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Thermodynamic behaviors of $SiCl_2$ in silicon deposition by gas phase zinc reduction of silicon tetrachloride ☆

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A B S T R A C T

The modified Siemens process, which is the major process of producing polycrystalline silicon through current technologies, is a high temperature, slow, semi-batch process and the product is expensive primarily due to the large energy consumption. Therefore, the zinc reduction process, which can produce solar-grade silicon in a cost effective manner, should be redeveloped for these conditions. The $SiCl_2$ generation ratio, which stands for the degree of the side reactions, can be decomposed to $SiCl_4$ and $ZnCl_2$ in gas phase zinc atmosphere in the exit where the temperature is very low. Therefore, the lower $SiCl_2$ generation ratio is profitable with lower power consumption. Based on the thermodynamic data for the related pure substances, the relations of the $SiCl_2$ generation ratio and pressure, temperature and the feed molar ratio (n_{Zn}/n_{SiCl_4}) are investigated and the graphs thereof are plotted. And the diagrams of K_p^Θ–T at standard atmosphere pressure have been plotted to account for the influence of temperature on the $SiCl_2$ generation ratio. Furthermore, the diagram of K_p^Θ–T at different pressures have also been plotted to give an interpretation of the influence of pressure on the $SiCl_2$ generation ratio. The results show that $SiCl_2$ generation ratio increases with increasing temperature, and the higher pressure and excess gas phase zinc can restrict $SiCl_2$ generation ratio. Finally, suitable operational conditions in the practical process of polycrystalline silicon manufacture by gas phase zinc reduction of $SiCl_4$ have been established with 1200 K, 0.2 MPa and the feed molar ratio (n_{Zn}/n_{SiCl_4}) of 4 at the entrance. Under these conditions, $SiCl_2$ generation ratio is very low, which indicates that the side reactions can be restricted and the energy consumption is reasonable.

1. Introduction

Research into alternative energy sources for electricity production is of considerable value globally in view of the ever-increasing cost and diminishing supply of petroleum fuels. As a result, high-efficiency solar energy conversion has become a subject receiving attention due to being environmentally friendly process and having no impact on the thermal balance of the planet [1,2]. Polycrystalline silicon is presently one of the best materials for application in photovoltaic energy conversion. Other materials may be found as the primary material instead of silicon in the photovoltaic industry in the next at least 50 years [3, 4]. The cost of raw material-polycrystalline silicon-amounts to about 20% of the cost of a silicon solar cell [5–8]. Therefore, the cost of polycrystalline silicon has a considerable influence on the cost of the solar cell. Solar energy power technology has developed quickly, which results in the cost of polycrystalline silicon increasing quickly in recent years. Therefore, the photovoltaic industry was inhibited [9]. The modified Siemens process is the primary technology for manufacturing polycrystalline silicon production at present [10]. However, the technology is controlled by seven companies around the world, having a silicon yield of 76.7% of the total [11]. The modified Siemens method has some advantages, for example safety, mature technology, and high purity of product. However, the cost is high with the current technologies. At present, intensive research efforts have been concentrated on reducing the cost of polycrystalline silicon with this method. However, efficient results have not been achieved presently [12,13]. Therefore, it is very important to find new technologies for silicon production for high-efficiency solar cells to lower the manufacturing cost of high-purity silicon. Although the gas phase zinc reduction method had

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been developed over nearly 50 years, it was displaced by the Siemens method due to the purity of silicon being not up to electro-grade. However, Battelle's Columbus laboratories restudied the method upon an urgent request to curb the cost of polycrystalline silicon. The results show that the efficiency of web-dendrite solar cells made from the material by gas phase zinc reduction process is indistinguishable from that of those made from semiconductor-grade silicon [14]. A thorough study into the process was started by an SST company in Japan and the purity of silicon above 6N (99.9999%) silicon was obtained [15]. Presently, the industrialization research on the process is being developed by three companies in Japan, achieving silicon purity up to 8N (99.999999%) [16]. From the analysis above, it is obvious that the zinc reduction process has been developed as an important method for manufacturing a low-cost polycrystalline silicon. The main side-reactions are $SiCl_4(g) + Zn(g) \rightarrow SiCl_2(g) + ZnCl_2(g)$ and $SiCl_4(g) + Si(s) \rightarrow SiCl_2(g)$ reported by Hou [17]. It is noted that $SiCl_2$ is the main by-product in zinc reduction process and it, as we know, can decompose into $SiCl_4$ and $ZnCl_2$ in gaseous zinc atmosphere. The process is a consumption of material and power. So the thermodynamic behavior of $SiCl_2$ is very important in gas phase zinc reduction of $SiCl_4$ process for manufacturing polycrystalline silicon. Thereby, the thermodynamic behavior of $SiCl_2$ is studied in the paper and the interesting results of the optimum conditions, under which the by-product $SiCl_2$ can be restricted, are hoped to be obtained.

2. Thermodynamic Characters in Zinc Reduction Process

Hou [17] has reported that there may be 10 kinds of components when the reactions, which are present in the gas phase zinc reduction of $SiCl_4$ process for manufacturing polycrystalline silicon, reach equilibrium, for example, Si(s), $ZnCl_2$(g), $SiCl_4$(g), Zn(g), $SiCl_2$(g), Zn_2Cl_4(g), ZnCl(g), $SiCl_3$(g), SiCl(g), Cl(g) and Cl_2(g). Among the above components, the first five are the main ones. The other components are scarce and can be neglected in the equilibrium gas phase composition analysis. And the reactions, which may occur in gas phase zinc reduction of $SiCl_4$ for manufacturing polycrystalline silicon, have been obtained as following [17]:

