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Reduction Behavior of $SiCl_4$ During its Aluminothermic Reduction

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Abstract. With a long term aim of utilization of $SiCl_4$ as a resource for solar grade silicon, we have investigated the aluminothermic reduction of $SiCl_4$. The rate-controlling step for reduction of $SiCl_4$ with liquid aluminum with the gas flow at the melt surface was estimated to be mass transfer in the liquid aluminum. When the Ar-$SiCl_4$ gas was either blown onto or injected into the liquid aluminum, the maximum silicon contents obtained were below the saturated silicon content, and the formation of solid silicon precipitates was not observed. This was believed to be because solid silicon film forms at the gas/liquid interface and acts as a protective layer, stopping further reaction. To overcome this, the injection of Ar-$SiCl_4$ gas into liquid aluminum kept under a temperature gradient was conducted, and the precipitation of solid silicon during the reaction was achieved.

Keywords. Solar grade silicon, $SiCl_4$, aluminothermic reduction.

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1 Introduction

The production of crystalline silicon solar cells has increased significantly this decade. However, the supply of silicon feedstock has been unstable, and sudden increases in feedstock price have occurred, particularly over the last five years. This feedstock problem arises because the industry is reliant on expensive, off-spec semiconductor-grade silicon (SEG-Si). Although construction of silicon production plants has accelerated worldwide, the development of a low-cost silicon production process is essential for the sustainable development of silicon solar cells.

Purification of silicon through metallurgical treatments is a promising way for mass production of solar grade silicon (SOG-Si) from metallurgical grade silicon (MG-Si). Solidification of silicon is a well known process for removing metallic impurities such as iron and titanium which have strong segregation tendencies from silicon. However, removal of phosphorus and boron, which are important dopants in silicon, is practically impossible during solidification because their segregation coefficients are not sufficiently small ($k_P = 0.35$, $k_B = 0.8$ [1]). Vacuum melting and oxidation treatment are often employed to remove phosphorus [2] and boron [3]. However, these processes require high temperatures and long times, leading to a high price for the silicon produced. If silicon raw material with phosphorus and boron levels below 1 ppma can be supplied at a low price, the situation for silicon solar cells will change dramatically.

$SiCl_4$ gas mixture is generated as a by-product during the production of high purity quartz or semiconductor silicon. Although it is generally recycled through a special treatment which consumes a vast amount of energy, it may be possible to be used as a source of SOG-Si. Recently, metallothermic reduction of $SiCl_4$ for producing SOG-Si has been investigated using sodium [4], zinc [5, 6] and aluminum [7] as reductants. Sodium vapor can be supplied for the reduction of $SiCl_4$, which is favorable for the reaction rate. However, there is strong disquiet for the handling of sodium vapor in mass production because of its high chemical reactivity. Zinc can also reduce $SiCl_4$ in the gas phase due to its high vapor pressure, and fibrous silicon or silicon deposition can be obtained [5, 6]. Yoshizawa [8] conducted aluminothermic reduction of $SiCl_4$ in the 1960s, and showed the formation of a mixture of solid silicon along with liquid Al-Si alloy. Although the mixed product is generally a disadvantage for separation of silicon product, we can expect further precipitation of silicon to occur during cooling of the alloy. More importantly, silicon can be highly purified during the partial solidification from the alloy, as reported by the authors [9–15]. Hence, the reduction of $SiCl_4$ with pure aluminum, followed by the partial solidification of silicon, is considered to be a promising process to produce SOG-Si. The phenomena during the aluminothermic reduction of $SiCl_4$, however, were not well understood.

In the present work, we have investigated the aluminothermic reduction of $SiCl_4$ by blowing and injecting Ar-$SiCl_4$ gas into the liquid aluminum. The influence of adding copper to the melt, which is regarded as not harmful

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for SOG-Si due to its moderate allowable content [16] as well as ease of removal during the gettering process [17], was also examined. Furthermore, the injection of Ar-$SiCl_4$ gas into the liquid aluminum under a temperature gradient was conducted, with the aim of precipitating silicon in the melt during the reaction.

