Solubilities and Equilibrium Distribution Coefficients of Oxygen and Carbon in Silicon

Takayuki Narushima, Atsushi Yamashita *, Chiaki Ouchi and Yasutaka Iguchi

Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Solubilities of oxygen and carbon in solid silicon at 1673 K were determined by using a chemical equilibrium technique. Solid silicon was heated at 1673 K in an oxygen atmosphere for 1800 ks, and then oxygen content in the solid silicon equilibrated with silica was measured by the inert gas fusion-IR absorption method. Carbon content in the solid silicon equilibrated with silicon carbide after heating at 1673 K in an Ar–5%CO atmosphere for 4860 ks was measured by the combustion-IR absorption method. Comparing these solubility values in solid silicon with those in liquid silicon that were previously reported by the present authors, the equilibrium distribution coefficients of oxygen and carbon in silicon at the melting point were evaluated to be 0.85 ± 0.08 and 0.30 ± 0.16, respectively.

(Received May 10, 2002; Accepted June 12, 2002)

Keywords: silicon, carbon, oxygen, distribution coefficient, thermodynamics, solubility, segregation

1. Introduction

Oxygen is one of the most important impurity elements in silicon single crystals grown by the Czochralski (CZ) method. It is well known that oxygen is introduced to silicon melt due to dissolution of a silica crucible, and then distributed to the CZ silicon single crystal at the melting point.1) Oxygen in the CZ silicon crystal plays an important role for intrinsic gettering or for suppression of dislocation motion in silicon wafers. Therefore, the homogeneity of oxygen in CZ silicon wafers has been required for optimization of VLSIs’ characteristics.

Recently, a pyrometallurgical process for manufacturing solar grade (SOG) silicon from metallurgical grade (MG) silicon has been noted because of its mass-production ability in low cost. Since the MG silicon is produced by carbon reduction of silica, the total carbon content in the MG silicon is much higher than 100 mass ppm. The carbon concentration in the SOG silicon is required to be less than 5 mass ppm,2) and the decarburation of MG silicon is one of the key technologies in a pyrometallurgical process. Kato et al.3) proposed the pyrometallurgical process, in which polycrystalline silicon ingots were manufactured by directional solidification after a decarburation process using plasma for silicon melt. Therefore, the final carbon content in the silicon ingot is determined by the distribution between crystal and melt.

There have been many studies on the equilibrium distribution of oxygen and carbon between crystal and melt at the melting point because of their importance in silicon production processes. The reported equilibrium distribution coefficients of oxygen ranged widely from 0.2 to 1.25,4–12) and the values of the equilibrium distribution coefficient of carbon were reported to be less than 0.1.13–16) The crystal-growth-related techniques, such as the zone melting process and the CZ process, were employed to prepare the specimens for oxygen or carbon analysis in the experimental studies on the distribution.5–11,14) The equilibrium distribution of oxygen or carbon between crystal and melt has been assumed in these studies.

The present authors have reported the solubilities of oxygen,17) nitrogen18) and carbon19) in liquid silicon equilibrated with silica, silicon nitride and silicon carbide, respectively, and clarified the effect of alloying elements on oxygen and carbon solubilities.20,21) In the present work, solubilities of oxygen and carbon in the solid silicon equilibrated with silica and silicon carbide at 1673 K, respectively, were measured by using a chemical equilibrium technique and gas fusion-IR absorption methods for oxygen and carbon analyses. The equilibrium distribution coefficients of oxygen and carbon in silicon at the melting point were determined by comparing the solubility values in solid silicon with those in liquid silicon previously reported by the present authors.

2. Experimental

The silicon single crystal prepared by the floating zone (FZ) method was used as a source material for specimens in the equilibrium experiment. The FZ silicon single crystal was cut into plates. The silicon crystal plate size was 10 mm × 15 mm × 1.5 mm (W × L × T). Both of initial oxygen and carbon contents in the specimens were less than 5 mass ppm. The FZ crystal is considered to be suitable for the equilibrium experiment because of less initial oxygen precipitates in the body than those in CZ crystal. The silicon crystal plates were heated at 1673 K in an oxygen atmosphere or an Ar–5%CO atmosphere in order to form silica or silicon carbide film on their surface. The specimen temperature was maintained at 1673 ± 1 K using a PID controller, and monitored with two Pt-Pt13Rh thermocouples set near the specimen. Since the silica and silicon carbide films on specimens are expected to be protective,22) the equilibria represented by eqs. (1) and (2) are established at the SiO2/Si and SiC/Si interfaces, respectively.

