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Kyoto University
Silicon Electrodeposition in a Water-Soluble KF–KCl Molten Salt: Utilization of SiCl4 as Si Source

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The electrodeposition of Si was investigated in a molten KF–KCl salt mixture (eutectic composition, 45:55 mol%) after the introduction of SiCl4 to demonstrate a new production method for solar cell substrates. Gaseous SiCl4 was introduced directly into the molten salt at 1023 K by a vapor transport method using Ar as a carrier gas. The dissolution efficiency of SiCl4 exceeded 80% even when a simple tube was used for bubbling. Galvanostatic electrolysis was conducted at 923 K on a Ag substrate at 155 mA cm−2 for 20 min in the molten KF–KCl salt mixture after the dissolution of 2.30 mol% SiCl4. Although a compact Si layer was formed, its smoothness was inferior to that obtained from the melt after the addition of K2SiF6. The molar fraction of the fluoride anion is suggested as one of the factors affecting the morphology of the deposits.

The current production method for the Si substrates used in photovoltaic cells consists of multiple processes, including a slicing step of the high-purity Si ingots produced by the Siemens process. This method has several drawbacks in terms of energy efficiency and yield because of the low productivity of the Siemens process and the considerable kerf loss in the slicing step. Thus, the development of an alternative efficient process for manufacturing crystalline Si substrates is necessary to enable significant improvements for the photovoltaic industry.

The direct formation of Si films has been investigated as one of the alternative methods for producing polycrystalline Si solar cells. The electrodeposition of crystalline Si using high-temperature molten salts has been reported by several researchers since the 1970's.1–10 The use of fluoride-based molten salts, such as LiF–KF and LiF–NaF–KF, is effective for obtaining compact and smooth Si films.12,5,9,10 However, previous investigations that employed fluoride-based molten salts found that the low solubility of LiF and NaF in water makes the removal of the salt that adheres to the deposited Si a major problem.10,11 Another essential problem is the lack of high-purity and low-cost Si sources, on which the process previously studied was based. Conventionally, either K2SiF6 or the anodic dissolution of a Si rod was utilized as the supply of Si ions. However, the low-cost preparation of K2SiF6 and Si rods of solar-grade purity is difficult.

We proposed and investigated a new electrodeposition process for the formation of Si films from a molten KF–KCl electrolyte with high-purity gaseous SiCl4 as a Si source (Fig. 1), with the aim of developing a new method for the production of polycrystalline Si films for solar cells.12,14 In this process, gaseous SiCl4 is dissolved into the molten salt to form Si(IV) complex ions. Si films are then electrodeposited onto the cathode of an appropriate substrate, and Cl2 gas is evolved at a carbon anode. The salt that adhered to the Si deposit is easily removed by washing with water.

\[
\text{SiCl}_4 \text{ dissolution: } \text{SiCl}_4 (g) + 6 \text{F}^- \rightarrow \text{SiF}_6^{2-} + 4 \text{Cl}^- + 3 \text{e}^- \quad [1]
\]

\[
\text{Cathodic reaction: } \text{SiF}_6^{2-} + 4 \text{e}^- \rightarrow \text{Si} (s) + 6 \text{F}^- \quad [2]
\]

\[
\text{Anodic reaction: } 4\text{Cl}^- \rightarrow 2\text{Cl}_2 (g) + 4 \text{e}^- \quad [3]
\]

Figure 1. A schematic illustration of the principle of electroplating process of Si in KF–KCl molten salt.12,13

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Figure 2. A schematic drawing of the experimental apparatus for the introduction of SiCl$_4$ by a vapor transport method.

