Oscillatory Behavior in Electrochemical Deposition Reaction of Polycrystalline Silicon Thin Films through Reduction of Silicon Tetrachloride in a Molten Salt Electrolyte

Toshihiko Matsuda, Shinsuke Nakamura, Ken-ichiro Ide, Kazuiku Nyudo, Shinji Yae, and Yoshihiro Nakato*
Department of Chemistry, Faculty of Engineering Science, and Research Center for Photoenergetics of Organic Materials, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560

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A new electrochemical oscillation is found for reduction reaction of silicon tetrachloride on a partially immersed single crystal n-Si electrode in a lithium chloride-potassium chloride eutectic melt electrolyte. The reduction of $SiCl_4$, which is almost insoluble in the electrolyte, occurs mainly near the upper edge of an electrolyte meniscus on the electrode, and it is discussed that the oscillation is caused by a change in the height of the meniscus due to a change in the chemical structure (and hence the interfacial tension) of the electrode surface with progress of the silicon deposition reaction.

Polycrystalline silicon (Si) thin films have attracted growing attention as the most promising semiconductor material for low-cost and high-efficiency solar cells. Several preparation methods, physical,[1-3] chemical[4,5] and electrochemical,[6-9] have been reported. The electrochemical method is of much interest because it has potential advantages that the deposition reaction proceeds under a well-regulated current density (*i.e.*, deposition rate) at a relatively low temperature with a cheap gas such as $SiCl_4$ as the Si source. To date, the electrochemical reduction of K_2SiF_6 in molten fluorides was reported,[6] but this method needed a high temperature of 750 °C. The electrochemical reduction of $Si(OC_2H_5)_4$[7] and silicon halides[8,9] in non-aqueous organic solvents gave only amorphous films. We have started to study a new electrochemical method for the Si deposition. In the course of the studies, we have found that the Si-depositing current shows prominent oscillatory behavior which gives useful information on the mechanism of the deposition reaction.

Figure 1 schematically shows an electrochemical cell used in the present work. Highly doped single crystal n-Si(111) wafers ($(0.1\text{-}1.0)\times10^{-3}$ Ωcm, 0.5 mm thick, Shin-Etsu Handotai Co. Ltd.) were used as the cathode (working electrode), which also acted as the substrate for the Si deposition. They were cut into pieces 4 cm high and 5 mm wide, rinsed in acetone, and etched in CP4A and 9 wt% HF. Ohmic contact was made by vacuum-deposition of a 150-nm thick aluminum layer on the upper part of the wafer, followed by attachment of a nickel wire with silver paste and covering with an aluminum oxide adhesive for insulation. The counter electrode was a glassy carbon rod (Tokai Carbon Co. Ltd.). The reference electrode was an Ag/Ag^+ electrode prepared in the following way: A LiCl-KCl eutectic melt containing 0.2 $mol kg^{-1}$ silver chloride was put in a glass tube having a very thin bottom layer and a silver wire was inserted in the melt.

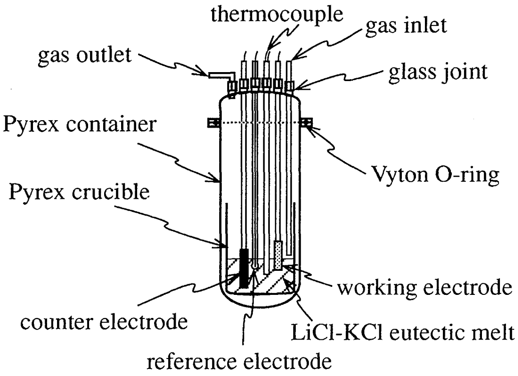

Figure 1. Schematic illustration of an electrochemical cell.