\[ \text{Si(s)} + 2\text{O}_{\text{in solid silicon}} = \text{SiO}_2(s) \quad (1) \]
\[ \text{Si(s)} + \text{C}_{\text{in solid silicon}} = \text{SiC}(s) \quad (2) \]

Oxygen and carbon potentials, i.e., oxygen and carbon concentrations in solid silicon, at the interface are constantly de-
Solubilities and Equilibrium Distribution Coefficients of Oxygen and Carbon in Silicon

2121

Fig. 1 Calculated oxygen contents in solid silicon equilibrated with silica at 1673 K.

determined by eqs. (1) and (2), respectively. In the present experiment, it was required that the oxygen or carbon concentration was homogeneous in the entire solid silicon at 1673 K. Figure 1 shows the calculated oxygen contents in solid silicon equilibrated with silica. The oxygen contents were calculated with the Fick’s second law assuming that oxygen content at the SiO$_2$/Si interface was 30 mass ppm and initial oxygen content in the solid silicon was 5 mass ppm. The thickness of solid silicon was 1.5 mm and the diffusivity of oxygen in solid silicon at 1673 K was assumed to be $3.5 \times 10^{-9} \text{ cm}^2\cdot\text{s}^{-1}$. According to Fig. 1, the establishment of equilibrium in the entire solid silicon is expected after heating for 1800 ks (500 h). On the other hand, the specimen was heated in an Ar–5%CO atmosphere up to 4860 ks (1350 h), which was longer than that in an oxygen atmosphere because the carbon diffusivity in solid silicon at 1673 K has ranged from $10^{-7}$ cm$^2\cdot\text{s}^{-1}$ to $10^{-10}$ cm$^2\cdot\text{s}^{-1}$.

After the equilibrium was established, oxygen or carbon content in the specimen was determined by inert gas fusion-IR absorption method (TC436, LECO) using the analytical conditions that were reported elsewhere. The analytical conditions for carbon in silicon were shown in Table 1.

Table 1 Analytical conditions for carbon in silicon.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baking of alumina crucible</td>
<td>1623 K</td>
<td>600 s</td>
</tr>
<tr>
<td>Baking of specimen and metal bath</td>
<td>923 K</td>
<td>600 s</td>
</tr>
<tr>
<td>Size of specimen block</td>
<td>1–3 mm (0.1 g)</td>
<td></td>
</tr>
<tr>
<td>Metal bath</td>
<td>Cu (501–623, LECO), 3 g</td>
<td></td>
</tr>
<tr>
<td>Fe standard sample</td>
<td>4.2 mass ppm (502–401, LECO)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 mass ppm (001–050, LECO)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 XRD pattern of silicon heated at 1673 K in an oxygen atmosphere for 1800 ks.

3. Results

Figure 2 demonstrates XRD pattern of the surface of the solid silicon after heating at 1673 K in an oxygen atmosphere for 1800 ks. Since silica (cristobalite) was found on the solid silicon, it was confirmed that the equilibrium reaction can be represented by eq. (1). The relationship between heating time and the oxygen contents in solid silicon is shown in Fig. 3. The analytical values of oxygen contents agreed within 2 mass ppm at each heating time. As shown in the figure, the equilibrium between solid silicon and silica was established and the constant oxygen content was obtained after 1000 ks. According to Fig. 3, the value of oxygen solubility in solid silicon equilibrated with silica at 1673 K was concluded to be $33 \pm 3$ mass ppm ($2.9 \times 10^{18}$ atoms$\cdot$cm$^{-3} \pm 2.6 \times 10^{17}$ atoms$\cdot$cm$^{-3}$).

Silicon carbide ($\beta$ type) was found on the surface of the solid silicon after heating at 1673 K in an Ar–5%CO atmosphere for 1800 ks as shown in Fig. 4. It was confirmed that the solid silicon coexisted with silicon carbide. Figure 5 shows the change of carbon contents in the solid silicon with heating time at 1673 K. The uncertainty in the analytical values of carbon contents increased with the increase of heating time. However, it is considered that the equilibrium between solid silicon and silicon carbide was established after 3000 ks because the average value of carbon contents appeared to be constant. Therefore, the value of carbon solubility in solid silicon equilibrated with silicon carbide ($\beta$ type) was taken as the analytical value for carbon in this experiment.
carbide at 1673 K was determined to be 24 ± 13 mass ppm (2.8 ± 10^{18} \text{ atoms} \cdot \text{cm}^{-3} \pm 1.5 \times 10^{18} \text{ atoms} \cdot \text{cm}^{-3}) by considering the uncertainty of analytical values of carbon contents.

