Electrochemical Reduction of Silicon Tetrachloride in an Intermediate-Temperature Ionic Liquid

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Electrochemical reduction of silicon tetrachloride has been investigated in an equimolar N-ethyl-N-methylpyrrolidinium chloride-zinc chloride melt at 423 K for low-cost production of silicon thin films. A dark-brown substance was formed preferentially on the Ni substrate near the electrode-gas-melt three-phase interface by potentiostatic electrolysis at 0 V vs Zn(II)/Zn. Both energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy suggested that some SiCl$_4$ was electrochemically reduced to amorphous Si in the present system. Cross-sectional observation of electrodeposited films by scanning electron microscopy suggested that the deposition rate in the present system is about 100-fold higher than that in the room-temperature system investigated in our previous study. Contrivances of the electrode configuration and the SiCl$_4$-supplying method enabled electrodепositing the Si-containing film on almost the whole Ni substrate.

Key Words : Electrodeposition, Silicon, Intermediate Temperature, Silicon Tetrachloride, Zinc Chloride-based Molten Salts

1 Introduction

Silicon is a key material to solve the environmental and energy issues. There is no doubt that the demand for Si thin films will continuously increase hereafter. In order to meet such a great demand, energetically-favored and inexpensive processes of Si thin films are highly desired.

We believe that an electrochemical process is one of the most attractive candidates because it can produce large-area thin films inexpensively without requiring any high-vacuum apparatus. However, it must be done in nonaqueous media due to thermodynamic restriction and instability of most Si compounds appropriate as Si precursors. So far, in our group, the electrodeposition of Si has been accomplished using SiCl$_4$ as a Si precursor in propylene carbonate (PC) containing tetrabutylammonium chloride$^1$ and in trimethyl-α-hexylammonium bis(trifluoromethylsulfonyl)amide (TMATFS$^2$) at room temperature. Besides, the electrodeposition of Si has been investigated by various research groups in organic solvents$^5$-$^7$ and in room-temperature ionic liquids (RTILs).$^8$-$^{11}$ Especially for the electrodeposition of Si in RTILs, Katayama et al. first attempted to electrodeposit Si in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (EMITFS$^2$) containing (EMI)$_2$SiF$_6$.$^9$ Endres et al. investigated the electrodeposition of Si in 1-buty1-1-methylpyrroolidinium bis(trifluoromethylsulfonyl)amide containing SiCl$_4$ mainly by using in situ scanning tunneling microscopy.$^{9,11}$ However, the electrodeposition of Si generally has a serious problem of low deposition rate.

Then, we considered that the rise in the operation temperature would overcome the problem. Electrodeposition of Si has been studied in high-temperature molten salts by many researchers.$^{12,13}$ Nakato et al. attempted electrodeposition of Si in the presence of gaseous SiCl$_4$ introduced in the LiCl-KCl eutectic melt at 723 K.$^{13}$ For high-temperature molten salts, however, there are disadvantages in the selection of cell and substrate materials. Hence, our interest in this study was focused on intermediate-temperature ionic liquids (ITILs).$^{14,16}$ It is expected that a moderate elevation of the operation temperature enhances the deposition rate and improves the quality of electrodeposited Si without causing the difficulty in the selection of materials for the cell and the substrate. We have developed a new ITIL, N-ethyl-N-methylpyrrolidinium chloride (EMPyrCl)-ZnCl$_2$, which enables the electrodeposition of refractory metals at 423 K.$^{16}$ This new ITIL was applied to Si electrodeposition.

In this study, the electrodeposition of Si was attempted in an equimolar EMPyrCl-ZnCl$_2$ melt at 423 K. Silicon tetrachloride was used as a Si precursor because high-purity SiCl$_4$ can be produced relatively easily and inexpensively. As far as we know, it was the first attempt to electrodeposit Si in ITIL using a gaseous Si precursor.

