Thermodynamic Behavior of SiCl₄ in Hydrogenation System of Siemens Process

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Abstract: The modified Siemens process is the major process of producing polysilicon through current technologies. The main by-production SiCl₄ converting to SiHCl₃ by hydrogenation process is an effective manner for reducing the cost. The temperature, pressure and initial molar ratio of H₂ to SiCl₄ have vital influence on the SiCl₄ converting ratio. When all of those are close to the practical production conditions, the residual ratio of SiCl₄ in the Siemens process for the production of polysilicon can be calculated. We mainly discuss that the temperature, pressure and initial molar ratio of H₂ to SiCl₄ have effect on the SiCl₄ converting ratio. The results show that the residual ratio of SiCl₄ decreases with increasing temperature when other conditions constant. The decreasing rate with increasing temperature is quicker when the constant initial molar ratio of H₂ to SiCl₄ is larger and the pressure is lower. The pressure has little effect on the residual ratio of SiCl₄ with other conditions remain unchanged. The initial molar ratio of H₂ to SiCl₄ has a negative effect on the residual ratio of SiCl₄ and the residual ratio of SiCl₄ decreases more slowly with the temperature higher, when other conditions constant. The residual ratio of SiCl₄ decreases more quickly with increasing the initial molar ratio of H₂ to SiCl₄ when the temperature is higher. However, the residual ratio of SiCl₄ decreases with almost a constant rate in any pressure when the initial molar ratio of H₂ to SiCl₄ increases.

1. Introduction
Polycrystalline silicon is the basic raw material in electronic and solar photovoltaic power generation industries. With the rapid development of the electronic industry, especially under the great foreground of photovoltaic (PV) industry, polysilicon manufacturing industry has increased with every year 15-30% speed in the last ten years[1]. The polysilicon production process mainly has the modified Siemens process, vapor-liquid deposition method[2], free-space method[3], metallurgy method[4] and fluidized bed method[5]. At present, polysilicon is mainly industrially produced by the modified Siemens
process, which is used to produce electronic grade polysilicon, and the production of polysilicon is the largest in the process of improving Siemens process, the production of polysilicon contributes approximately to 25-33% of the overall cost of the solar panels, and it requires about 30-40% of the total energy in their fabrication\cite{6}\cite{7}. Modified Siemens process based on the Siemens process technology, adding recycling system, reducing exhaust gas dry Si Cl$_4$ hydrogenation process, realized the closed cycle, also called (closed loop type Si HCl$_3$ hydrogen reduction method). The modified Siemens process main steps are the syntheses of SiHCl$_3$ by MG-Si reacting with HCl, (which is produced on-site as well by Cl$_2$ reacting with H$_2$), followed by the distillation purification of SiHCl$_3$, silicon deposition by SiHCl$_3$ reacting with hydrogen and hydrogenation of by-product SiCl$_4$ for recycle. It is noted that the process of the reduction of SiHCl$_3$ for deposition polysilicon is the heart of the Siemens process\cite{8}. However, how to increase the conversion ratio from SiCl$_4$ to SiHCl$_3$ is a challenge for other studies. Many preparation methods of trichlorosilane from silicon tetrachloride are presently being studied\cite{9}. However, few thermodynamic studies exist on the process. But the thermodynamic behavior of SiCl$_4$, which depicts the SiCl$_4$ converting ratio is very important. Therefore, the present study is aimed at investigating the thermodynamic behavior of SiCl$_4$ in the SiCl$_4$ hydrogenation system of the modified Siemens process in order to provide effective theory for the production process.

2. The Thermodynamic Characters in "Si-H-Cl"

Sirtl et al\cite{10}, Hunt and Sirtl\cite{11} proposed that there may be 15 reactions in the high temperature hydrogenation process. Based on the analysis of thermodynamics and actual chemicals, there may be dozen of components in the SiCl$_4$ hydrogenation system, for example, H$_2$(g), SiCl$_4$(g), HCl(g), SiHCl$_3$(g), SiCl$_2$(g), Si(s), SiH$_2$Cl$_2$(g), SiH$_3$Cl(g), SiH$_4$(g) and SiCl(g). Among the above components, the first and eight components are the main ones. Based on the method of Brinklev\cite{12}, five reactions are independent among the fifteen reactions that may exist in the SiCl$_4$ hydrogen system and the others are linear combinations of the five independent reactions. All of the reactions are gas phase reactions in the conversion process of SiCl$_4$ into SiHCl$_3$, and there is no solid silicon in the process. Furthermore, the main components in the reactions are SiCl$_4$, SiHCl$_3$ and SiH$_2$Cl$_2$. Therefore, the following 5 reactions can be selected as a group of independent reactions.