4. Discussion

4.1 Solubility of oxygen in solid silicon

The comparison of the reported\textsuperscript{5,11,24,30–34} and present oxygen solubilities in solid silicon equilibrated with silica is shown in Fig. 6. Several research groups\textsuperscript{24,32–34} evaluated the oxygen solubility by measuring the oxygen concentration profiles in the solid silicon after heating in various atmospheres. Yatsurugi et al.\textsuperscript{5} and Huang et al.\textsuperscript{11} measured the oxygen contents in the solid silicon crystals grown by a zone melting method in an oxygen atmosphere and a vertical freezing method in a silica ampoule, respectively. Hrostowski and Kaiser,\textsuperscript{30} and Bean and Newman\textsuperscript{31} annealed the CZ solid silicon crystals containing 1.4–1.6 × 10^{18} \text{ atoms} \cdot \text{cm}^{-3} as initial oxygen, and then measured the concentrations of soluble oxygen in the solid silicon using IR absorption method. The different principles and analytical techniques were employed in the experiments to determine the oxygen solubility. Nevertheless, almost all reported and extrapolated oxygen solubility in solid silicon at the melting point including the present data agreed in the range between 20 and 33 mass ppm. The solubility values reported by Mikkelsen, Jr.\textsuperscript{33} are lower than those reported by other research groups. It is suggested that the equilibrium between solid silicon and silica was not established by annealing in an inert gas atmosphere.\textsuperscript{33}
4.2 Solubility of carbon in solid silicon

Nozaki et al.\textsuperscript{16} zone-melted silicon rods on which carbon in aqueous suspension was painted. The zone melting was carried out in a vacuum. After a single zone pass, carbon contents in the silicon rod were determined as a function of the distance from top by CPAA (charged particle activation analysis) method. The carbon content just prior to the appearance of silicon carbide on the surface of silicon rods was concluded as the solubility of carbon in solid silicon at the melting point. Bean and Newman\textsuperscript{31} and Endo et al.\textsuperscript{35} annealed the carbon-rich silicon at various temperatures, and then the concentrations of soluble carbon were measured by IR absorption method. The value of carbon solubility obtained in the present work was higher than those reported by other research groups as shown in Fig. 7. Bean and Newman\textsuperscript{31} estimated the carbon solubility at the melting point (4.5 × 10\textsuperscript{17} atoms cm\textsuperscript{-3}) from their temperature dependence of carbon solubility. They stated, however, that the higher value than 4.5 × 10\textsuperscript{17} atoms cm\textsuperscript{-3} appeared to be more reasonable at the melting point because it was reported\textsuperscript{36,37} that carbon can be soluble in as-grown silicon crystals up to 2–3 × 10\textsuperscript{18} atoms cm\textsuperscript{-3}. Recently, Newman\textsuperscript{38} suggested that carbon solubility was enhanced by the presence of oxygen atoms in silicon crystal, which expanded the lattice of the silicon crystal. In the present work, oxygen contents in the solid silicon after heating in an Ar–5% CO atmosphere have not been analyzed. Further research on the interaction between oxygen and carbon in solid silicon is needed.

4.3 Equilibrium distribution coefficient of oxygen and carbon

The present authors have reported the oxygen and carbon solubilities in liquid silicon using a chemical equilibrium technique.\textsuperscript{17,19} The temperature dependence of oxygen and carbon solubilities in liquid silicon is represented as follows:\textsuperscript{17,19}

\[
\log(C_0/\text{mass%}) = -4620/T + 0.332(T : 1693–1823 K) \tag{3}
\]

\[
\log(C_l/\text{mass%}) = -9660/T + 3.63(T : 1723–1873 K) \tag{4}
\]

According to eqs. (3) and (4), the oxygen ($C_0$) and carbon ($C_l$) solubilities in liquid silicon at the melting point were calculated to be 38.9 and 79.1 mass ppm, respectively.

In the present work, the oxygen and carbon solubilities were measured at 1673 K. There have been several investigations on temperature dependence of oxygen and carbon solubilities in solid silicon as shown in Figs. 6 and 7. The relative difference in the values of oxygen and carbon solubilities between at 1673 K and at the melting point of silicon (1685 K) were no more than 5% and 10%, respectively. Therefore, the solubility values of oxygen ($C_0$) and carbon ($C_l$) in solid silicon at the melting point can be assumed to be the same as those at 1673 K. Using the solubilities at the melting point of silicon, the equilibrium distribution coefficients of oxygen ($k_O = C_0/C_l$) and carbon ($k_C = C_l/C_0$) were determined to be 0.85 ± 0.08 and 0.30 ± 0.16, respectively. The equilibrium distribution coefficients of oxygen and carbon in silicon reported in the past are summarized in Table 2.

