Electrochemical quartz crystal microbalance, X-ray photoelectron spectroscopy, and

Raman spectroscopy analysis of SiCl_4 reduction in ionic liquids

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Abstract

The reaction mechanism of Si electrodeposition in the ionic liquid trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl)imide (TMHATFSI) with SiCl₄ was investigated using an electrochemical quartz crystal microbalance (EQCM) and X-ray photoelectron spectroscopy (XPS). The deposited films were further characterized by Raman spectroscopy. The EQCM method measured the frequency change *in situ* during electrodeposition, whereas XPS provided the Si mass concentration in the electrodeposited films. By combining these results, the mass change due to SiCl₄ reduction was estimated. Then, the current efficiency for Si electrodeposition at various potentials was evaluated. The calculated current efficiency was almost 100% when it was assumed that SiCl₄ reduction progressed by four-electron electroreduction. The XPS and Raman results showed that the deposited films were composed primarily of amorphous Si with Si–Si bonds. Crystalline Si thin films were obtained after annealing in an Ar gas stream.

Keywords: Si electrodeposition, ionic liquids, EQCM, XPS, annealing

1. Introduction

Global environmental concerns caused by the fossil fuel economy urgently require renewable energy schemes such as ultralarge-scale photovoltaic power generation that guarantees a steady supply and very low cost in advanced countries. Among the various types of solar energy conversion, crystalline Si-based solar cells are attractive because the technology and its stability have been reliably established over many years [1–4]. With ever-increasing energy demand and movement toward a more sustainable society, Si thin film solar cells fabricated at extremely low cost are of great interest.

Si has been successfully electrodeposited using nonaqueous solvents (molten salt [5], organic solvents [6–10], and ionic liquids [11–18]). In particular, ionic liquids exhibit low volatility, a wide electrochemical window, and good electrochemical stability. Their major advantage over molten salts is the availability of room temperature deposition. These considerations highlight ionic liquids as a good candidate electrolyte for understanding the electrodeposition mechanism for highly reactive metals.

Four aspects were investigated in this study. First, films electrodeposited at several potentials are characterized. Second, X-ray photoelectron spectroscopy (XPS)

and electrochemical quartz crystal microbalance (EQCM) measurement are used to obtain the electrodeposition rate of Si in the films. Third, the electrodeposited films are characterized using Raman spectroscopy. XPS and Raman spectroscopy provide complementary information regarding Si electrodeposition, in particular ionic liquid inclusion into Si thin films and the possibility of its binding with the films. Fourth, the as-deposited film is annealed in an attempt to improve its crystallinity [15]. These analyses allow us to partially understand the Si electrodeposition reaction mechanism in ionic liquids.

2. Experimental

The ionic liquid trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl)imide (TMHATFSI) containing less than 30 ppm H₂O and less than 1 ppm Cl⁻ were used with 0.5 M SiCl₄ (99.98% purity) (Stella Chemifa). This ionic liquid is hydrophobic and exhibits high solubility of SiCl₄ up to 1.0 M. The working electrode (deposition substrate) was a 6 MHz AT-cut quartz crystal with Au contacts (Hokuto Denko). Its surface area was 1.32 cm². Pt wires 0.1 cm in diameter were used as a quasi-reference electrode (QRE) and as a coiled counter electrode. The Pt QRE was insulated by a heat-shrinkable tube, leaving the tip of the Pt wire exposed, and it was immersed

directly in the ionic liquid. The surface area of the QRE tip was 0.01 cm^2 , whereas that of the Pt wire coil counter electrode was about 5 times larger than that of the working electrode. The working electrode was pretreated in oxygen plasma for 2 min, and the Pt electrodes were pretreated in 20% sulfuric acid solution before electrodeposition.