\[
\begin{align*}
\text{SiCl}_4(g) + H_2(g) &= \text{SiHCl}_3(g) + HCl(g) \quad \text{(main reaction)} \\
\text{SiCl}_4(g) + H_2(g) &= \text{SiCl}_2(g) + 2HCl(g) \\
2\text{SiHCl}_3(g) &= \text{SiCl}_4(g) + \text{SiH}_2\text{Cl}_2(g) \\
\text{SiH}_2\text{Cl}_2(g) + H_2(g) &= \text{SiH}_3\text{Cl}(g) + HCl(g) \\
\text{SiHCl}_3(g) &= \text{SiCl}_2(g) + HCl(g)
\end{align*}
\]

Based on the thermodynamic data for the related pure matter reported by Kee et al\cite{13}, the amount of the species exist in the hydrogenation system can be calculated when the five reactions reach equilibrium.

3. The calculated results and analysis

The residual ratio of SiCl$_4$ ($y$) can be calculated using the following equation.

\[
y = \frac{n_{\text{SiCl}_4,\text{Eq}}}{n_{\text{SiCl}_4,\text{in}}}
\]

Here, $y$ is the residual ratio of SiCl$_4$, $n_{\text{SiCl}_4,\text{Eq}}$ is the molar content of SiCl$_4$ when the reactions reach equilibrium; and $n_{\text{SiCl}_4,\text{in}}$ is the feed molar content of SiCl$_4$.

3.1 Influence of Temperature on residual ratio of SiCl$_4$

The residual ratio of SiCl$_4$ ($y$) decreases, when increasing temperature when pressure and initial molar
ratio of H$_2$ to SiCl$_4$ is kept constant, as shown in Figure 1 and Figure 2. SiCl$_4$ which is reactant in reactions (1) and (2) decreases with increasing temperature because the value of $K_p^0$ for the main reaction (1) increases slightly and the value of $K_p^0$ for the side-reaction (2) reported by Y. Hou et. al[14] (2011). However the value of $K_p^0$ for the reactions (3) remains substantially constant reported by Y. Hou et. al[14], so the amount of SiCl$_4$ keeps unchanged with increasing temperature in the reactions (3). Therefore, the residual ratio of SiCl$_4$ ($y$) decreases with increasing temperature. It is obvious that the temperature has a positive effect on the hydrogenation process. However, it is noticed that the amount of SiCl$_2$ increasing quickly with increasing temperature due to the values of $K_p^0$ for reactions (2) and (5) increase quickly and upon quenching SiCl$_2$ goes to SiHCl$_3$ and SiCl$_4$ under hydrogenation atmosphere. Therefore, it is consumption of energy when the temperature is too high.

The residual ratio of SiCl$_4$ decreases more quickly when the initial molar ratio of H$_2$ to SiCl$_4$ is higher as shown in Figure 1, for example, the residual ratio of SiCl$_4$ decreases from 0.8565 to 0.3798 by decreasing ratio of 55.66% when the temperature increases from 800℃ to 1300℃ under 0.1MPa and $n_{H_2}/n_{SiCl_4}$ of 2 against decreasing ratio of 77.36% with from 0.7623 to 0.1726 under 0.1MPa and $n_{H_2}/n_{SiCl_4}$ of 6. Figure 2 illustrates the residual ratios of SiCl$_4$ are a constant under different press when the temperature is kept constant and decreases more quickly when the press is lower. The residual ratios of SiCl$_4$ are 0.8565 under 0.1MPa and 0.5MPa, but it is 0.3798 with decreasing 55.66% under 0.1MPa compared to 0.4960 with decreasing 42.1% under 0.5MPa at 800℃ and $n_{H_2}/n_{SiCl_4}$ of 2.

3.2 Influence of press on residual ratio of SiCl$_4$

Fig. 1 The diagrams of the residual ratio of SiCl$_4$ versus temperature at P=0.MPa (a), 0.3MPa(b), and 0.5MPa(c)

Fig. 2 The diagrams of the residual ratio of SiCl$_4$ versus temperature at $n_{H_2}/n_{SiCl_4}$ of 2(a), 4(b) and 6(c)
Fig. 3 The diagrams of the residual ratio of SiCl$_4$ versus press at $T=800^\circ$C(a), 1100 $^\circ$C(b), and 1300 $^\circ$C(c)

Fig. 4 The diagrams of the residual ratio of SiCl$_4$ versus press at $n_{H_2}/n_{SiCl_4}$ of 2(a), 4(b) and 6(c)

When the pressure increases with temperature and initial molar ratio kept constant, the residual ratio of SiCl$_4$ keeps constant at lower temperature and increases slightly when temperature is higher than 1000$^\circ$C as shown in Figure 3 and Figure 4. For the following reasons (1) For reactions (1), (3) and (4), the equilibrium constant $K$ kept constant when the pressure increases, because the total amount of gas does not change when the reactions reach a new equilibrium. However, reactions (2) and (5), the total amount of gas increases if the reactions goes towards the substance and reach a new equilibrium. So the equilibrium will change and the reactions go towards the reactant when the pressure increases. Therefore the residual ratio of SiCl$_4$ increases since SiCl$_4$ is the reactant in reaction (2) However, when the temperature is lower, the date of $K_p^*$ is small which is reported by Hou et. al [14]. That shows the amount of substance is very small. So the equilibrium change little when the pressure increases.