2 Principle

The reduction of $SiCl_4$ gas by liquid Al can be expressed as:

$$SiCl_4(g) + \frac{4}{3}Al(l) = Si(s) + \frac{4}{3}AlCl_3(g), \qquad (1)$$

$$\Delta G^\circ = -562{,}000 + 18.0T \quad (J/mol)\ [18]. \qquad (2)$$

Here, T is the temperature. As the standard Gibbs energy, ΔG° (Eq. (2)), for Eq. (1) is highly negative, we can expect the reduction to silicon as well as the formation of gaseous $AlCl_3$. However, there are other gaseous components in the Al-Si-Cl system besides $AlCl_3$ and $SiCl_4$. Thermodynamic analysis was thus carried out for gas formation using the thermodynamic software FactSage 5.5. The following conditions were assumed for the analysis: (i) total pressure is fixed to 1 atm, and the input gas is Ar-10mol%$SiCl_4$. (ii) The condensed phases are solid silicon and silicon-saturated Al-Si alloys since the interfacial reaction is assumed to proceed immediately. The activity of aluminum in the alloy was obtained from the data reported by Murray and McAlister [19].

The estimated partial pressures of gaseous species are shown in Figure 1. Since the partial pressure of $SiCl_4$ is much lower than the input pressure of 0.1 atm over the entire temperature range, it can be reduced to silicon even at the low aluminum content of the liquid alloy at high temperature (e.g. 1 mol% Al at 1680 K). Although $AlCl_3$ has the highest partial pressure, AlCl and $AlCl_2$ become major gaseous components along with $AlCl_3$ at high temperature. In addition, the partial pressure of $SiCl_2$ exceeds 10^{-6} atm above 1250 K. Hence, the loss of the formed silicon by the following reaction should be taken into account when the reduction is conducted at high temperature.

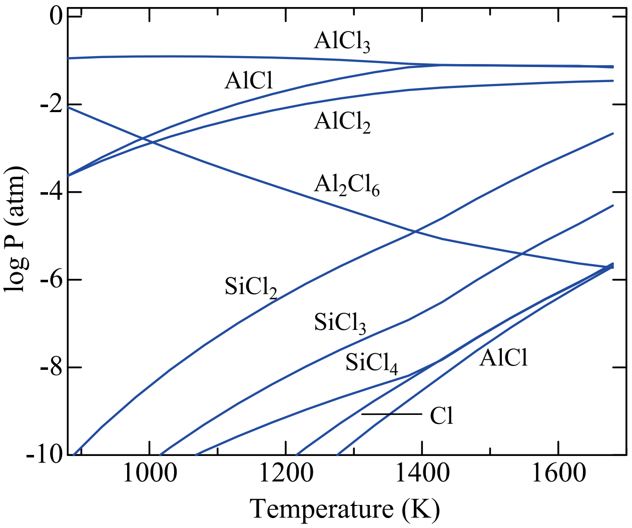

Figure 1. Estimated partial pressures of gaseous components when Ar-10%$SiCl_4$ gas was reacted with liquid aluminum to form solid silicon and silicon-saturated Al-Si melt.

$$SiCl_4(g) + Si(s) = 2SiCl_2(g), \qquad (3)$$

$$\Delta G^\circ = 318{,}000 - 19.8T \quad (J/mol)\ [18]. \qquad (4)$$

3 Experimental

The reduction of $SiCl_4$ gas by liquid aluminum was conducted in a vertical electric-resistance furnace. Pure aluminum or pre-melted Al-Cu alloy was cleaned with HF acid, and was charged in a graphite crucible. The crucible was inserted in a closed-end quartz or mullite reaction tube, and the tube was then purged with argon gas, which was passed through magnesium perchlorate, soda-lime and magnesium turnings heated at 823 K to remove moisture, CO_2 and oxygen, respectively. After the reaction tube was inserted into the furnace and the metal was melted, Ar-$SiCl_4$ gas was then supplied to the melt through a 3 mm diameter alumina nozzle. After the reaction, the sample was taken out from the reaction tube and quenched in water. Silicon and aluminum contents of the sample were determined by the SiO_2 gravimetric method and inductively coupled plasma (ICP) atomic emission spectroscopy, respectively.

