1, 2 and 3, respectively. The analytical value (C_C or C_X) is defined as the mean values of carbon contents or alloying element con-

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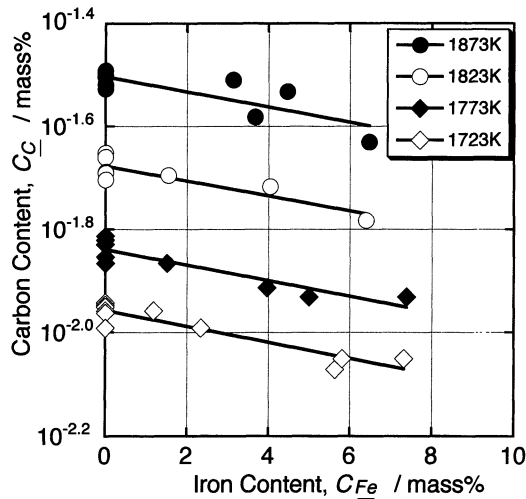


Fig. 1 Effect of iron content on carbon solubility.

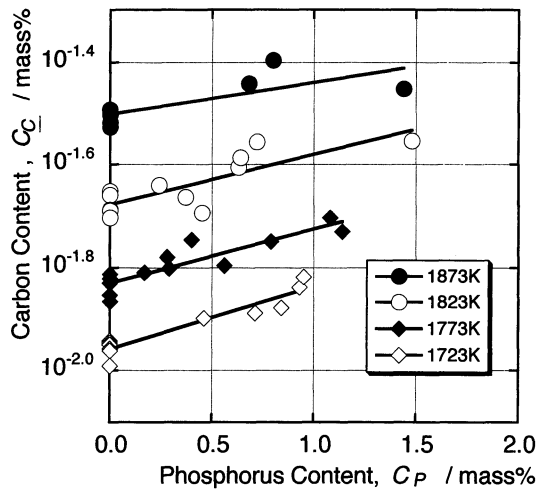


Fig. 2 Effect of phosphorus content on carbon solubility.

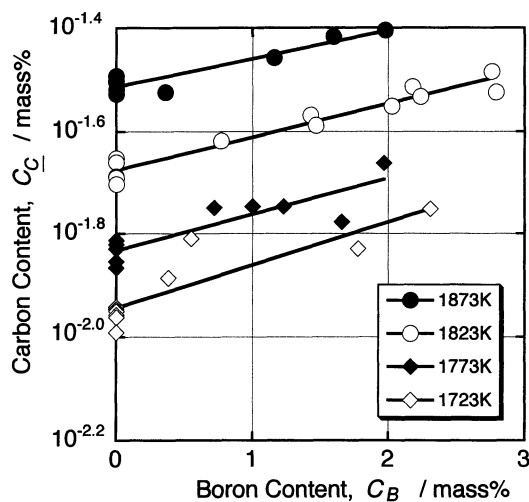


Fig. 3 Effect of boron content on carbon solubility.

tents found in several analyses of one experimental run. The points plotted at $C_X=0$ in these figures represent the previously reported experimental values for carbon con-

tents in pure liquid silicon⁽⁶⁾. Carbon contents in the liquid Si-X alloys decreased with increasing Fe content in the temperature range examined, but increased with increasing P or B content. Assuming a linear relationship between $\log(C_C/\text{mass}\%)$ and $C_X/\text{mass}\%$, eqs. (1)–(12) can be obtained using both the present and previous analytical values⁽⁶⁾.

Si-Fe system ($C_{Fe}/\text{mass}\%=0-8$)

$$1723 \text{ K: } \log(C_C/\text{mass}\%) = -1.96 - 0.0154[C_{Fe}/\text{mass}\%] \quad (1)$$

$$1773 \text{ K: } \log(C_C/\text{mass}\%) = -1.84 - 0.0151[C_{Fe}/\text{mass}\%] \quad (2)$$

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0146[C_{Fe}/\text{mass}\%] \quad (3)$$

$$1873 \text{ K: } \log(C_C/\text{mass}\%) = -1.50 - 0.0147[C_{Fe}/\text{mass}\%] \quad (4)$$

Si-P system ($C_P/\text{mass}\%=0-1.5$)

$$1723 \text{ K: } \log(C_C/\text{mass}\%) = -2.00 + 0.123[C_P/\text{mass}\%] \quad (5)$$

$$1773 \text{ K: } \log(C_C/\text{mass}\%) = -1.83 + 0.105[C_P/\text{mass}\%] \quad (6)$$

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 + 0.0976[C_P/\text{mass}\%] \quad (7)$$

$$1873 \text{ K: } \log(C_C/\text{mass}\%) = -1.50 + 0.0626[C_P/\text{mass}\%] \quad (8)$$