The experimental setup is schematically illustrated in Fig. 2. Reagent-grade KF (Wako Pure Chemical Co. Ltd., >99.0%) and KCl (Wako Pure Chemical Co. Ltd., >99.5%) were mixed to form a eutectic mixture (45 mol% KF + 55 mol% KCl, melting point = 878 K\textsuperscript{16}) and loaded in a graphite crucible (Toyo Tanso Co. Ltd., o.d.: 90 mm, i.d.: 80 mm, height: 120 mm). The mixture in the crucible was first dried under vacuum at 453 K for 72 h to remove residual moisture. The crucible was placed at the bottom of a quartz vessel in an air-tight Kanthal container with a stainless-steel lid. The salt was further dried under vacuum at 673 K for 24 h. The experiments were conducted in a dry Ar atmosphere at 923 K or 1023 K. Liquid SiCl$_4$ (Aldrich, 99.998%) held in a Duran bottle (100 mL) was maintained at 293 K in a water bath using a thermostat (As-one, Cool Circulator CH-202). Pyrex pipes (o.d.: 6 mm, i.d.: 4 mm) connected to perfluoroalkoxy alkane (PFA) tubes (o.d.: 6.35 mm, i.d.: 4.35 mm) were attached to the screw cap (As-one, pipe diameter: 6–8 mm) of the bottle. The mixed Ar–SiCl$_4$ gas was prepared by bubbling Ar gas (20 mL min$^{-1}$, Kyoto Teisan, Inc., >99.998%) into liquid SiCl$_4$ using a Pyrex pipe. The mixed gas was bubbled into the molten eutectic KF–KCl (200 g) at 1023 K with a graphite pipe (Toyo Tanso Co., Ltd., ISO-68TS, o.d.: 12 mm, i.d.: 5 mm, length: 470 mm). After bubbling the mixed gas for the predetermined period, the lower end of the pipe was removed from the melt and the flow gas was switched to pure Ar. Then, the temperature of the melt was lowered to 923 K, at which the electrochemical measurements were carried out. The working electrodes were Ag wire (Nilaco Corp., diameter: 0.1 mm, 99.98%) and Ag flag electrodes (Nilaco Corp., thickness: 0.1 mm, 99.98%).\textsuperscript{13} A glass-like carbon rod (Tokai Carbon Co., Ltd., diam.: 5.0 mm) was used as the counter electrode. A Pt wire (Tanaka Kikinzoku Kogyo, >99.95%, diameter: 1.0 mm) was employed as a quasi-reference electrode. The potential of the reference electrode was calibrated with reference to a dynamic K$^+/K$ potential, which was prepared by the electrodeposition of metallic K on a Ag wire. The electrolyzed samples were soaked in hot distilled water at 333 K for 24 h to remove the salt adhered to the deposits and dried under vacuum for 12 h. The samples were analyzed by cross-sectional scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

Thermodynamic Calculation

Figure 3 shows the Gibbs energies for the reactions of the chlorides with fluorine gas to form the fluorides and chlorine gas.\textsuperscript{17}

\[
\frac{2}{x} \text{SiCl}_x (l, g) + F_2 (g) = \frac{2}{x} \text{SiF}_x (l, g) + \text{Cl}_2 (g) \quad (x = 1, 2, 3, 4) \tag{5}
\]

\[
2 \text{KCl} (s, l) + F_2 (g) = 2 \text{KF} (s, l) + \text{Cl}_2 (g) \tag{6}
\]

As indicated in the figure, the Gibbs energy change for the formation of SiF$_x$ and Cl$_2$ from SiCl$_4$ and F$_2$ is much more negative than for the reaction of KF + Cl$_2$ to form KCl + F$_2$. Thus, the
conversion of SiCl₄ to SiF₄ in the reaction with KF is thermodynamically favorable.¹⁷

\[
\frac{1}{2} \text{SiCl}_4 (g) + 2 \text{KF}(l) = \frac{1}{2} \text{SiF}_4 (g) + 2 \text{KCl}(l) \\
\Delta G^\circ = -221.17 \text{kJ at } 923 \text{ K} \quad [7]
\]

These thermodynamic calculations suggest that the SiCl₄ gas introduced into the KF–KCl melt is expected to dissolve to produce SiF₆²⁻ complex ions, which are highly stable in molten salts.

\[
\text{SiCl}_4(g) + 4 \text{KF}(l) \rightarrow \text{SiF}_4(g) + 4 \text{KCl}(l) \quad [8]
\]

\[
\text{SiF}_4(g) + 2 \text{KF}(l) \rightarrow 2 \text{K}^+ + \text{SiF}_6^{2-} \quad [9]
\]

**Results and Discussion**

**Vapor transport of SiCl₄**—The SiCl₄ was supplied via a vapor transport method utilizing Ar as a carrier gas and the apparatus shown in Fig. 2. The flow rate of Ar gas and the partial pressure of SiCl₄ in the mixed Ar–SiCl₄ gas were used to modulate the vapor transport rate, and these factors were controlled using a gas flow meter and a thermostat, respectively. The vapor pressure of SiCl₄, \( P_{\text{SiCl}_4} \), is determined by the temperature, \( T \), according to the following equations.¹⁸

\[
P_{\text{SiCl}_4} = 10^{(4.0977 - \frac{273}{T})} \quad (275 < T < 330 \text{ K}) \quad [10]
\]