Ar-$SiCl_4$ gas was prepared by injecting argon gas into liquid $SiCl_4$ at a controlled flow rate. The temperature of liquid $SiCl_4$ was controlled to 273 K or 298 K by iced water or a controlled temperature bath, respectively. Partial pressure of $SiCl_4$ in the gas mixture can be controlled by the saturated vapor pressure of $SiCl_4$ according to the following equation:

$$SiCl_4(l) = SiCl_4(g), \qquad (5)$$

$$\Delta G^\circ = 29{,}670 - 89.8T \quad (kJ/mol)\ [20]. \qquad (6)$$

$SiCl_4$ partial pressures are calculated to be 10.4 kPa at 273 K and 31.2 kPa at 298 K, respectively. The generation of the equilibrium vapor pressure of $SiCl_4$ was confirmed prior to the experiment. When argon was flown at the flow rate, V_{Ar} (ml/min), the theoretical evaporation rate of $SiCl_4$, V_{SiCl_4} (ml/min), can be expressed by Eq. (7).

$$V_{SiCl_4} = \frac{P^\circ_{SiCl_4}}{1 - P^\circ_{SiCl_4}} V_{Ar} \quad (ml/min), \qquad (7)$$

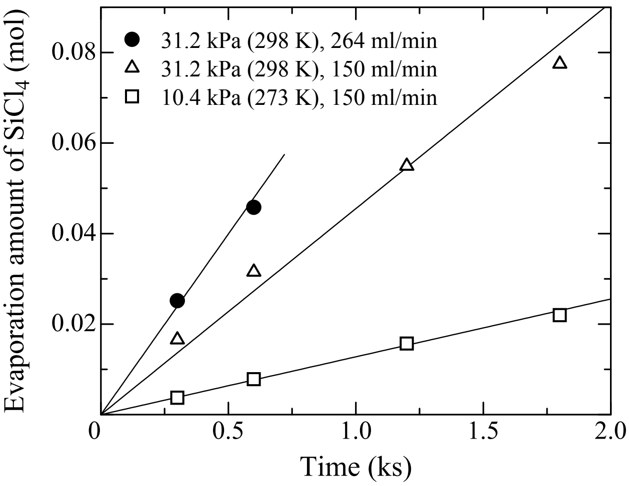

Figure 2. Evaporation rate of $SiCl_4$ during injecting of argon gas into liquid $SiCl_4$. Lines are calculated using Eq. (8).

where $P^{\circ}_{SiCl_4}$ is the saturated vapor pressure of $SiCl_4$. Its evaporation rate on a mole basis is given by Eq. (8), derived from the ideal gas equation.

$$n_{SiCl_4} = \frac{P^{\circ}_{SiCl_4} V_{Ar}}{1000(1 - P^{\circ}_{SiCl_4})RT} \quad \text{(mol/min)}. \qquad (8)$$

Here, R is the gas constant. Argon gas was injected into liquid $SiCl_4$ at 273 K or 298 K, and was then passed through pure water. The content of chloride ion in the water was measured by an ion meter. The measured $SiCl_4$ amounts calculated from the chloride content are shown in Figure 2, together with the estimated lines from Eq. (8). As the measured amounts were well in accordance with theoretical lines, Ar-$SiCl_4$ gas was determined to be saturated with $SiCl_4$ at the controlled temperature.