The EQCM apparatus was mounted in an aluminum block, and the electrolyte temperature was maintained at $40\text{ }^{\circ}\text{C}$ during all the experiments using this Al thermo-block (NISSIN, COOL/HEAT BLOCK NDC-100). After the measurements, all the electrodes were cleaned by rinsing with 99.5% dimethyl carbonate (JUJO) and dried in vacuum for 10 min.

The electrochemical operations were performed in an Ar-filled glove box. The potential of ferrocenium/ferrocene (Fc^+/Fc) was measured to be $-0.23\text{ V}_{\text{vs. Pt QRE}}$ [Fig. 1]. Cyclic voltammetry (CV) and constant potential measurements were then performed using a potentiostat/galvanostat (Hokuto Denko, HZ-5000). EQCM (Hokuto Denko quartz crystal mount and Agilent Technologies Frequency Analyzer, E5061A) measurement was also performed. CV was conducted from open circuit potential (OCP) to $-3.0\text{ V}_{\text{vs. Pt QRE}}$ at a scan rate of 10 mV s^{-1} , and constant potential electrodeposition was performed at -2.0 , -2.5 , and $-3.0\text{ V}_{\text{vs. Pt QRE}}$. The reproducibility of the OCP measurement was within 50 mV at $-0.20\text{ V}_{\text{vs. Pt QRE}}$ in the ionic liquid containing 0.5 M

SiCl₄.

XPS (ULVAC, PHI 5000 Versa Probe WS) using Al-K α irradiation and 4 kV Ar ion etching was employed to measure the concentration profiles of elements. One minute of Ar sputter time etches approximately 50 nm in SiO₂. A transfer vessel was used to prevent Si thin films from oxidizing in the air before XPS measurement. The XPS peaks were fitted using the MultiPak software utility (ULVAC, PHI 5000 Versa Probe WS).

The electrodeposited thin films were also characterized using focused ion beam scanning electron microscopy (SEM, HITACHI, NB 5000) with Ga ion etching to measure cross-sectional views, as well as by Raman spectroscopy (TOKYO INSTRUMENTS SOLAR TII, Nanofinder 30). Detailed analysis of the Raman spectra was performed using Origin (OriginLab Corporation). It can compensate for the background noise level in each measurement so that the modified spectrum represents the essential chemical signal strength corresponding to each peak.

As-deposited Si films were subjected to rapid thermal annealing (ULVAC, MILA 3000) in Ar atmosphere at 700 °C for 1 h.

3. Results and Discussion

3.1 Electrochemical Measurement

Figure 2 illustrates the current transient and EQCM measurement along the dotted line during the anodic scan in the ionic liquid alone (containing no SiCl_4). The increase in the cathodic current density and decrease in the mass recorded at $-3.8 \text{ V}_{\text{vs. Pt QRE}}$ stemmed from decomposition of the ionic liquid. Then, EQCM measurement during CV measurement was conducted in the ionic liquid with 0.5 M SiCl_4 . In the EQCM analysis, the Sauerbrey equation [Eq. (1)] and the related equations for damping [Eqs. (2), (3)] were used to calculate the mass change during electrodeposition [18].

$$\Delta f_{\text{mass}} = \frac{-2f_s^2 \Delta m}{A(\mu_q \rho_q)^{1/2}} \quad (1)$$

$$\Delta f_{\text{viscosity}} = \frac{-\Delta w}{2} = \frac{-f_s^{3/2} [\Delta(\eta\rho)]^{1/2}}{(\pi\mu_q \rho_q)^{1/2}} \quad (2)$$

$$\Delta f_s = \Delta f_{\text{mass}} + \Delta f_{\text{viscosity}} = \Delta f_{\text{mass}} - \frac{\Delta w}{2} \quad (3)$$

where

Δf_{mass} is the resonance frequency change deriving from the mass,

$\Delta f_{\text{viscosity}}$ is the resonance frequency change deriving from viscous damping,

Δf_s is the series resonance frequency change (frequency of peak in conductance),

Δm is the mass change,

A is the surface area,

$\mu_q \rho_q$ is the product of the quartz crystal's shear modulus and density,

Δw is the change in the half-width at half-maximum of the conductance peak, and

$\eta \rho$ is the product of the ionic liquid's viscosity and density.