An eutectic mixture of 59 mol% LiCl and 41 mol% KCl (analytical grade) as the electrolyte was put in a Pyrex crucible, which was placed in a sealed Pyrex container, and kept under a high-purity argon (Ar) atmosphere. After the mixture was melted by heating with an electric furnace, high-purity hydrogen chloride (HCl) was bubbled through the melt for dehydration. Residual HCl in the melt was removed by further bubbling with Ar. Then, the melt was pre-electrolyzed and purified using glassy carbon and tungsten electrodes. Current-potential (*j-E*) curves were measured with the working electrode (cathode) partially immersed in the electrolyte whose temperature was kept at 450 °C (cf. Figure 1). $SiCl_4$ (99.9999%) was introduced into the gas phase of the Pyrex container with Ar as a carrier gas.

Figure 2(a) shows a *j-E* curve for an n-Si electrode (cathode) in the absence of $SiCl_4$. When the potential was scanned from the rest potential around -0.5 V toward the negative under a potential-controlled condition, no current was observed down to ca. -2.2 V, at which a current due to the deposition of Li-Si alloy started to flow as reported in the literature.[10] On the other hand, in the presence of $SiCl_4$, a cathodic current, attributable to the $SiCl_4$ reduction, was observed in potentials more negative than -1.5 V,

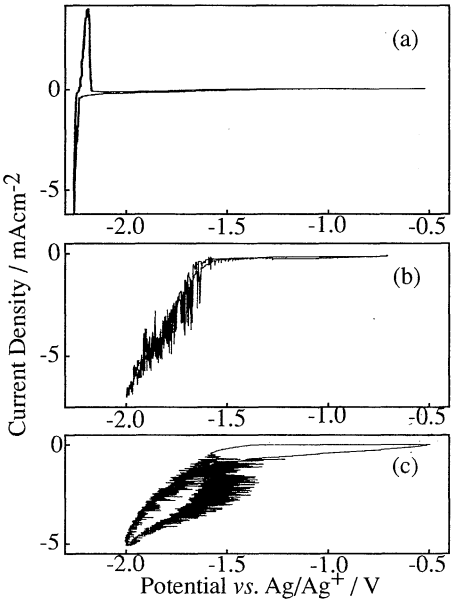

Figure 2. Current-potential (*j-E*) curves for an n-Si(111) electrode; (a) before introducing $SiCl_4$ in The electrochemical cell, whereas (b) and (c) after introducing $SiCl_4$ in the cell. Curves (a) and (b) were obtained by potential scanning at a rate of 10 mV/s, whereas curve (c) was obtained by current scanning at a rate of 25 μA/s.

accompanied by pronounced oscillations, as shown in Figure 2(b). The current oscillation *vs.* time at a constant potential in the potentials below -1.5 V was of non-periodic nature and the average frequency became larger as the electrode potential got more negative. In case where the current was scanned at a rate of 25 μA/s under a current-controlled condition, the oscillation of the electrode potential was observed as shown in Figure 2(c).

Scanning electron microscopic inspection of the n-Si electrode surface after the *j-E* curve measurements showed that a mixture of polycrystalline- and sponge-like films was deposited but only on the electrode surface near the electrode/electrolyte/gas contact line. Similar deposits were obtained on nickel electrodes, and their X-ray photoelectron spectra showed strong Si2p peaks, clearly indicating that the deposits were composed of Si. These results indicate that $SiCl_4$ can be reduced electrochemically but only near the upper edge of a meniscus of the electrolyte on the electrode surface, most probably because $SiCl_4$ is hardly dissolved in the LiCl-KCl eutectic melt.

In agreement with the above argument, it was seen by eyes that an upward meniscus of the electrolyte started to be formed on the n-Si electrode at *ca.* -1.5 V, just at the same potential as the onset potential of the reduction current (cf. Figure 2(b)). The meniscus height became higher with shifting the potential toward the negative. The electrolyte was almost flat between -1.5 V and -0.5 V, but at potentials more positive than -0.5 V, a downward meniscus was formed. The formation of the upward meniscus at the negative potentials can be explained as due to the formation of an electrical double layer of a form, $\equiv Si_S^- \cdots Li^+$ (or K^+), at the Si/molten salt interface, where $\equiv Si_S$ refers to a surface Si atom. The formation of such a layer will lead to a decrease in the interfacial tension at the Si/molten salt interface and an increase in the meniscus height. On the other hand, the formation of the downward meniscus at the positive potentials can be explained as due to the formation of $\equiv Si_S$–Cl bonds at the Si surface, leading to a large increase in the interfacial tension at the Si/molten salt interface.