4 Results and Discussion

4.1 Flowing $SiCl_4$ Gas onto the Melt

The reduction behavior of $SiCl_4$ gas during the Ar-$SiCl_4$ gas flow above the liquid aluminum was investigated at 1125 K with different gas supply conditions. For experiments FL01–09, the tip of a gas nozzle was placed 20 mm above the melt surface, and Ar-10.4%$SiCl_4$ gas flowed at 50–150 ml/min. For experiments BL01–03, Ar-10.4%$SiCl_4$ gas was blown onto the melt surface from a nozzle tip set just above the surface. Aluminum was charged in a graphite crucible of 8 mm inner diameter and the melt depth was controlled to around 10 mm. The results are summarized in Figure 3 and Table 1. Upon increasing the Ar-$SiCl_4$ gas flow rate during the FL series of tests, the silicon content of the melt also increased. In addition, the silicon content increased remarkably when the gas was blown onto the surface. As discussed in Section 2, the vapor pressure of $AlCl_3$ is extremely large during the reaction between liquid Al and $SiCl_4$ gas. Henceforth, the mass transfer of the gaseous $AlCl_3$ formed would possibly be the rate determining step in the reaction, at least for experiments FL01–09.

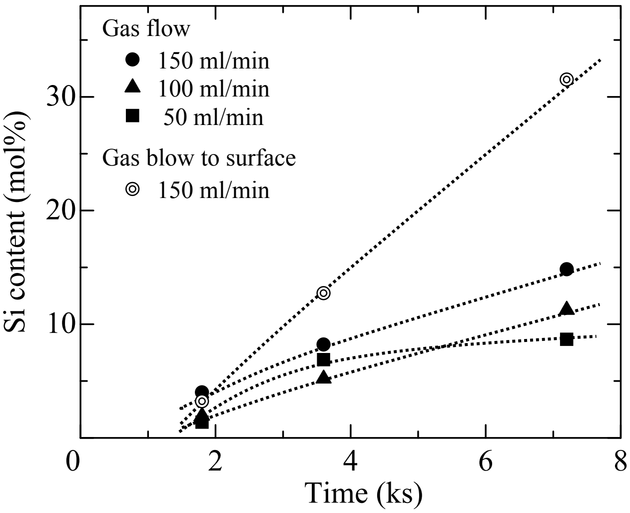

Figure 3. Change in silicon contents of liquid aluminum during flow of Ar-10.4%$SiCl_4$ gas onto the melt at 1125 K.

The effect of copper addition to the melt on the reaction was examined by blowing Ar-$SiCl_4$ onto the melt surface. The conditions were identical with those used for experiments BL01–03. Al-5mol%Cu and Al-10mol%Cu alloys were used as starting materials and their melt depths were adjusted to 10 mm by estimating the specific gravities of Al-Cu alloys from those of pure aluminum and copper [21]. Figure 4 shows the change in silicon contents during the reaction. As the copper content of the melt increased, the silicon content became smaller. Hence, copper addition was detrimental to the aluminothermic reduction of $SiCl_4$.

The reduction kinetics of $SiCl_4$ under gas blow conditions are now discussed. It was expected that the mass transfer in the gas was enhanced sufficiently by blowing the gas onto the melt surface. The mass transfer in the liquid phase was assumed to be rate determining, presuming adequate chemical reaction at the interface because of the high temperature. The surface composition of the melt is considered to be in saturation with silicon due to the exchange reaction between $SiCl_4$ and Al, and dissolved silicon diffuses inside the melt. By integrating Fick's 2nd law with the initial condition of no silicon content in the entire melt and the boundary condition of silicon saturation at the surface, $C^{\text{satd.}}_{Si}$, the silicon content of the melt, C_{Si}, can be described