In the present experiment system, the total gas pressure was 1 atm,

\[
P_{\text{Ar}} + P_{\text{SiCl}_4} = 1 \text{ atm} \quad [11]
\]

where \( P_{\text{Ar}} \) is the partial pressure of Ar. Thus, the flow volume rate of SiCl₄, \( f_{\text{SiCl}_4} \), is expressed as a function of the flow volume rate of Ar, \( f_{\text{Ar}} \), at 298 K.

\[
f_{\text{SiCl}_4} = f_{\text{Ar}} \cdot \frac{P_{\text{SiCl}_4}}{P_{\text{Ar}}} = f_{\text{Ar}} \cdot \frac{P_{\text{SiCl}_4}}{1 - P_{\text{SiCl}_4}} \quad [12]
\]

Thus, the transport rate of SiCl₄, \( v_{\text{SiCl}_4} \), is

\[
v_{\text{SiCl}_4} = \frac{P_{\text{Ar}}}{R} \cdot f_{\text{SiCl}_4} = \frac{P_{\text{Ar}}}{RT} \cdot \frac{P_{\text{SiCl}_4}}{1 - P_{\text{SiCl}_4}} \cdot f_{\text{Ar}} \quad [13]
\]

where \( R \) is the gas constant, and \( P_0 \) is the ambient atmospheric pressure (1.013 \times 10^5 \text{ Pa}).

The above relationships are valid only when the gas is ideal, and the evaporation is fast enough to reach equilibrium. The validity of these conditions was confirmed by flowing Ar gas (20 mL min⁻¹) into liquid SiCl₄ for 50 min at 293 K, where the value of \( P_{\text{SiCl}_4} \) is 0.257 atm, and measuring the resulting weight change. The transport rate of SiCl₄, \( v_{\text{SiCl}_4} \), is calculated from Eqs. 14 and 15.

\[
W_{\text{SiCl}_4, \text{trans}} = W_{\text{SiCl}_4, \text{bef}} - W_{\text{SiCl}_4, \text{aft}} \quad [14]
\]

**Table I. The transport rate of SiCl₄ by the vapor transport method.**

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Temperature of SiCl₄ T/K</th>
<th>Vapor pressure of SiCl₄ ( P_{\text{SiCl}_4}/\text{atm} )</th>
<th>Ar flow rate at 298 K ( f_{\text{Ar}}/\text{mL min}^{-1} )</th>
<th>Reaction time ( t/\text{min} )</th>
<th>Before reaction ( W_{\text{SiCl}_4, \text{bef}} )</th>
<th>After reaction ( W_{\text{SiCl}_4, \text{aft}} )</th>
<th>Transported ( W_{\text{SiCl}_4, \text{trans}} )</th>
<th>Transport rate ( v_{\text{SiCl}_4}/\text{mol min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td># VT-1</td>
<td>293</td>
<td>0.257</td>
<td>20</td>
<td>50</td>
<td>250.55</td>
<td>248.12</td>
<td>2.43</td>
<td>2.86 \times 10^{-4}</td>
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<td></td>
<td></td>
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<tr>
<td># VT-2</td>
<td>293</td>
<td>0.257</td>
<td>20</td>
<td>50</td>
<td>310.00</td>
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</table>

\( ^a P_{\text{SiCl}_4} = 10^{(4.0977 - \frac{273}{T})} \)

\( ^b W_{\text{SiCl}_4, \text{trans}} = W_{\text{SiCl}_4, \text{bef}} - W_{\text{SiCl}_4, \text{aft}} \)

\( ^c v_{\text{SiCl}_4} = \frac{W_{\text{SiCl}_4, \text{trans}}}{W_{\text{SiCl}_4, \text{bef}} - W_{\text{SiCl}_4, \text{aft}}} \)

\( ^d v_{\text{SiCl}_4} = \frac{P_{\text{Ar}}}{RT} \cdot f_{\text{SiCl}_4} \cdot 10^{-6} = \frac{P_{\text{Ar}}}{RT} \cdot \frac{P_{\text{SiCl}_4}}{1 - P_{\text{SiCl}_4}} \cdot f_{\text{Ar}} \cdot 10^{-6} \)