$$SiCl_4 + 2Zn \rightarrow Si + 2ZnCl_2 \text{(main reaction)} \quad (1)$$

$$SiCl_4(g) + Zn(g) \rightarrow SiCl_2(g) + ZnCl_2(g) \quad (2)$$

$$SiCl_4(g) + Si(s) \rightarrow 2SiCl_2(g) \quad (3)$$

It is noted that $SiCl_2$ is the main product in the Side-reactions (2) and (3). $SiCl_4$ is converted into $SiCl_2$ in Reduction reaction (2) by gas phase zinc. It is a waste of $SiCl_4$. And the solid silicon is eroded by $SiCl_4$ in Reaction (3) in which $SiCl_2$ is the only product. It is noted that $SiCl_2$ can decompose into $SiCl_4$ and $ZnCl_2$ in gaseous zinc atmosphere and the process is a consumption of material and power. Thus, it not only is a waste of material $SiCl_4$ but also increases the power consumption when the Reactions (2) and (3) occur. Furthermore, the productive ratio of silicon decreases since the side-reactions occur in the process. Therefore, the thermodynamic behaviors of $SiCl_2$ have a great effect on gas phase zinc reduction of $SiCl_4$ process for manufacturing polycrystalline silicon.

Based on the thermodynamic data for the related pure substances listed in Table 1, the thermodynamic behaviors of $SiCl_2$ can be analyzed in the gas phase zinc reduction of $SiCl_4$ process for manufacturing polycrystalline silicon.

Table 1
Thermodynamic data for related pure substances (Sp.); all data are taken from compilation of Ye and Hu [18]; enthalpies and entropies are refereed to stand conditions (*i.e.*, 0.1 MPa and 298 K) and are expressed in J/mol and in J/mol K: specific heats can be calculated from the reported values as: $C_p = C_{p,m} = A_1 + A_2 \times 10^{J\cdot mol\text{-}1\cdot K\text{-}13}\ T + A_3 \times 10^5\ T^{-2}$

Sp.	$\Delta_f H_m^\Theta$/ $J\cdot mol^{-1}$	S_m^Θ/ $J\cdot mol^{-1}\cdot K^{-1}$	A_1/ $J\cdot mol^{-1}\cdot K^{-1}$	A_2/ $J\cdot mol^{-1}\cdot K^{-1}$	A_3/ $J\cdot mol^{-1}\cdot K^{-1}$	T/K
Si	0	18.828	22.803	3.849	−3.515	298–1685
			27.196	0	0	1685–3492
$ZnCl_2$	−416,308	108.366	60.668	23.012	0	298–519
			100.834	0	0	519–1005
			60.250	0.837	0	1005–2000
$SiCl_4$	−687,640	239.743	146.440	0	0	298–334
			101.462	6.862	−11.506	334–2000
Zn	0	41.631	20.736	12.510	0.833	298–693
			31.380	0	0	693–1184
			20.786	0	0	1184–2000
$SiCl_2$	−164,431	281.834	57.572	0.377	−5.648	298–2200

3. Thermodynamic Behaviors of $SiCl_2$

$SiCl_2$ generation ratio (x), which can be calculated from the following equation, is employed to describe the degree of Side-reactions (2) and (3).

$$x = n_{SiCl_2-Eq}/n_{SiCl_4-in} \quad (4)$$

where x is the $SiCl_2$ generation ratio, n_{SiCl_2-Eq} is the molar content of $SiCl_2$ when the reactions reach equilibrium and n_{SiCl_4-in} is the feed molar content of $SiCl_4$.

$SiCl_2$ generation ratio can indicate the degree of side reactions in gas phase zinc reduction process. Smaller $SiCl_2$ generation ratio, which shows the side reactions are restricted, stands for the higher polycrystalline silicon yield ratio. Thus, $SiCl_2$ generation ratio can also been employed to describe the polycrystalline silicon yield ratio.

3.1. Influence of temperature on $SiCl_2$ generation ratio

$SiCl_2$ generation ratio was analyzed while changing the temperature with the pressure and the molar ratio unchanged. Because the reactant must be in the gaseous state, the minimum temperature for analysis should be up to the boiling point of zinc (1184 K). Diagrams of $SiCl_2$ generation ratio x *versus* temperature can be plotted under 0.1 MPa, 0.3 MPa and 0.6 MPa, and feed molar ratios (x_{SiCl_4}/x_{Zn}) of 1:2, 1:4 and 1:8 as shown in Figs. 1 and 2, respectively.

$SiCl_2$ generation ratio increases with increasing temperature when pressure and feed molar ratio of Zn to $SiCl_4$ are kept as a constant as shown in Figs. 1 and 2. And $SiCl_2$ generation ratio increases slowly when the temperature is lower and becomes more quick when the temperature is higher. The reasons for that should be addressed from equilibrium constant (K_p^Θ). Based on the thermodynamic data for the related pure components listed in Table 1, the relations of standard free energy ($\Delta_r G_m^\Theta$) *versus* temperature for Reactions (1)–(3) can be calculated, as shown in the following equations:

$$\Delta_r G_m^\Theta(1) = -0.269T\ln T + 0.7 \times 10^{-3}T^2 - 3.996 \times 10^5 T^{-1} - 159662 + 116.772T \quad (5)$$

$$\Delta_r G_m^\Theta(2) = 4.426T\ln T + 2.824 \times 10^{-3}T^2 - 2.929 \times 10^5 T^{-1} + 85374 - 51.733T \quad (6)$$

$$\Delta_r G_m^\Theta(3) = 9.121T\ln T + 4.979 \times 10^{-3}T^2 - 1.863 \times 10^5 T^{-1} + 330410 - 220.237T \quad (7)$$

where T is the temperature.

It is noted that the numbers (1, 2, 3) in the brackets on the left hand of Eqs. (5)–(7) stands for Reactions (1), (2) and (3),