Sample	Condition	System	Weight of Al(g)	Ar flow rate (ml/min)	Partial pressure of $SiCl_4$ (kPa)	Time (ks)	Diameter (mm)	Si content (mol%)
FL01	Flow	Al	1.17	50	10.4	1.8	8	1.11
FL02	Flow	Al	1.16	50	10.4	3.6	8	9.45
FL03	Flow	Al	1.16	50	10.4	7.2	8	17.8
FL04	Flow	Al	1.16	100	10.4	1.8	8	1.87
FL05	Flow	Al	1.17	100	10.4	3.6	8	5.02
FL06	Flow	Al	1.16	100	10.4	7.2	8	10.9
FL07	Flow	Al	1.17	150	10.4	1.8	8	3.86
FL08	Flow	Al	1.17	150	10.4	3.6	8	7.91
FL09	Flow	Al	1.16	150	10.4	7.2	8	14.3
BL01	Blow	Al	1.27	150	10.4	1.8	8	3.10
BL02	Blow	Al	1.27	150	10.4	3.6	8	12.3
BL03	Blow	Al	1.27	150	10.4	7.2	8	30.7
BL04	Blow	Al-5%Cu	1.37	150	10.4	1.8	8	0.74
BL05	Blow	Al-5%Cu	1.37	150	10.4	3.6	8	10.7
BL06	Blow	Al-5%Cu	1.37	150	10.4	7.2	8	21.4
BL07	Blow	Al-10%Cu	1.27	150	10.4	1.8	8	1.15
BL08	Blow	Al-10%Cu	1.27	150	10.4	3.6	8	9.80
BL09	Blow	Al-10%Cu	1.27	150	10.4	7.2	8	18.4
BL10	Blow	Al	0.40	150	31.2	6.3	8	29.8
BL11	Blow	Al	0.40	150	31.2	9.0	8	29.2
BL12	Blow	Al	0.40	150	31.2	14.4	8	30.4

Table 1. Experimental conditions and results for experiments flowing and blowing Ar-$SiCl_4$ gas onto the melt at 1125 K.

by Eq. (9).

$$C_{\mathrm{Si}} = C_{\mathrm{Si}}^{\mathrm{satd.}}\left[1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left\{-D_{\mathrm{Si}}\frac{(2n+1)^2\pi^2 t}{4L^2}\right\} \times \cos\frac{(2n+1)\pi x}{2L}\right]. \tag{9}$$

Here, D_{Si}, L, t and $x$denote the diffusion coefficient of silicon in the melt and depth of the melt, reaction time and the distance from the gas/liquid interface, respectively. The average content of silicon, $C_{\mathrm{Si}}^{\mathrm{ave.}}$, is expressed by Eq. (10) (from integration of Eq. (9)).

$$C_{\mathrm{Si}}^{\mathrm{ave.}} = C_{\mathrm{Si}}^{\mathrm{satd.}}\left[1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2} \times \exp\left\{-D_{\mathrm{Si}}\frac{(2n+1)^2\pi^2 t}{4L^2}\right\}\right]. \tag{10}$$

The saturated silicon contents are 31.3, 27.8 and 24.2 mol% for aluminum, Al-5mol%Cu and Al-10mol%Cu alloys, respectively, from the phase diagrams for binary Al-Si [19] and ternary Al-Cu-Si [22] systems. Petrescu [23] reported the temperature dependence of the diffusion coefficient of silicon in the eutectic Al-12.9mol%Si alloy as given by Eq. (11).

$$D_{\mathrm{Si,Al\text{-}12.9\%\,Si}} = 2.03 \times 10^{-7}\exp\left(\frac{25{,}700}{RT}\right) \quad (\mathrm{m^2/s}). \tag{11}$$

The diffusion coefficient of silicon is assumed to be constant for the composition range until silicon saturation. Furthermore, we used the data for the Al-Si alloy to estimate the diffusion coefficients of Si in Al-Cu alloys. Calculated silicon contents from Eq. (7) are shown as solid lines in Figure 4. In addition, silicon contents were estimated for the case where the reaction started at 1600 s (dotted lines on Figure 4), since it seems that the measured silicon contents at 1800 s are rather small and that the reaction start is delayed. The measured silicon contents are roughly consistent with the calculated results. Hence, the rate of reduction of $SiCl_4$ gas by liquid aluminum during blowing of Ar-$SiCl_4$ gas is mainly influenced by the mass transfer in the melt. In addition, the decrease in the silicon content upon copper

