Time and Temperature Dependence of the Solubility of Carbon in Liquid Silicon Equilibrated with Silicon Carbide and Its Dependence on Boron Levels

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The solubility of carbon in liquid silicon equilibrated with silicon carbide has been studied in the temperature region 1414–1559°C. High purity silicon was melted in graphite crucibles under Ar atmosphere with various boron additions. The equilibrium was observed to be established within minutes, after which no evolution with time could be observed. The addition of boron to the system was found to increase the carbon solubility, and an equation was derived describing the solubility as a function of both temperature and boron content. The solubility of carbon in pure liquid silicon was determined to be 65 ppm mass at the melting point of silicon. Expressions for the dissolution energy of carbon and the B-C interaction coefficient were also derived. [doi:10.2320/matertrans.M2009034]

(Received February 3, 2009; Accepted February 23, 2009; Published April 8, 2009)

Keywords: silicon, carbon, boron, solubility, thermodynamics

1. Introduction

The casting of multi crystalline silicon ingots for solar applications typically take place in induction furnaces where both the susceptor and a large portion of the insulation are made from graphite. This rich environment enriches the silicon melt to such an extent that carbide particles and filaments are often observed throughout the finished ingot. The carbide particles can act as nucleation sites for dislocations, which are detrimental to solar cell operation. Also, the filaments—growing parallel to the direction of crystal growth—can penetrate the pn-junction of a finished cell and cause shunting.

In understanding and preventing the formation of silicon carbide particles and filaments, the solubility limit of carbon in liquid silicon is an important figure. It is also important to understand how carbon interacts with other impurities, and how this may affect the solubility. Boron is both a common dopant element and also one of the more difficult impurities to remove from silicon. The compensated material that have been introduced lately have even higher boron contents. Carbon-boron interactions will therefore virtually always be present in the solidification process of silicon ingots.

In the current work, a liquid silicon melt containing from 0–2 mass% boron has been equilibrated with silicon carbide, and samples have been extracted and analysed. The results have been discussed with respect to the time and temperature dependency of the carbon solubility, and the effect of boron additions.

2. Experimental Setup

In each experiment, approximately 75 g of high purity polycrystalline silicon feedstock with starting carbon content 9 ± 3 ppm was charged in a high density graphite (Tanso IG-610) crucible. The silicon was then melted in an argon atmosphere in a resistance heated tube furnace. In five experiments, 0.25–2.00 mass% crystalline boron powder of 99.9% purity, (Alfa Aesar, product number 44257) was added to the feedstock, while in four experiments there were no boron additions. For the experiments with boron additions, a holding period of four hours was included after the silicon was melted in order to facilitate boron dissolution.

Once the silicon had melted, it reacted with the graphite crucible and formed a layer of silicon carbide along the crucible-melt interface. An equilibrium was then established between carbon in the form of silicon carbide and carbon in solution:

\[
Si(l) + C(l) = SiC(s)
\] (1)

Carbon would continue to enter the melt until the liquid was saturated locally. The melt flow would then transport carbon away from the area near to the crucible wall, allowing more carbon to enter into solution. This process would continue until the carbon content of the melt was uniform and equal to the saturation limit.

The top flange of the furnace has three inlets, one of which was used for argon flow into the furnace. Of the remaining two inlets, one was used for an alumina sheath, inside which was nested a type S Pt-Pt10%Rh thermocouple measuring the melt temperature. Another thermocouple was placed near the hottest point on the heating spiral, and used to control the furnace temperature with a Eurotherm 903P temperature controller. All temperature measurements in this article refer to the melt temperature.

The final inlet was used for the sample taking and was fitted with a ball valve, a 115 mm long steel tube, and a sealing mechanism with two o-rings. The samples were extracted using \( \phi_{in} = 2 \, mm \times \phi_{ext} = 4 \, mm \) quartz tubes fitted with a syringe. In each sampling, ~0.5 mL (~1 g) melt was sucked into the tube, meaning that roughly 137 mm of the tube was filled with silicon. Since the distance between the ball valve and the bottom o-ring was 160 mm, this prevented damage to the o-ring seal, as the valve could be closed beneath the nozzle of the sampling tube with all the hot silicon inside the metal tube still below the o-ring.

As samples were extracted at different temperatures during one experimental run, the samples were always taken in order of increasing temperature. This was done to avoid carbon entering into solution at high temperature and then precipitating as SiC once the temperature decreased. Such SiC precipitates would give too high carbon levels during analysis.
The samples were etched in concentrated HF for a couple of days in order to completely get rid of the quartz tubes. The silicon was then rinsed in distilled water, and sent to analysis at Elkem Research where they were analysed for carbon using a Leco C200 combustion IR-spectrometer. It was confirmed through microprobe analysis that no SiC precipitated on the quartz tubes, and no carbon was lost during the etching process.