Si-B system ($C_B/\text{mass}\%=0-3$)

$$1723 \text{ K: } \log(C_C/\text{mass}\%) = -1.95 + 0.0836[C_B/\text{mass}\%] \quad (9)$$

$$1773 \text{ K: } \log(C_C/\text{mass}\%) = -1.83 + 0.0706[C_B/\text{mass}\%] \quad (10)$$

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 + 0.0648[C_B/\text{mass}\%] \quad (11)$$

$$1873 \text{ K: } \log(C_C/\text{mass}\%) = -1.51 + 0.0544[C_B/\text{mass}\%] \quad (12)$$

The carbon solubilities in other systems at 1823 K are expressed as follows:

Si-Al system ($C_{Al}/\text{mass}\%=0-5$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 + 0.0147[C_{Al}/\text{mass}\%] \quad (13)$$

Si-Ca system ($C_{Ca}/\text{mass}\%=0-6$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 + 0.0195[C_{Ca}/\text{mass}\%] \quad (14)$$

Si-Ti system ($C_{Ti}/\text{mass}\%=0-7$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0086[C_{Ti}/\text{mass}\%] \quad (15)$$

Si-V system ($C_V/\text{mass}\%=0-8$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0107[C_V/\text{mass}\%] \quad (16)$$

Si-Cr system ($C_{Cr}/\text{mass}\%=0-5$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0143[C_{Cr}/\text{mass}\%] \quad (17)$$

Si-Mn system ($C_{Mn}/\text{mass}\%=0-6$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0278[C_{Mn}/\text{mass}\%] \quad (18)$$

Si-Co system ($C_{Co}/\text{mass}\%=0-7$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0162[C_{Co}/\text{mass}\%] \quad (19)$$

Si-Ni system ($C_{Ni}/\text{mass}\%=0-7$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0223[C_{Ni}/\text{mass}\%] \quad (20)$$

Si-Cu system ($C_{Cu}/\text{mass}\%=0-7$)

$$1823 \text{ K: } \log(C_C/\text{mass}\%) = -1.68 - 0.0273[C_{Cu}/\text{mass}\%] \quad (21)$$

The relationship between $\log(C_C/\text{mass}\%)$ and $C_X/\text{mass}\%$ in all the systems at 1823 K is shown in Fig. 4. Oxygen impurities in the liquid silicon may have affected the carbon content levels due to the formation of CO gas in the liquid silicon or SiO₂ at the liquid silicon-silicon

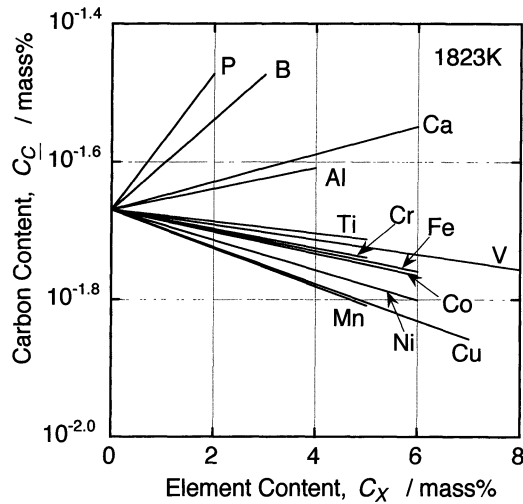


Fig. 4 Effect of alloying elements on carbon solubility.

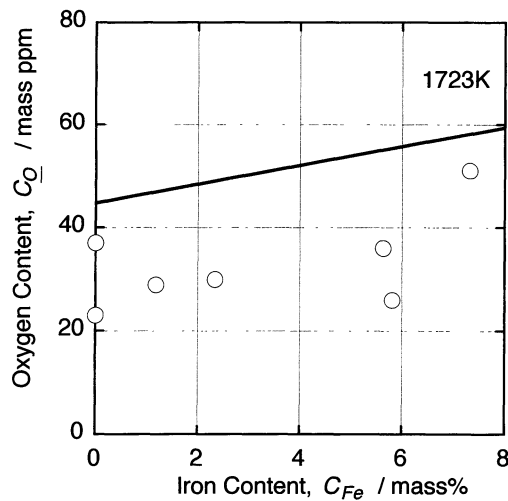
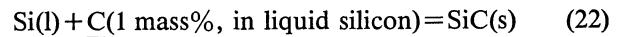


Fig. 5 Oxygen content in liquid Si-Fe.

carbide interface. **Figure 5** shows the level of oxygen impurities in a liquid Si-Fe alloy which has been analyzed by the inert-gas-fusion IR absorption method (TS-436E, LECO). The straight line in Fig. 5 shows oxygen solubility in the liquid Si-Fe alloy that has been estimated from the oxygen solubility in pure liquid silicon⁽⁷⁾ and the effect of iron on oxygen solubility in the liquid Si-Fe alloy⁽⁸⁾. In the present work, the levels of oxygen impurities were suppressed so as to be much lower than those allowed by the solubility values, and the effect of the oxygen impurities on carbon solubility appeared to be negligible as a result. Since the most of the sample was used for carbon determination, the reproducibility of oxygen determination was not high and was within ± 5 –10 ppm. It might be not serious for confirmation of the negligible effect of oxygen on carbon solubility.