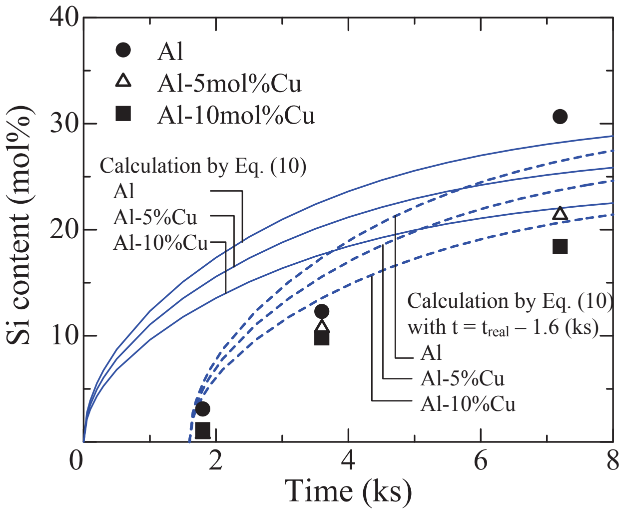

Figure 4. Change in silicon contents of liquid aluminum and Al-Cu alloys during blowing of Ar-10.4%$SiCl_4$ gas onto the melt surface at a flow rate of 150 ml/min at 1125 K.

addition shown in Figure 4 can be explained by the decrease in the saturated silicon content of the melt.

To achieve the maximum possible silicon content during blowing of Ar-$SiCl_4$ onto the melt, experiments were carried out with a smaller mass of the sample, higher $SiCl_4$ partial pressure in the reaction gas and for longer reaction time (BL10–12). The silicon content, however, was almost constant throughout the reaction time and slightly below the liquidus composition. Although the aluminum activity at the silicon-saturated composition was still sufficient for further reduction of $SiCl_4$ as mentioned in Section 2, reaction was almost stopped. This may be caused by the formation of a solid silicon film at the surface which acts as a protective layer and blocks further reaction. Hence, it was determined that the reduction of $SiCl_4$ is limited to the melt composition becoming saturated with silicon when $SiCl_4$ gas is blown onto the melt surface.

4.2 Injection of $SiCl_4$ Gas to the Melt

To obtain a silicon content after the reaction higher than the silicon saturation level, injection of Ar-$SiCl_4$ gas into the liquid aluminum was conducted, in an attempt to increase the reaction area and also stir the melt more effectively to enhance the mass transfer. The gas nozzle tip was immersed in the melt and set just above the bottom. The gas flow rate, $SiCl_4$ partial pressure in the gas and mass of the melt were varied (tests IJ01–IJ09). The experimental conditions and results are summarized in Table 2. The measured silicon contents are plotted in Figure 5 on the Al-Si binary phase diagram [19]. The reduction rate of silicon was higher than that achieved with gas blow, which may be due to the enhancement of the mass transfer in the liquid. However, the silicon contents again did not exceed silicon saturation. This would be because the "protective silicon film" formed even at the surface of gas bubbles, and, as before, restricted further reaction. Hence, it is difficult in practice to obtain a silicon content significantly above silicon saturation, which means no precipitation of silicon occurs during the reaction, under isothermal conditions.

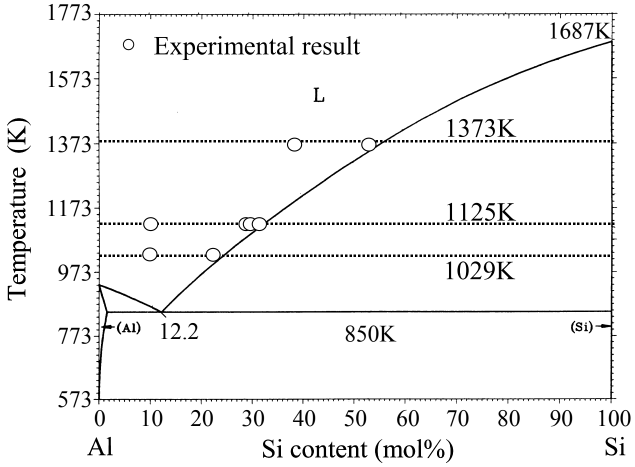

Figure 5. Silicon contents after experimental injection of Ar-$SiCl_4$ gas into the melt.