**Figure 4.** Cyclic voltammograms for a Ag flag electrode in molten KF–KCl–K₂SiF₆ (2.0 mol%) at 923 K and molten KF–KCl at 923 K after the introduction of SiCl₄. Scan rate: 0.50 V s⁻¹.
direction, a cathodic current peak is observed at 0.57 V vs. K+/K+, which corresponds to the deposition of Si. Additionally, a small cathodic current shoulder is observed at −0.8 V, which is likely caused by the reduction of impurities. The voltammogram was compared with one that was previously obtained for the melt after the addition of 2.0 mol% K2SiF6, as indicated by the broken curve in Fig. 4. The corresponding peak current densities for Si deposition are −1.742 A cm−2 and −1.521 A cm−2 in the solid curve (SiCl4) and the broken curve (K2SiF6), respectively. Since the peak current density is proportional to the Si ion concentration, we estimated that the concentration of SiF62− ions was 2.30 mol%. Thus, a melt with the optimum Si ion concentration (2.0–3.5 mol%) for the electrodeposition of compact films was successfully prepared.

The dissolution efficiency of SiCl4 (2.30 mol% dissolved) was calculated to be 80% of the supplied amount (2.86 mol%). In contrast, the supplied SiCl4 scarcely dissolved into the melt in the molten LiCl–KCl system at 723 K. Notably, we achieved a high dissolution efficiency even when a simple pipe with an inner diameter of 5 mm was used for bubbling. We expect that the time between SiCl4 gas contacting and reacting with the KF–KCl molten salt was very short in our experimental system.

The high dissolution rate of SiCl4 to the melt demonstrates that the use of SiCl4 and a KF–KCl molten salt as the Si source and electrolyte, respectively, for Si electrodeposition is highly feasible. The high reactivity is explained by the large thermodynamic driving force of the reaction between SiCl4 and KF, as shown by the thermodynamic calculation in Fig. 3 and Eq. 7. The use of a porous gas bubbler to produce finer bubbles is expected to improve the dissolution efficiency.

**Electrodeposition of Si.**—Since the voltammetry suggested the existence of some impurities in the melt, pre-electrolysis was carried out to remove them. After electrolysis at 0.95 V vs. K+/K+ for 88 min, a black deposit was obtained on a Ag wire electrode. The deposit was found to consist mainly of iron metal by EDX. A small leakage in the gas supply system would lead to the reaction of SiCl4 and moisture to form SiO2 and hydrogen chloride. The hydrogen chloride gas probably corroded a stainless-steel connector between the PFA tube and the graphite pipe, introducing iron chlorides into the molten salt.

After pre-electrolysis, the electrodeposition of Si was carried out by galvanostatic electrolysis at −155 mA cm−2 for 20 min in molten KF–KCl at 923 K after the introduction of SiCl4.

Table II. The anionic fraction of the melt after the addition of 2.00 mol% K2SiF6 and the introduction of 2.30 mol% SiCl4 into KF–KCl molten salt.

<table>
<thead>
<tr>
<th>Si source</th>
<th>F−</th>
<th>Cl−</th>
<th>SiF6²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2SiF6 (2.00 mol%)</td>
<td>44.1</td>
<td>53.9</td>
<td>2.0</td>
</tr>
<tr>
<td>SiCl4 (2.30 mol%)</td>
<td>31.6</td>
<td>66.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 5. Cross-sectional SEM images of the sample obtained by the galvanostatic electrolysis of a Ag wire electrode at −155 mA cm−2 for 20 min in molten KF–KCl at 923 K after the introduction of SiCl4.
Conclusions

The dissolution of SiCl\textsubscript{4} gas into a KF–KCl molten salt and the electrodeposition of Si from the melt were investigated. A mixed Ar–SiCl\textsubscript{4} gas containing 14.90 g of SiCl\textsubscript{4} was introduced by a gas transport method into a eutectic KF–KCl melt (200 g) at 1023 K. Cyclic voltammetry indicated that a melt with 2.30 mol\% of Si ion concentration was produced. The dissolution efficiency of SiCl\textsubscript{4} was calculated to be 80\% from measurements of the amount of SiCl\textsubscript{4} that was supplied (2.86 mol\%) and that dissolved (2.30 mol\%). A Si film was deposited on a Ag substrate at 923 K by galvanostatic electrolysis at $-155$ mA cm\textsuperscript{-2} for 20 min. Cross-sectional SEM observation confirmed that a compact Si deposit was achieved. The observed granular morphology may have been caused by the molar ratio of F– and Cl– anions, which will be confirmed in future investigations.

Acknowledgments

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References