![Fig. 7 Comparison of the reported and present carbon solubilities in solid silicon equilibrated with silicon carbide.](image)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Distribution coefficients</th>
<th>Authors</th>
<th>Distribution coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trumbore (1960)</td>
<td>0.5</td>
<td>Haas et al. (1969)</td>
<td>0.1</td>
</tr>
<tr>
<td>Yatsurugi et al. (1973)</td>
<td>1.25 ± 0.17</td>
<td>Nozaki et al. (1970)</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Murgai et al. (1979)</td>
<td>&gt; 1</td>
<td>Kolbesen and Mühlbauer (1982)</td>
<td>0.058 ± 0.005</td>
</tr>
<tr>
<td>Lin et al. (1983)</td>
<td>0.25–0.3</td>
<td>Durand and Duby (1999)</td>
<td>0.034</td>
</tr>
<tr>
<td>Inno et al. (1993)</td>
<td>0.2–0.4</td>
<td>Present work</td>
<td>0.30 ± 0.16</td>
</tr>
<tr>
<td>Kakimoto and Ozoe (1998)</td>
<td>0.35–0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huang et al. (1998)</td>
<td>0.8 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xu (1999)</td>
<td>0.998</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>0.85 ± 0.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
distribution at the interface between crystal and melt. It is suggested that the achievement of equilibrium distribution between crystal and melt is difficult in the crystal-growth-related processes. They reported $k_0 = 0.35–0.8$ in the silicon crystal growth under vertical magnetic fields at 0.3 T to prevent melt flow in radial directions. Huang et al.\textsuperscript{11} determined the value of $k_0$, 0.8±0.1, at the melting point by comparing the oxygen solubility in the silicon crystal with that in the silicon melt.\textsuperscript{40} The value of $k_0$ in the present work agreed well with that reported by Huang et al.,\textsuperscript{11} who used a small silica ampoule to ensure the equilibrium in the SiO$_2$(s)–Si(s,l)–SiO(g) system.

The values of $k_c$ reported by other research groups are less than the present data as shown in Table 2. Durand and Duby\textsuperscript{16} selected the carbon solubilities in solid and liquid silicon from the literatures, and the value of $k_c$ was evaluated to be 0.034 at the melting point of silicon. Other three research groups\textsuperscript{13–15} experimentally measured the carbon contents in the silicon after zone melting, and the values of $k_c$ were reported in the range between 0.058 and 0.1. Since the zone melting is a dynamic process, it may be difficult to achieve the equilibrium distribution between crystal and melt especially at high temperatures, even if the zone traveling velocity is extrapolated to zero.\textsuperscript{14, 15} In addition, it was reported that carbon content in silicon was affected by the ambient atmosphere during the zone melting process.\textsuperscript{34} The accuracy of the $k_c$ value obtained in the present work depends on that of the carbon solubility in solid silicon. The equilibrium between solid silicon and silicon carbide was confirmed, but as described in 4.2, the effect of oxygen atoms in solid silicon on the carbon solubility should be clarified in order to evaluate the accuracy of the present $k_c$ value in detail.

5. Conclusions

The oxygen and carbon contents in the solid silicon crystals after heating at 1673 K in an oxygen atmosphere and an Ar–5%CO atmosphere, respectively, were measured and the following results were obtained.

(1) The solubility values of oxygen and carbon in solid silicon at 1673 K were 33 ± 3 mass ppm (2.9 × 10$^{18}$ atoms·cm$^{-3}$ ± 2.6 × 10$^{17}$ atoms·cm$^{-3}$) and 24 ± 13 mass ppm (2.8 × 10$^{18}$ atoms·cm$^{-3}$ ± 1.5 × 10$^{18}$ atoms·cm$^{-3}$), respectively.

(2) The equilibrium distribution coefficients of oxygen and carbon in silicon at the melting point were concluded to be 0.85 ± 0.08 and 0.30 ± 0.16, respectively, by comparing the solubilities at 1673 K with those in liquid silicon that were previously reported by the present authors.

Acknowledgments

This work was partly supported by KAWASAKI STEEL 21st Century Foundation and the New Energy and Industrial Technology Development Organization (NEDO) through the Japan Space Utilization Promotion Center (JSUP).

REFERENCES