The evaporation loss from the sample may be discussed here. Non-negligible decrease of sample weight was observed above 1373 K, whereas it was not significant below 1125 K. For example, the sample weight loss for IJ06 was up to 39.7 %, and the sample was completely lost in test IJ07. As described in Section 2, chloride components besides $AlCl_3$ form during the reaction between liquid aluminum and $SiCl_4$ gas. In particular, the partial pressure of $SiCl_2$ is significant at high temperature. Accordingly, the formation of gaseous $SiCl_2$ is the dominant factor in evaporation of the sample, suggesting that the reaction should be conducted at a sufficiently low temperature to allow an adequate fraction of the silicon to be recovered.

4.3 Reduction of $SiCl_4$ by Gas Injection into the Melt Under a Temperature Gradient

To drastically increase the silicon content during the reaction between Al and $SiCl_4$, a method for continuous reduction of $SiCl_4$ and precipitation of silicon particles away from the reaction interface was considered. The liquid aluminum was placed in a temperature gradient, and Ar-$SiCl_4$ gas was injected slightly above the bottom of the melt. By controlling the top of the melt to be at a lower temperature, it was expected that dissolved silicon in the melt would transfer upwards and solidify at the upper part of the melt. The temperature distribution in the furnace was examined prior to experiments, and the temperatures of the top and

Sample	Weight of Al(g)	Temperature (K)	Ar flow rate (ml/min)	Partial pressure of $SiCl_4$ (kPa)	Time (ks)	Diameter (mm)	Si content (mol%)
IJ01	1.76	1029	50	10.4	7.2	11	9.75
IJ02	1.75	1029	50	10.4	30.6	11	22.1
IJ03	1.34	1125	150	10.4	10.8	8	31.1
IJ04	12.7	1125	150	31.2	18	28	28.0
IJ05	14.3	1125	250	31.2	3.6	28	10.6
IJ06	14.0	1125	250	31.2	7.2	28	28.3
IJ07	1.40	1373	150	10.4	7.2	8	38.5
IJ08	12.6	1373	150	31.2	10.8	28	51.7
IJ09	1.18	1673	150	10.4	10.8	8	–

Table 2. Experimental conditions and results for experiments injecting Ar-$SiCl_4$ gas into the melt.

Sample	Weight of Al(g)	Ar flow rate (ml/min)	Partial pressure of $SiCl_4$ (kPa)	Time (ks)	Diameter (mm)	Si content (mol%)	
						Lower part	Upper part
TG01	30.93	150	10.4	12.6	20	27.3	35.8
TG02	30.07	150	10.4	25.2	20	40.1	35.7
TG03	29.73	150	10.4	37.8	20	38.3	36.7
TG04	4.16	150	10.4	25.2	8	53.5	35.0

Table 3. Experimental conditions and results for experiments injecting Ar-10.4%$SiCl_4$ gas into the melt placed in a temperature gradient.

bottom positions of the melt were measured as 980 K and 1223 K, respectively. The melt depth in the graphite crucible was controlled to around 40 mm.