3. Results and Discussion

From four experimental runs with pure silicon, 39 samples were analysed, while from the five experiments with boron additions, 67 samples were analysed. The samples were analysed in one to four parallels, depending on the amount of sample available in each case.

The parallels were grouped according to boron level and the $3^\circ C$ temperature interval in which they were extracted. Any parallel that deviated from the mean of its temperature group by more than two standard deviations was deemed an outlier, and removed from the data set. All parallels removed from the data set in this way showed a positive deviation, indicating carbon contamination. Figure 1 shows all parallels for all experiments, including the excluded outliers.

3.1 Time dependency

For each sample, the settlement time for which the melt had been held at the sampling temperature was recorded so that any evolution of carbon solubility with time could be investigated. Samples were extracted with settlement times ranging from 3 to 158 minutes, and no dependence of the carbon levels on the settlement time could be detected. Thus it was concluded that equilibrium is established rapidly, within a couple of minutes at most. Hence no samples were left out of the discussion based on a too short settlement time.

3.2 Temperature dependency

The complete data set for the experiments with pure silicon were fitted to an Arrhenius expression using the method of least squares. The best fit gave, in mass%:

$$C_C(T) = 839.4 \exp(-19856/T)$$

($T : 1687–1832 K$)

Figure 2 shows the best fit equation together with all the considered experimental values. At the melting point of silicon ($1414^\circ C$), the model gives a solubility of 65 ppm mass carbon in liquid silicon. Figure 3 shows the best fit graph compared with those reported by other authors. All results have been extrapolated to the melting point of silicon for reference.

The present work shows good agreement with the works of Yanaba et al., Hall and Ottem, while poor agreement is seen with the results of Durand and Duby; Oden and McCune; and Scace and Slack. The work of Durand and Duby is a review article based on the data of Kleykamp and Schumacher; Hal; and Dash. As was pointed out by Søiland, their published equation gives a higher solubility at $1414^\circ C$ than any of the publications on which they base their review.

Scace and Slack investigated rapidly quenched liquid samples in equilibrium with a silicon carbide layer. As was pointed out by Olesinski and Abbaschian, this silicon

Fig. 1 Overview of all analysed parallels for all experiments. Red markers indicate outliers that have been excluded from the discussion. Note the logarithmic scale on the y-axis.

Fig. 2 Carbon concentration as function of temperature. The experimental points are shown together with the plot of the best fit Arrhenius equation, the dashed curves representing a 95% confidence interval.

Fig. 3 Log-plot comparison with previously reported results. The lines are marked with their references. Dotted lines indicate extrapolations beyond the temperature regions in which the experiments were run.
carbide layer would have functioned as a growth substrate for diffusing carbon during quenching. As this layer was removed before carbon analysis, the carbon content may have been underestimated.

The work of Oden and McCune was carried out at high temperatures, between 1700–2150 °C, so the extrapolation of their results to the melting point is inherently uncertain. Furthermore, they also employed rapid quenching of graphite crucibles followed by diamond grinding of the silicon ingot. Thus the issues of lost silicon carbide in the work of Scace and Slack may also apply here.

### 3.3 Dissolution energy of carbon

\( \Delta G_1^0 \), the standard change in Gibbs energy of reaction 1, is given by the expression

\[
\Delta G_1^0 = -RT \ln(K_1),
\]

(3)

where \( R \) is the gas constant, and \( K_1 \) is the equilibrium constant of the reaction, given by

\[
K_1 = \frac{a_{\text{SiC}}}{a_{\text{Si}}a_{\text{C}}},
\]

(4)

Here, \( a_X \) is the activity of substance \( X \). Since the silicon and silicon carbide are virtually pure, their activities can be set as equal to one, and the equilibrium constant becomes the inverse of the carbon activity. For the low concentrations of carbon in these experiments, it is natural to assume that the carbon activity follows Henry’s law. If the mass% carbon in liquid silicon is chosen as the standard state for carbon, the carbon activity can be replaced with the carbon concentration. Combining eq. (2) with eqs. (3) and (4) gives, in J/mol,

\[
\Delta G_1^0 = -1.65 \times 10^5 + 56.0T
\]

(5)

for the Gibbs energy change of reaction (1). The standard Gibbs energy of formation of silicon carbide in J/mol is given by Ref. 15:

\[
\Delta G_1^0 = -1.13 \times 10^5 - 11.4T \log T + 75.7T
\]

(6)