From the above arguments, we can expect that the current oscillation in Figure 2 is caused by an oscillatory change in the height of the upward meniscus with progress of the Si deposition reaction. At the negative potentials, the Si surface has an electrical double layer of the form, $\equiv Si_S^- \cdots Li^+$ (or K^+), as mentioned above, and an upward meniscus is formed. The $\equiv Si_S^-$ is regarded as a Lewis base, whereas $SiCl_4$ is regarded as a Lewis acid. Thus, in the presence of $SiCl_4$, the $\equiv Si_S^-$ undergoes an electrophilic attack of $SiCl_4$, and changes into $\equiv Si_S$–$SiCl_3$ with a release of Cl^-. Such a reaction increases the interfacial tension of the Si/molten salt interface, leading to a decrease in the height of the upward meniscus, accompanied by a decrease in the current. Too much decrease of the meniscus height will make the electrode surface electrochemically unstable and induce a sudden reduction reaction of $\equiv Si_S$–$SiCl_3$ to the $\equiv Si_S$–$SiCl_2^- \cdots Li^+ + Cl^-$, accompanied by recovery of the meniscus height and an increase in the current. Similar mechanism was reported for oscillating behavior of anodic dissolution of iron electrodes in aqueous H_2SO_4 solutions.[11] The aforementioned non-periodic (random) oscillation may be caused by inhomogeneous nature of the Si surface.

According to the above explanation, the onset potential of the reduction current of $SiCl_4$ observed in Figure 2 (*ca.* -1.5 V) is given by the onset potential of the formation of the upward meniscus, not representing the "true" onset potential for the $SiCl_4$ reduction. This expectation was supported by the measurements of *j-E* curves corresponding to the dissolution and deposition of an n-Si electrode in the LiCl-KCl melt (Figure 3). An anodic current peak at a potential of *ca.* -0.1 V was accompanied by gas evolution on the electrode, suggesting that this current corresponds to anodic Si dissolution giving rise to $SiCl_4$. It is reported that the equilibrium potential for chlorine evolution lies at a much more positive potentials of *ca.* 1.1 V,[12] and we confirmed this fact using a glassy carbon electrode. The addition of 3 mol% LiF to the electrolyte much increased the anodic current peak, accompanied by violent gas evolution, suggesting that F^- anions act as a catalyst for the Si dissolution. Also, the onset potential for this anodic current lying at -0.5 V is in harmony with the aforementioned fact that the downward meniscus starts to be formed at -0.5 V. On the other hand, a cathodic current peak at *ca.* -1.2 V was accompanied by disappearance of the gas bubbles formed on the n-Si electrode by the anodic current at -0.1 V, suggesting that this current corresponds to the reduction of $SiCl_4$. These results indicate that the equilibrium potential for the $SiCl_4$ reduction lies around -0.5 V, much more positive than the aforementioned potential of -1.5 V.

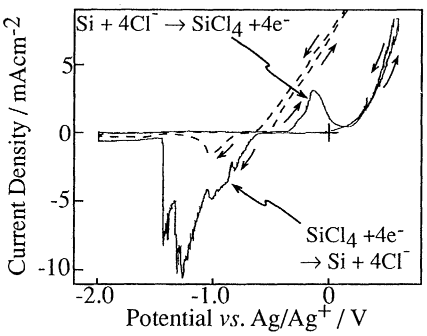

Figure 3. Current-potential (*j-E*) curves for an n-Si electrode(—) in a LiCl-KCl eutectic melt and (- - -) in a LiCl-KCl-LiF (mole ratio: 56:41:3) melt with no intentional introducing of $SiCl_4$. Scan rate: 20 mV/s.

In conclusion, the oscillatory behavior found in the present work is closely related to the mechanism of the Si deposition reaction and suggests that the reaction is initiated by an electrophilic attack of $SiCl_4$ to the Si substrate. Such knowledge is useful in search for conditions to get high-quality polycrystalline Si films.

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