Effect of hydrogen radical on decomposition of chlorosilane source gases

Masatomo Sumiya¹*, Tomohiro Akizuki¹,², Kenji Itaka³, Makoto Kubota¹,², Kenta Tsubouchi⁴, Takamasa Ishigaki²,⁵, and Hideomi Koinuma⁴,⁶

¹ Widegap Materials group, National Institute for Materials Science, Tsukuba, 305-0044, Japan
² Department of Materials Chemistry, Hosei University, Koganei Tokyo, 184-8584, Japan
³ North Japan Research Institute for Sustainable Energy, Hirosaki University, 2-1-3, Matsubara, Aomori, 030-0813, Japan
⁴ Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, 277-8568, Japan
⁵ Department of Chemical Science and Technology, Hosei University, Koganei Tokyo, 184-8584, Japan
⁶ Department of Cogno-Mechatronics Engineering, Pusan National University, Miryang 627-706, South Korea

*Email: SUMIYA.Masatomo@nims.go.jp

Abstract. The effect of hydrogen radical on production of Si from chlorosilane sources has been studied. We used hydrogen radical generated from pulsed thermal plasma to decompose SiHCl₃ and SiCl₄. Hydrogen radical was effective for lowering the temperature to produce Si from SiHCl₃. SiCl₄ source, which was chemically stable and by-product in Siemens process, was decomposed effectively by hydrogen radical. The decomposition of SiCl₄ was consistent with the thermo-dynamical calculation predicting that the use of hydrogen radical could drastically enhance the yield of Si production rather than case of H₂ gas.

1. Introduction

Photovoltaic cells have attracted more attentions and demand of solar grade silicon (SOG-Si) has rapidly increased. SOG-Si is purified either by metallurgical or by chemical process. In metallurgical process, re-solidification and other various processes are used for obtain “six nines (6N)” grade silicon. In chemical process, metal-grade silicon (~99%) is converted to volatile compound such as SiHCl₃ for making purification by distillation, which produces highly pure semiconductor-grade Si (SEG-Si) with ~12N orders of magnitudes.

Siemens process¹ has been widely used for producing SEG-Si. In Siemens process, SiHCl₃ decomposes on heated high-purity Si rod in reducing ambient of H₂ gas under pressure of ~1atm. Drawbacks of Siemens process are considered to be (1) batch process and (2) low yield of ~25 %, because by-product of SiCl₄ can be more favorably generated. To overcome these issues, fluidized bed reactor² and vapor liquid reaction³ processes have been developed for enhancing its production rate and for realizing continuous production. However, there are still difficulties in these processes with respect to the unavoidable impurity incorporation from reactor and low yield. Because reducing reaction of Si production depends on thermal decomposition of source gas in H₂ ambient.

It is necessary to develop process for producing SOG-Si with much higher yield, which must result in reduction of its cost. We have proposed the use of hydrogen radical instead of H₂ gas. Thermodynamic calculation has been carried out to predict the effect of hydrogen radical on the decomposition of chlorosilane sources. Based on this calculation, we have experimentally investigated Si production from SiHCl₃ and SiCl₄ reacting with hydrogen radical generated from thermal pulsed plasma in this study.
2. Experiments

The schematic of the plasma torch is shown in Fig. 1, of which structures are described in detail elsewhere. The solid state amplifier (MP-22CY, Denki Kogyo Co., Ltd.) was employed for the pulsing plasma generation. The inverter-type power source continuously supplies the electric power of 22 kW with a nominal frequency of 1 MHz, and has a high electric energy efficiency up to 90%. The electric matching with a load is attained by the phase locked loop with variable frequency and an LC matching circuit. The rf power was pulse modulated by imposing the external pulsed signal to switch a static induction transistor. The pulsing rise time of power source is less than 1 msec. The external signal was generated by a pulse generator (HP 8116A) with a response time of 6 ns.

The rf power was modulated with the pulse of on-time of 10 msec and off-time of 5 msec as the optimized condition. The sheath gas was composed of Ar and H₂ at the flow rate of 98 SLM and/or 6 SLM, respectively. The flow rate of H₂ gas was maximum to generate the pulsed thermal plasma. Hydrogen atom density was numerically simulated to be in range of 2.1~4.5x10¹⁶ cm⁻³ throughout a pulse cycle. The plasma was first generated at the continuous power level of 10 kW and the pulse mode plasma was generated at low power level of 7.8 kW. By applying pulsed mode in the plasma, a high flux (order of 10¹⁷ cm⁻³ of hydrogen in ZnO film) of chemically active species can be achieved as reported in ZnO treatment.