2 Experimental

All electrolyses were conducted in a three-electrode cell. A Ni wire (1 mmφ × 10 mm, Nilaco Corp.) or a Ni plate (3 mm × 20 mm, Nilaco Corp.) was employed as a working electrode. Its surface was mechanically polished to a mirror finish, and then electrochemically polished in 50 wt% H$_2$SO$_4$ aqueous solution beforehand. The Ni substrate was surrounded by a glass tube to keep SiCl$_4$ gas in the vicinity of the electrode-gas-melt interface. Liquid SiCl$_4$ (Wako Pure Chemical Industries, Ltd.) was introduced into the glass tube immersed in the melt just before starting electrolysis. It was immediately trans-
formed into gas because the operation temperature (423 K) was higher than its boiling point (330 K). The reference electrode was a Zn(II)/Zn electrode. It was composed of a Zn wire (1 mm x 10 mm, Nilaco Corp.) immersed into the equimolar EMPyCl-ZnCl₂ melt separated from the bulk melt by a Porex® filter (Porex Corp.). All the potentials in this paper are described with reference to that of the Zn(II)/Zn electrode. A Zn coil (1 mm x 100 mm, Nilaco Corp.) was used as a counter electrode.

The equimolar EMPyCl-ZnCl₂ melt (m.p. 318 K) was employed as an electrolyte of the electrolytic bath. EMPyCl (Yoyulabo Corp.) was refined by a recrystallization method using acetonitrile (Wako Pure Chemical Industries, Ltd.) and ethyl acetate (Wako Pure Chemical Industries, Ltd.). Then, it was dried in a vacuum at 423 K for more than 48 hours to remove traces of water and organic solvents. ZnCl₂ (Wako Pure Chemical Industries, Ltd.) was dried in a vacuum at 453 K for more than 48 hours. They were mixed in an equimolar ratio and melted at 423 K in a 20-mL Pyrex® beaker placed in a five-necked separable flask on a heating plate in an Ar-filled vacuum glove box.

Electrochemical measurement and sample preparation was performed at 423 K in an Ar-filled glove box by using a potentiostat-galvanostat (Hokuto Denko Co., Ltd., HA-301) and a data logger (Keyence Corp., NR-2000). A function generator (Hokuto Denko Co., Ltd., HB-104) was also used in cyclic voltammetric studies. All samples for characterization were prepared by potentiostatic electrolysis. After the electrolysis, a sample electrodeposited on a Ni substrate was immersed in PC (Wako Pure Chemical Industries, Ltd.) and subsequently in dimethyl carbonate (Wako Pure Chemical Industries, Ltd.) to rinse out a melt on the sample surface. It was followed by drying the sample in a vacuum for 30 minutes. The dried sample was inserted in a sealed bag with oxygen absorbent (L.S.O., Inc., A-500HS) to prevent its oxidation in the air during transferring it to the chambers of analyzers.

Surface and cross-sectional morphologies of the electrodeposited samples were observed by using a scanning electron microscope (SEM, Hitachi, Ltd., S-2600H). The composition of a microscopic region was analyzed by energy-dispersive X-ray spectroscopy (EDX, Horiba Co., Ltd., EMAX ENERGY EX-200), simultaneously with SEM observation. The binding energy of the inner electron shell of Si in the electrodeposited sample was investigated by X-ray photoelectron spectroscopy (XPS, JEOL, Ltd., JPS-9010MC).

3 Results and Discussion

Prior to sample preparation, cyclic voltammetry (CV) was performed to determine the electrode potential appropriate to Si electrodeposition in the present system. Figure 1 shows cyclic voltammograms of a Ni wire measured in the EMPyCl-ZnCl₂ melt at 423 K before and after the introduction of SiCl₄. In this figure, the dotted and the solid lines correspond to before and after introducing SiCl₄ to the melt, respectively. Both the voltammograms were recorded at a scan rate of 10 mV s⁻¹. As for the voltammogram of the blank system, the cathodic and anodic current peaks around 0 V correspond to the deposition and dissolution of Zn, respectively. Meanwhile, a slight increase of cathodic current from 0.20 V are due to the formation of Ni-Zn alloys and the anodic current peaks at 0.20 V and 0.35 V are assigned to the dissolution of Zn from Ni-Zn alloys. After introducing SiCl₄ to the vicinity of the Ni substrate, rest potential shifted to a more positive value and cathodic current began to flow immediately after a scan was started from the rest potential. The cathodic current observed at potentials from 0.70 to 0.20 V possibly corresponds to the reduction reactions involving SiCl₄. However, the standard potential of the following reaction