The experimental conditions are summarized in Table 3. Since the sample was expected to have a distribution of silicon content due to the temperature gradient inside, it was divided into upper and lower parts and then subjected to chemical analysis. Figure 6 shows the change in the silicon content during reaction of the sample with 20 mm diameter (TG01–03). The silicon content of the lower parts of the sample remained almost constant. Since the measured contents are between the liquidus compositions at 1223 K and 1100 K, (the bottom and middle temperatures in the melt), it can be considered that the lower melt was almost saturated with silicon during the reaction. The silicon content of the upper parts of the sample increased in the initial stages before becoming almost constant. The silicon content at this constant level was larger than the content of the lower part of the sample, and beyond the liquidus silicon content at 1100 K. It can be determined that silicon particles precipitated at the upper part of the sample during the reaction. When the experiment was carried out with a smaller sample (TG04, 8 mm diameter) for 25,200 s, the silicon content of the lower part of the sample was comparable to that of TG01–03. On the other hand, a much higher content was obtained for the upper part of sample TG04. The temperature gradient in the melt can be considered to be larger with the smaller sample due to the more efficient heat transfer inside against the surrounding temperature. Thus we speculate that the mass transfer was enhanced and further precipitation of silicon was obtained with a larger temperature gradient in sample TG-04.

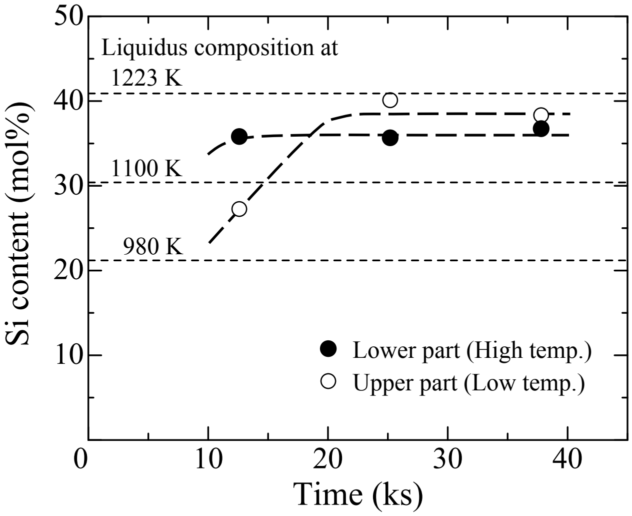

Figure 6. Change in silicon contents of upper and lower parts of the sample upon injection of Ar-10.4%$SiCl_4$ gas when the sample was under a temperature gradient.

The reduction of $SiCl_4$ gas with liquid aluminum can be enhanced by placing the melt under a temperature gradient to accelerate the silicon precipitation away from the gas-liquid reaction interface. If the separation of precipitated silicon as well as simultaneous supply of aluminum can be accomplished during the $SiCl_4$ reduction in the liquid under a temperature gradient, we can develop a continuous silicon production process using aluminothermic reduction of $SiCl_4$.

5 Conclusions

With the eventual aim of using $SiCl_4$ as a resource for solar grade silicon (SOG-Si), we have investigated the reduction behavior of gaseous $SiCl_4$ by liquid aluminum in the present work. The following results were obtained.

(1) The silicon content obtained in the melt when Ar-$SiCl_4$ gas flowed near it was smaller than that obtained when the gas was blown directly onto the melt surface. In addition, the silicon content was increased by increasing the gas flow rate during the flowing condition. Thus, the mass transfer of the $AlCl_3$ gas formed could be rate determining for the reaction under sufficient gas flow at the melt surface.

(2) The silicon content of the melt during blowing Ar-$SiCl_4$ gas onto its surface was roughly coincident with the result predicted using the unsteady-state diffusion equation. Hence, the rate-controlling step for the reaction with sufficient gas flow to the melt surface was estimated to be mass transfer in the liquid.

(3) Copper addition to the melt decreased the silicon content of the liquid, probably because of the decrease in the saturation content of silicon in the melt.

(4) With both blowing Ar-$SiCl_4$ gas onto and injecting it into the liquid aluminum, the maximum silicon contents obtained were below the saturation silicon content. It was supposed that a solid silicon film forms on the gas/liquid interface and acts as a protective layer, preventing further reaction.

(5) When Ar-$SiCl_4$ gas was injected to the liquid aluminum under a temperature gradient, the reduction proceeded furthermore, and the precipitation of solid silicon during the reaction was achieved.

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