The reactor pressure was controlled at 200 Torr. SiHCl₃ or SiCl₄ source in cylinder was kept at 10 °C and -10 °C, and it was introduced into the chamber from side port by Ar carrier gas in the range from 50 to 75 sccm corresponding to amount of supplying Si from 340 to 510 μmol/min. Sapphire and silicon substrates were placed on the position at 10 cm below the bottom of rf coil. Temperature near the substrate was ~1000°C detected by thermo couple. In order to supply more H₂ gas, it was also introduced from side port, not through the plasma region. The plasma was characterized by optical emission spectroscopy (Stellarnet Bluewave UVNb). Materials deposited on the substrates were characterized by Raman spectroscopy (Nihon Bunko, NR-1800) and x-ray diffraction (XRD).

3. Results and discussion

3.1 Effect of hydrogen radical on decomposition of SiHCl₃ source

Figure 2 shows Raman spectra for materials deposited on sapphire substrates in the thermal plasma under three kinds of sheath gas condition, when SiHCl₃ source gas was introduced for 5 min. Under the continuous plasma of only Ar sheath gas, H₂ and H₃ emissions are not observed, and Raman peak at around 520 cm⁻¹ corresponding to crystalline silicon is not detected (Fig. 2(a)). When H₂ gas of 5 SLM was introduced from the side port (not through the plasma), H₆ and H₈ peaks are observed, implying that hydrogen radical may be generated by the Ar plasma (Fig. 2(b)).

The Raman peak at 520 cm⁻¹ is clearly detected. Temperature near the substrate was 700 °C under the continuous Ar sheath gas plasma. Although Si was hardly generated at this temperature in Siemens process, Si was confirmed to be produced under hydrogen radical. This indicates that hydrogen radical must enhance the reducing reaction of SiHCl₃ source at lower temperature. Furthermore, H₂ gas was added into Ar sheath gas to increase hydrogen radical as shown in Fig. 2(c). Si production was confirmed not only from Raman spectrum but also from XRD as shown in the inset of Fig. 2(c).
3.3 Comparison between SiHCl₃ and SiCl₄

Alternatively, SiCl₄ source was introduced into the pulsed thermal plasma. Raman spectra of materials grown on sapphire substrate exhibits a sharp peak at 520 cm⁻¹ as shown in Fig. 3, compared to that from SiHCl₃ supplied with the same amount. Si material from SiCl₄ shows better crystalline quality than that from SiHCl₃.

In order to understand the effect of hydrogen radical qualitatively, thermodynamic calculations were performed for the reactions of reducing chlorosilane gases in H₂ and hydrogen radical in follow.

\[
\begin{align*}
    \text{H}_2(\text{g}) + \text{SiHCl}_3(\text{g}) & \rightarrow \text{Si}(\text{s}) + 3\text{HCl}(\text{g}) & (1) \\
    2\text{H}_2(\text{g}) + \text{SiCl}_4(\text{g}) & \rightarrow 4\text{HCl}(\text{g}) + \text{Si}(\text{s}) & (2) \\
    2\text{H}(\text{g}) + \text{SiHCl}_3(\text{g}) & \rightarrow \text{Si}(\text{s}) + 3\text{HCl}(\text{g}) & (3) \\
    4\text{H}(\text{g}) + \text{SiCl}_4(\text{g}) & \rightarrow \text{Si}(\text{s}) + 4\text{HCl}(\text{g}) & (4)
\end{align*}
\]

For thermodynamic calculation, standard formation enthalpy (\(\Delta H^\circ\)) and standard entropy (\(S^\circ\)) of reaction species are necessary. Temperature dependence of Gibbs Energy was calculated using stored data in the program, MALT-2 [10].

![Figure 3](image.png)

**Figure 3** Raman spectra for samples prepared on c-plane sapphire substrates from SiHCl₃ (blue) and SiCl₄ (red) source supplied with the same amount.
calculation parameters for partial pressure of H$_2$, H, HCl, SiHCl$_3$, and SiCl$_4$ were determined from the actual experimental condition of the pulsed thermal plasma. It was assumed that hydrogen radical might be generated at rate of ~2%.

Open and closed circles in Fig. 4 are calculated $\Delta G$ of the reaction (1) and (2), respectively. Since the value of $\Delta G$ is negative at temperatures higher than 600 °C, it suggests the possibility of Si production from SiHCl$_3$ and SiCl$_4$ under H$_2$ partial pressure of 5.7x10$^{-2}$ atm. Since $\Delta H^\circ$ of hydrogen radical at 298.15 K is 218.0 kJ/mol, which is much larger than that of H$_2$ gas, it can be expected that reduction of SiHCl$_3$ can be accelerated by using hydrogen radical. $\Delta G$ of reaction (3) shows much lower than those of reaction (2). This tendency is remarkable for SiCl$_4$ source gas, because $\Delta G$ becomes much further lower. This indication is qualitatively consistent with the experimental results using hydrogen radical as reduction gas.