Considering that the carbon dissolution reaction can be written as eq. (1) subtracted from the formation of silicon carbide:

\[
\begin{align*}
C(s) + \text{Si}(l) & \rightleftharpoons \text{SiC}(s) \\
-C(s) + \text{Si}(l) & \rightleftharpoons \text{SiC}(s)
\end{align*}
\]

(1)

the Gibbs energy change in J/mol of the carbon dissolution can be found as a function of temperature by combining eqs. (5) and (6):

\[
\Delta G_2^0 = 5.2 \times 10^4 - 11.4T \log T + 19.7T
\]

(9)

This expression gives the dissolution energy of carbon at the melting point of silicon as 23.2 kJ/mol. Yanaba et al. found 20.4 kJ/mol for the same value. 4)

### 3.4 The effect of boron content

An Arrhenius expression showing the temperature dependence of the carbon solubility was constructed from the experimental data for each of the different levels of boron additions. Figure 4 shows the plots of the best fit equations together with the result for the pure silicon as discussed in the previous section. It can be seen that for all cases the carbon solubility is greater with boron additions present compared to the case of pure silicon. Also, apart from the case of 0.25%/0.50%, the carbon concentration increases with increasing boron content. From these observations it is natural to attempt to describe the carbon solubility as a function not only of temperature but also of boron content.

As justified above, the equilibrium constant of eq. (1) is equal to the inverse of the carbon activity. With the activity of carbon equal to the product of the activity coefficient and the concentration of carbon, the logarithm of the equilibrium constant becomes:

\[
\log(K) = -\log(f_C) - \log(C_C)
\]

(10)

Here, \( f_C \) is the activity coefficient of carbon. Using interaction coefficients, the activity coefficient of carbon is given by

\[
\log(f_C) = e_C^CC_C + e_B^BC_B
\]

(11)

Where \( e_C^C \) and \( e_B^C \) are the interaction coefficients describing the carbon-carbon and carbon-boron interactions respectively. Since the carbon activity has been assumed to follow Henry’s law in the boron-free system, it follows that the carbon-carbon interactions are insignificant, and \( e_C^C \) is equal to zero. With these assumptions, eq. (10) can be rearranged to

\[
\log(C_C) = -\log(K) - e_B^BC_B
\]

(12)

Since, as the boron level approaches zero the function \( C_C(T,B) \) must approach the function \( C_C(T) \) found above, \(-\log(K)\) can be replaced by \( \log(839.4 \exp(-19856/T)) \). Assuming that the temperature dependence of the interaction parameter \( e_B^C \) can be described by a first order Taylor polynomial, the final form of the expression describing the carbon solubility as a function of temperature and boron content becomes:

\[
\log(C_C(T,B)) = 0.9240 - 8623.4/T - (\alpha + \beta T)C_B
\]

(13)

The constants \( \alpha \) and \( \beta \) were determined by fitting the experimental data using the method of least squares. The resulting expression was
rapidly at higher temperatures. A positive interaction agreement at low temperatures, but then diverges rather apparent that the two predictions are within reasonable formula:  

$$\log(C_C(T, B)) = 0.9240 - \frac{8623.4}{T}$$  \hspace{1cm} (14)  

$$- (-0.2 + 3.87 \times 10^{-5}T)C_B$$  

$$T : 1687\text{–}1832 \text{ K;} \ B : 0\text{–}2 \text{ mass\%}$$  

This function is illustrated in Fig. 5 as 2D projections of the function at certain constant boron levels.  

For boron additions between 1 to 5 ppm, eq. (14) predicts increases in carbon solubility of 2 to 27 ppm in the temperature range 1414\text{–}1600 \text{ °C. Thus the increased solubility is negligible for solar purposes.}  

The boron-carbon interaction coefficient $e^B_C$ can be read out of eq. (14) to be  

$$e^B_C = -0.20 + 3.87 \times 10^{-5}T$$  \hspace{1cm} (15)  

This means that the boron-carbon interaction coefficient is negative for all temperatures below the boiling point of silicon. This is at variance with the results of Yanaba et al.,\textsuperscript{16} who found an expression indicating a positive interaction parameter above 1982 \text{ °C. Figure 7 shows a comparison of the current results with those found by Yanaba et al. It is apparent that the two predictions are within reasonable agreement at low temperatures, but then diverges rather rapidly at higher temperatures. A positive interaction parameter as predicted by the model of Yanaba et al. at high temperatures would imply a decrease in carbon solubility with increased boron content.  