\[
\text{SiCl}_4 + 4e^- = \text{Si} + 4\text{Cl}^- \tag{1}
\]

is thermodynamically calculated to be 0.239 V vs. Zn(II)/Zn at 423 K by using the values \(\Delta G^\circ(\text{SiCl}_4, g) = -605.79 \text{ kJ mol}^{-1}\) and \(\Delta G^\circ(\text{ZnCl}_2, l) = -349.09 \text{ kJ mol}^{-1}\). Thus, the cathodic current found at more positive potentials than 0.239 V may be attributed to the formation of partially reduced silicon chloride complexes, SiₙCl₄⁻, [n/m < 4] or EMPySiCl₄ [y−1/x < 4], though these compounds have not been identified in this study. From these results, it follows that SiCl₄ dissolves into the melt at 423 K, and that the electrochemical reduction of SiCl₄ proceeds. Actually, the solubility of SiCl₄ in the EMPyCl-ZnCl₂ melt at 423 K was measured to be 0.47 mol% by atomic absorption spectroscopy. Meanwhile, the anodic current density found in the presence of SiCl₄ was generally lower than that in the blank system although the cathodic current density was higher. It indicates that the electrochemical reduction of SiCl₄ is irreversible in the present system.

On the basis of voltammetric results, potentiostatic electrolysis was performed at 0.20 V or 0 V in the presence of SiCl₄. These two potentials for electrolysis were selected for the following reasons. The former potential (0.20 V) is a little more negative than the theoretical standard potential for the reduction of SiCl₄ to Si (0.239 V/mole).
V). At 0 V, on the other hand, the electrodeposition of Zn would proceed slowly in addition to the electrochemical reduction of SiCl₄. In this case, Si is expected to be produced by the following chemical reaction

\[ \text{SiCl}_4 + 2\text{Zn} = \text{Si} + 2\text{ZnCl}_2 \]  (2)

This reaction is considered to be effective to obtain Si in the case that the overpotential for the reduction of SiCl₄ to Si on a Ni substrate is considerably large.

As a result, a dark-brown substance was electrochemically formed on a Ni substrate around the electrode-gas-melt three-phase interface at 0 V (Fig. 2). The average current was \(-20\ \mu\text{A}\) for a dipped area of 0.30 cm² though the area of the three-phase interface was much smaller. Meanwhile, there was almost no change in appearance of a Ni substrate in the case of 0.20 V.

Figure 3 shows surface and cross-sectional SEM images of the dark-brown substance. The deposited layer has the maximum thickness of 10 µm. This deposition rate is about 100-fold higher than that in TMHATFSFA at room temperature.\(^{9}\) Furthermore, the electrodeposited film appears to be dense and adhesive to the substrate but the surface is somewhat rough, compared with that formed in the RTIL system.\(^{4}\) EDX studies indicated that the dark-brown substance contains Si. Oxygen and chlorine exist in the deposit as well. However, standardless quantitative analysis confirmed that SiCl₄ is electrochemically reduced because the oxidation number of Si was estimated to be less than IV (the atomic ratios of O/Si and Cl/Si were 1.2 and 0.12, respectively). Therefore, the detected O and Cl were probably derived from oxidation in the air, and entanglement of the melt or partial reduction of SiCl₄, respectively.

Figure 4 shows an XPS spectrum of Si 2p core level for the dark-brown substance formed on a Ni wire by the electrolysis at 0 V for two hours in the equimolar EMPreCl-ZnCl₂ melt in the presence of SiCl₄ at 423 K. The sample was etched by Ar⁺ before the analysis.

Fig. 2 A photograph of a Ni wire after the electrolysis at 0 V for one hour in the equimolar EMPreCl-ZnCl₂ melt in the presence of SiCl₄ at 423 K.

Fig. 3 SEM images of a dark-brown substance formed on a Ni wire by the electrolysis at 0 V for one hour in the equimolar EMPreCl-ZnCl₂ melt in the presence of SiCl₄ at 423 K: (a) surface and (b) cross-sectional views.

Fig. 4 An XPS spectrum of Si 2p core level for a dark-brown substance formed on a Ni wire by the electrolysis at 0 V for two hours in the equimolar EMPreCl-ZnCl₂ melt in the presence of SiCl₄ at 423 K. The sample was etched by Ar⁺ before the analysis.