In order to explain better crystalline quality of Si from SiCl$_4$, the intensities of H$_\alpha$ and Cl at 542.5nm emissions in the plasma were measured. Figure 5 shows the relationship between H$_\alpha$ and Cl intensities emitting from the pulsed plasma for 10 min. Both H$_\alpha$ and Cl are generated more for SiCl$_4$ rather than SiCl$_3$ source. This implies that SiCl$_4$ must react more intensively with hydrogen radical, which is consistent with the thermodynamic calculation. Through reacting with hydrogen radical, chlorosilane can deposit Si containing partially hydrogenated amorphous Si on substrate. Assuming that Cl$^-$ ion could etch the amorphous Si, better crystalline quality was obtained for the case of SiCl$_4$ source.

### 3.4 Mass analysis in SiHCl$_3$ and SiCl$_4$ plasma

Since the amount of chlorosilane gas was less by four orders magnitudes than that of Ar gas in the pulsed thermal plasma, it was difficult to detect the mass numbers related to the source. We used typical capacitance-coupled plasma to investigate the reaction with hydrogen radical. SiHCl$_3$ or SiCl$_4$ source was introduced by using Ar or H$_2$ carrier gas of 30 sccm. RF (13.56 MHz) power was applied with 0–90 W under 20 mTorr of pressure. By using quadrupole mass spectroscopy from 1 to 200 amu (MKS e-Vision$^\text{Tm}$), the reducing reaction in the plasma were analyzed. Simultaneously, the optical

![Figure 4](image)

**Figure 4.** Thermodynamic calculation for SiHCl$_3$ and SiCl$_4$ reacting with H$_2$ and hydrogen radical, taken partial pressures of H$_2$ (5.7x10$^{-2}$ atm), H (1.2x10$^{-3}$ atm), HCl, SiHCl$_3$, and SiCl$_4$ (1.2x10$^{-4}$ atm) under conditions close to the pulsed thermal plasma.

![Figure 5](image)

**Figure 5** Relationship between H$_\alpha$ and Cl intensity in optical spectroscopy detected from the pulsed thermal plasma under SiHCl$_3$ and SiCl$_4$ source. The detecting time was 10 min after the source was introduced. Plasma lower power was 7.8 kW, and on-time of 10 msec and off-time of 5 msec.
spectroscopy was also observed. When SiHCl$_3$ or SiCl$_4$ source was introduced, the intensity of mass number at 36.5 amu corresponding to HCl was increased. We used this variation of HCl intensity as the index for the analysis of reaction. Figure 6(a) shows the variation of HCl and SiHCl$_3$ with and without H$_2$ ambient as a function of rf power. Intensity of SiHCl$_3$ is constant over 20W without H$_2$ gas, while it occurs continuously decreased with increase of rf power under H$_2$ ambient. The effect of H$_2$ ambient was remarkable in SiCl$_4$ as shown in Fig. 4(b). While no decomposition of SiCl$_4$ is confirmed under no H$_2$ gas, the reaction is enhanced due to H$_2$ ambient. Figure 7 shows the variation of H$_\alpha$ intensity under the gas conditions. With increase of RF power, the intensity gradually enhanced. However, the intensity of H$_\alpha$ emission drops at the same rf power when SiHCl$_3$ or SiCl$_4$ source was put into the plasma. Assuming that hydrogen radical must decompose SiHCl$_3$ or SiCl$_4$ before emitting H$_\alpha$, it is considered that the depression of H$_\alpha$ intensity indicates the effectiveness of hydrogen radical for the decomposition. The H$_\alpha$ intensity was much decreased in case of SiCl$_4$ source. The effect of hydrogen radical seems to be remarkable for SiCl$_4$. It is expected that hydrogen radical can be used to produce Si effectively from SiCl$_4$ which is by-product in Siemens process.

Figure 6. Variation of mass numbers corresponding to HCl and chlorosilane source of (a) SiHCl$_3$ and (b) SiCl$_4$ as a function of rf power applied to capacitance coupled plasma generated in 20 mTorr with and without H$_2$ gas.

Figure 7. Correlation between H$_\alpha$ intensity and RF power under the conditions of 20mTorr, H$_2$ and Ar of 30 sccm, respectively. Source materials of SiHCl$_3$ and SiCl$_4$ were carried by Ar of 30sccm.
4. Conclusions
We have proposed the use of hydrogen radical to improve the yield of Si production in Siemens process. When hydrogen radical generated from pulsed thermal plasma was applied, it made the temperature of Si production lower for SiHCl$_3$ source. It was found that hydrogen radical worked well for decomposition of SiCl$_4$ by-product in Siemens process. This was consistent with the thermodynamic calculation predicting that the use of hydrogen radical instead of H$_2$ gas could drastically enhance the yield of Si production.

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