3.5 Random and systematic error  

The three dimensional nature of eq. (14) makes a visual comparison between the model and the experimental data difficult. For that reason Fig. 6 is included to more clearly illustrate this point. It shows a plot of modelled versus experimental data for all boron levels where both the modelled and the experimental data have been scaled to give a value between one and unity after the following formula:  

$$C' = \frac{(C - C_{\min})}{(C_{\max} - C_{\min})}$$  \hspace{1cm} (16)  

For a model that follows the experimental data perfectly, all data points should lie on the line $y = x$. The data points in Fig. 6 clearly follow this trend, albeit with some scatter.  

The reasons behind the scatter can be many and complex, but it is likely that the inherent difficulty of analysing low amounts of carbon in silicon plays a significant role. As discussed in the results-section, some data points deviate so much as to be defined as outliers. As was mentioned, these outliers are probably caused by carbon contamination. It is possible that certain other samples are also contaminated, but to a much smaller degree, and that this is a cause for some of the scatter.  

It is likely that at least some aluminium is present in the melt because of the presence of alumina in the furnace interior and the thermocouple sheath. According to Yanaba et al.,\textsuperscript{16} an aluminium content of 0.1 mass% will increase the carbon solubility by ~0.3% at 1550 \text{ °C. An aluminium content of 0.1 mass% in a 75 g silicon melt corresponds to 0.075 g, which would represent a noticeable consumption of alumina. No such consumption has been observed, and it is believed that the real aluminium content in the melt is far below 0.1 mass% and the effect on the carbon solubility negligible.}  

Another concern is the oxygen content in the melt and in the samples. A few samples were analysed for oxygen content, and were found to be close to the solubility limit in liquid silicon. The formation of SiO\textsubscript{2} at the Si-SiC interface could disturb the Si-SiC equilibrium. No SiO\textsubscript{2}-particles have been detected in the microprobe analysis of the samples.
or the used crucibles. Furthermore, the presence of SiO$_2$ particles have been known to facilitate the precipitation of SiC particles, and no SiC-particles were detected in the samples. While nucleation can of course have been suppressed by a variety of effects, the lack of SiC substantiates our assumption that no SiO$_2$ nucleates in the melt.

When it came to the dissolved oxygen, Yanaba et al.\textsuperscript{16) }assumed that it did not influence the carbon solubility, and indeed the database created by SINTEF\textsuperscript{17) }predicts that an oxygen content of 50 ppm will decrease the carbon solubility in the melt by 0.12%. Thus the oxygen levels in the current work does not significantly influence the carbon solubility and can be ignored.

4. Conclusions

The time and temperature dependence of the solubility of carbon in liquid silicon equilibrated with silicon carbide have been investigated. No time dependence of the solubility limit could be detected, and it was concluded that equilibrium is rapidly established.

The temperature dependence of the solubility was investigated at various boron levels. In the case of pure silicon, the solubility was found to follow

$$C(T) = 8.394 \times 10^6 \times \exp\left(\frac{-19856}{T}\right)$$

$$\text{(} T : 1687–1832 \text{K)}$$

At the melting point of silicon, this gives a solubility limit of 65 ppm mass, near to the average of previously reported values.

From this expression, the $\Delta G^0$ of the dissolution of carbon was derived via a simple thermodynamic derivation to obtain:

$$C(s) \rightleftharpoons C(l)$$

$$\Delta G = 5.2 \times 10^4 - 11.4T \log T + 19.7T$$

At the melting point of silicon, this equation predicts a dissolution energy of 23.2 kJ/mol.

It was observed that the carbon solubility increased with increasing boron levels present in the melt. A multivariate expression was derived describing the solubility as dependent on temperature and boron content:

$$\log(Ct(T,B)) = 0.9240 - 8623.4/T$$

$$- (-0.2 + 3.87 \times 10^{-5}T)C_B$$

$$\text{(} T : 1414–1559 \text{Â°C; } C_B : 0–2 \text{ mass%)}$$

From this expression, it is clear that the carbon-boron interaction parameter in silicon depends on temperature in the following manner:

$$e_{C}^B = -0.20 + 3.87 \times 10^{-5}T$$

It was also predicted that the increase in carbon solubility will be in the ppb-range for a boron content in the low ppm-range, and will thus be negligible in solar applications.

Acknowledgements

The authors wish to thank The Norwegian Research Council, The Norwegian Ferroalloy Producers Research Association (FFF) and all other financial contributors to the ThermoTech project through which the current work has been performed. Heartfelt thanks are also due Elkem for the performance of chemical analysis without charge.

REFERENCES

17) K. Tang, E. J. Øvrelid, G. Tranell and M. Tangstad: Thermochemical and kinetic databases for the solar cell silicon materials, Crystal growth of Si for solar cells, (Springer) Accepted for publication.