Fig. 5 Contrivances for the electrodeposition using a gaseous precursor. (a) A substrate is continually moved up vertically to the gas-melt interface during electrolysis. (b) SiCl₄ gas is continuously supplied to the vicinity of a substrate.

and Cl/Si were 1.2 and 0.12, respectively). Therefore, the detected O and Cl were probably derived from oxidation in the air, and entanglement of the melt or partial reduction of SiCl₄, respectively.

Figure 4 shows an XPS spectrum of Si 2p core level for the dark-brown substance formed at 0 V. The spectrum was recorded after two-minute Ar⁺ etching at a discharge voltage of 400 V and a discharge current of 6.4 mA. The detected spectrum is considered to be assigned to Si and several silicon oxides. That is, the spectrum was separated into three peaks centered at 99.2, 100.95, and 103.1 eV, which correspond to the oxidation numbers of 0, II, and IV, respectively.\(^{28}\) It is considered from its peak position (99.2 eV) and its relatively large full width at half maximum (1.55 eV) that Si(0) exists in the amorphous phase of Si. Some of the Si atoms are in the state of oxidation number II, which suggests the existence of partially reduced Si compounds. Nevertheless, most of the Si atoms exist in the form of oxidation number IV, which is probably due to the oxidation of amorphous Si (a-Si) and partially reduced Si compounds during the treatment after electrolysis. However, the important thing to note is that SiCl₄ is electrochemically reduced to form a-Si, though the total amount was small after the washing treatment, preferentially on the Ni substrate near the three-phase interface.
Although the deposition rate in the present ITIL system is about 100-fold higher than that in RTIL, the present system also has a disadvantage that the electrochemical deposition reaction progresses only near the three-phase interface. It is because SiCl₄ is mainly supplied to the cathode from the gas phase existing above the melt.

Then, we attempted to overcome the disadvantage by improving the electrode configuration and the SiCl₄-supplying method as schematically described in Fig. 5. Firstly, the substrate was continually moved up vertically to the gas-melt interface at intervals of 20 minutes during electrolysis (Fig. 5 (a)). As a result, current increased from 25 to 30 µA at a maximum by pulling up the substrate during electrolysis, although this action decreased the apparent dipped area varied from 0.36 to 0.24 cm². It is probably caused by the generation of a new three-phase interface. Figure 6 shows a photograph of a Ni substrate after the electrolysis. A dark-brown deposit was formed on most of the substrate surface, in contrast to Fig. 2.

The way of supplying SiCl₄ gas to the cathode was also contrived to enhance the deposition rate as well as to accomplish the uniform electrodeposition on a Ni substrate (Fig. 5 (b)). Firstly, the EMPyrCl-ZnCl₂ melt was saturated with SiCl₄, and left for 12 hours to achieve equilibrium. Then, electrolysis was performed with immersing the whole surface of a Ni substrate in the melt. In this case, current density was 0.07 mA cm⁻². The continuous supply of SiCl₄ gas to the vicinity of the cathode increased current density up to 0.17 mA cm⁻². After the electrolysis, a dark-brown substance was produced on most of the cathode surface like Fig. 6. The measured XPS spectrum of Si 2p core level was similar to Fig. 4. The above results demonstrate that Si-containing film can be uniformly formed on the whole Ni substrate by improving the electrode configuration and the SiCl₄-supplying method.

4 Conclusion

Electrodeposition of Si was attempted in the equimolar EMPyrCl-ZnCl₂ melt at 423 K using SiCl₄ as a Si precursor for the first time. Cyclic voltammetric studies suggested that SiCl₄ is electrochemically reduced in the present system. Potentiostatic electrolysis at 0 V vs Zn(II)/Zn gave a dark-brown substance well adhering to a Ni substrate. EDX and XPS analyses demonstrated that, at least, some SiCl₄ was electrochemically reduced to a-Si. Cross-sectional SEM images indicated that the deposition rate in the present system is about 100-fold higher than that in the room-temperature system investigated in our previous study. Although the electrodeposition occurs preferentially near the three-phase interface, the disadvantage is overcome by controlling the electrode configuration and the SiCl₄-supplying method.

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References

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