2. Thermodynamics

The equilibrium reaction between liquid silicon and silicon carbide can be expressed by eq. (22):



The equilibrium constant (K_{22}) for eq. (22) can be written by eq. (23):

$$K_{22} = a_{\text{SiC}} / a_{\text{C}} \cdot a_{\text{Si}} \quad (23)$$

a_{SiC} and a_{Si} are the activities of SiC and Si referred to pure solid silicon carbide and pure liquid silicon, respectively. a_{C} is the carbon activity in liquid silicon and its standard state in liquid silicon is taken as 1 mass%. Since the maximum content of the alloying element in a liquid silicon is around 7 mol% (Si-B system), the activity of silicon can be assumed to be unity. Since carbides of alloying elements could not be detected in the surface film on the liquid silicon by X-ray diffraction, the activity of silicon carbide can be assumed to be unity. Then, eq. (23) can be rewritten as eq. (24):

$$\begin{aligned} K_{22} &= 1 / a_{\text{C}} \\ &= 1 / (f_{\text{C}} \cdot [C_{\text{C}} / \text{mass\%}]) \end{aligned} \quad (24)$$

where f_{C} is an activity coefficient of carbon in a liquid silicon. Equation (24) gives eq. (25):

$$\log K_{22} = -\log (f_{\text{C}}) - \log ([C_{\text{C}} / \text{mass\%}]) \quad (25)$$

The activity coefficient of carbon can be expressed as eq. (26) using interaction parameters, i.e., e_{C}^{C} and e_{C}^{X} .

$$\log (f_{\text{C}}) = e_{\text{C}}^{\text{C}} [C_{\text{C}} / \text{mass\%}] + e_{\text{C}}^{\text{X}} [C_{\text{X}} / \text{mass\%}] \quad (26)$$

Since, in the present work, the carbon contents in a liquid silicon were lower than 400 ppm, the term of $e_{\text{C}}^{\text{C}} [C_{\text{C}} / \text{mass\%}]$ in eq. (26) can be ignored. When eq. (26) is substituted in eq. (25), eq. (27) can be obtained:

$$\log ([C_{\text{C}} / \text{mass\%}]) = -\log (K_{22}) - e_{\text{C}}^{\text{X}} [C_{\text{X}} / \text{mass\%}] \quad (27)$$

It follows that the interaction parameters (e_{C}^{X}) can be calculated using eqs. (1)–(21) and eq. (27), and correspond to the slopes of lines in Figs. 1, 2, 3 and 4. **Figure 6** shows the relationship between the interaction parameters (e_{C}^{X}) and the reciprocal of temperature ($1/T$)^{(9)–(11)}. No clear temperature dependence of the interaction parameters (e_{C}^{X}) was detected in the Si-Fe system, and it can be con-

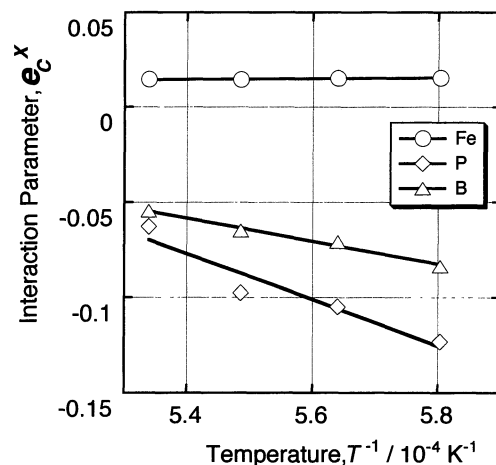


Fig. 6 Temperature dependence of the interaction parameters.

Table 1 Interaction parameters in Si-C-X system.