The pressure have little effect on the residual ratio of SiCl$_4$. But it is noticed that the amount of SiHCl$_3$ which is reactant in reaction (5) increases when the pressure increases. So increasing pressure properly is necessary in the actual Hydrogenation process.

3.3 Influence of initial molar ratio of H$_2$ and SiCl$_4$ on residual ratio of SiCl$_4$
When temperature and pressure kept constant, the initial feeding molar ratio of H₂ and SiCl₄ must increase with decreasing the residual ratio of SiCl₄ when there are only H₂ and SiCl₄ as reactant as shown in Figure 3 and Figure 4. For main reaction (1) in hydrogenation system of Siemens process, increasing $n_{H_2}/n_{SiCl_4}$ must force the reaction towards the substance. Thus the amount of SiCl₄ decreases and the amount of SiHCl₃ increases. And for reactions (1) and (2), the amount of HCl increases with $n_{H_2}/n_{SiCl_4}$ increases. Thus for reaction (5), the reaction goes towards reactant which is SiHCl₃. The amount of intermediate SiCl₂ decreases and the amount of SiHCl₃ increases. It is obvious that increasing the initial molar ratio of H₂ and SiCl₄ has a positive effect on the hydrogenation process.

Fig. 5 The diagrams of the residual ratio of SiCl₄ versus $n_{H_2}/n_{SiCl_4}$ at $T=800^\circ$C (a), $1100^\circ$C (b), and $1300^\circ$C (c)

Fig. 6 The diagrams of the residual ratio of SiCl₄ versus $n_{H_2}/n_{SiCl_4}$ at $P=0.1$ MPa (a), 0.3 MPa (b), and 0.5 MPa (c)

The residual ratio of SiCl₄ decreases more slowly with the temperature increases higher. For example, the residual ratio of SiCl₄ decreases from 0.6723 to 0.5671 with decreasing 15.65% when $n_{H_2}/n_{SiCl_4}$ increases from 2 to 4 against 12.33% with from 0.5671 to 0.4972, when $n_{H_2}/n_{SiCl_4}$ increases from 4 to 6 under 1100°C and 0.3 MPa. Therefore the initial molar ratio of H₂ and SiCl₄ should be controlled proper scope or there exists the next problems: (1) Increasing $n_{H_2}/n_{SiCl_4}$ has only a slight positive effect on the conversion ratio from SiCl₄ to SiHCl₃. Thus, the mass of H₂ should be handled as exhaust with the other by-products. The cost in the conversion from SiCl₄ to SiHCl₃ must rise greatly. (2) The molar concentration of by-product HCl also increases with increasing the initial molar ratio ($n_{H_2}/n_{SiCl_4}$). That makes it more difficult to deal with by-products. (3) The separation of HCl from H₂ is difficult with the current technology and the cost is high.
The residual ratio of SiCl₄ decreases more quickly with increasing $n_{\text{H}_2}/n_{\text{SiCl}_4}$ at higher temperature as shown in Figure 6, for example, the residual ratio of SiCl₄ decreases from 0.8579 to 0.7646 with decreasing 10.88% at 800°C against 45.49% from 0.4641 to 0.253 at 1300°C under 0.3MPa when from $n_{\text{H}_2}/n_{\text{SiCl}_4}$ 2 to 6. However the residual ratio of SiCl₄ decrease with almost a constant rate in any press when the initial molar ratio of H₂ to SiCl₄ increases, as shown in Figure 5.

4. Conclusions

(1) The residual ratio of SiCl₄ decreases with increasing temperature when the pressure and initial molar ratio of H₂ to SiCl₄ is kept constant. The decreasing rate with increasing temperature is quicker when the constant initial molar ratio of H₂ to SiCl₄ is larger and the pressure is lower.

(2) The pressure has little effect on the residual ratio of SiCl₄ with temperature and initial molar ratio of H₂ to SiCl₄ unchanged.

(3) When the temperature and pressure are kept constant, the initial molar ratio of H₂ to SiCl₄ has a negative effect on the residual ratio of SiCl₄ and the residual ratio of SiCl₄ decreases more slowly with the temperature increases higher.

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