Element (X)	B	Al	P	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic number	5	13	15	20	22	23	24	25	26	27	28	29
Atomic weight	10.81	26.98	30.97	40.08	47.88	50.94	52.00	54.94	55.85	58.93	58.69	63.55
e_C^X	-0.065	-0.015	-0.098	-0.02	0.0086	0.011	0.014	0.028	0.015	0.016	0.022	0.027
ε_C^X	-5.8	-3.3	-24.9	-6.6	3.4	4.6	6.0	12.6	6.9	7.7	10.6	14.0

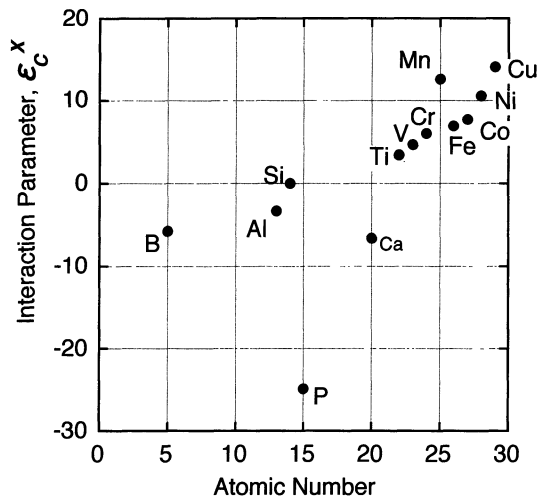


Fig. 7 Relationship between atomic number and the interaction parameters.

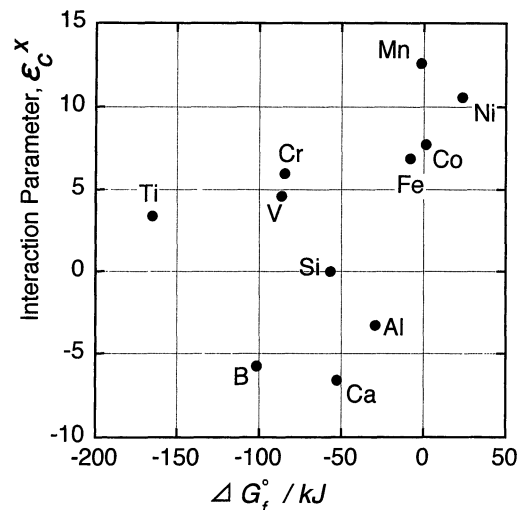


Fig. 8 Relationship between the standard free energy change of formation of metal carbide (per mol of carbon) at 1800 K and the interaction parameters.

cluded that $e_C^{\text{Fe}}=0.15$. Equations (28) and (29) can then be obtained, assuming a linear relationship between the interaction parameters and $1/T$ in the Si-P and Si-B systems, respectively.

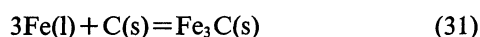
$$e_C^{\text{P}}=0.576-1.21 \times 10^3/T \quad (T: 1723 \sim 1873 \text{ K}) \quad (28)$$

$$e_C^{\text{B}}=0.267-6.02 \times 10^2/T \quad (T: 1723 \sim 1873 \text{ K}) \quad (29)$$

e_C^X and the interaction parameters (ε_C^X), which were calculated with eq. (30) at 1823 K, are summarized in Table 1.

$$\varepsilon_C^X=230(M_X/28.09)e_C^X+(28.09-M_X)/28.09 \quad (30)$$

where M_X is the atomic mass of X. Figure 7 shows the relationship between the atomic numbers of X and ε_C^X . For the most part, ε_C^X increased as the atomic number of the transition metal increased. The same tendency was found in an Fe-C-X system⁽¹²⁾⁽¹³⁾. A further study of other systems is necessary in order to clarify whether or not the interaction parameter in an Si-Mn or Si-P system is reasonable. Figure 8 demonstrates the correlation between ε_C^X and the standard free energy of the formation of a metal (X) carbide (ΔG_f^0 , per mol of carbon) at 1800 K⁽¹⁴⁾⁽¹⁵⁾, i.e., for Fe, the standard free energy change of eq. (31):



It was suggested that ε_C^X increased with increasing ΔG_f^0 in the Si-transition metal systems.

IV. Conclusions

Carbon solubilities in liquid Si-X (X=B, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni and Cu) alloys equilibrated with silicon carbide for the first time were determined in the temperature range between 1773 and 1873 K in the present work, yielding the following findings.

(1) At 1823 K the carbon solubility increased as B, Al, P and Ca contents increased in the liquid silicon, but decreased as Ti, V, Cr, Mn, Fe, Co, Ni and Cu contents increased.

(2) The temperature dependence of interaction parameters (e_C^X) in the Si-Fe, Si-P and Si-B systems was expressed as follows:

$$e_C^{\text{Fe}}=0.15 \quad (T: 1723 \sim 1873 \text{ K})$$

$$e_C^{\text{B}}=0.267-6.02 \times 10^2/T \quad (T: 1723 \sim 1873 \text{ K})$$

$$e_C^{\text{P}}=0.576-1.21 \times 10^3/T \quad (T: 1723 \sim 1873 \text{ K})$$

(3) The interaction parameters (ε_C^X) in Si-transition metal systems increased as both atomic number and the standard free energy of formation of X carbide (per mol of carbon) at 1800 K increased.

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