The uncommon parameters are described in Fig. 3. In the above equations, f_s represents the series resonance frequency, and Δf_s represents the series resonance frequency change, which is equal to the sum of the contributions to the resonance shift from the mass and viscosity: Δf_{mass} and $\Delta f_{\text{viscosity}}$, respectively (assuming that $\Delta f_{\text{viscosity}} \ll \Delta f_{\text{mass}}$). This viscosity component is almost equivalent to the change in the half-width at half-maximum of the conductance peak relative to the quartz crystal in air (no liquid contact). The viscosity of the electrolytes appears to change during electrodeposition in ionic liquids. Therefore, the resonance frequency change deriving from the viscosity must be calibrated in order to calculate the mass gain.

The cathodic current starts to increase slightly from -1.0 to -1.5 V_{vs. Pt QRE} and then rises significantly around -2.0 V_{vs. Pt QRE}, as seen in the inset of Fig. 2. Two current peaks, on the other hand, appear around -2.5 and -3.0 V_{vs. Pt QRE} with an associated mass increase that is likely due to SiCl₄ reduction. These EQCM results suggest that SiCl₄

reduction may progress in multiple stages, i.e., via intermediary electroreduction reactions, although further detailed study is necessary to clarify the stages of SiCl_4 reduction.

Next, the mass change during potentiostatic electrodeposition at three potentials was investigated using the EQCM. Figure 4 shows the transient variations in the current density and charge density at each potential. The current density recorded at -2.0 and -2.5 $V_{\text{vs. Pt QRE}}$ over the initial 400 to 600 s is negligibly small. An incubation period for Si electrodeposition may be expected.

After this incubation period, a current increase is observed from 400 to 1250 s at both potentials. Two solid curves reach the minimum values around 1250 s, indicating that the current tends to decrease after 1300 s. On the other hand, the current density rapidly increases just after potentiostatic electrodeposition starts, with a quite short incubation period, at -3.0 $V_{\text{vs. Pt QRE}}$. It increases in a zigzag manner over the initial 300 s, and then the current tends to increase more smoothly. (Three peaks are observed, which represent reactions that are difficult to identify at present.) These current increases are surely attributed to the electroreduction of SiCl_4 . Morphological variations in Si films electrodeposited at the three potentials were examined at 500 mC cm^{-2} (Fig. 5). A cross-sectional image of a compact, dense Si film on a Au substrate is observed at -2.0

$V_{vs. Pt QRE}$. A much thicker film with some pores in its cross section appears at $-2.5 V_{vs. Pt QRE}$. The surface morphology is rather uniformly composed of precipitated grains 50 nm in diameter. This surface roughness may be enhanced by coagulated precipitated grain ensembles with submicron diameter at $-3.0 V_{vs. Pt QRE}$.

The current density starts to decrease after 1300 s at -2.0 and $-2.5 V_{vs. Pt QRE}$, as seen in Fig. 4. This decreasing tendency may be caused by the resistance of the electrodeposited dense Si thin films, as Si is a semiconductor. On the other hand, the current density continues to increase as electrodeposition progresses, accompanying the formation of a porous film structure at $-3.0 V_{vs. Pt QRE}$. The porous film structure enhances the effective electrode surface area, increasing the current density under potentiostatic electrolysis.

3.2 Deduction of $SiCl_4$ Reduction Reaction Based on XPS and EQCM Measurements

Si thin films electrodeposited at each potential were measured by XPS. Figure 6 shows the composition depth profiles of thin films produced at each potential. In these depth profiles, the Au substrate was detected only after around 4 min of Ar sputtering (Au content not shown in this figure). The profiles are divided into three regions, (1),

(2), and (3), in this figure. Region (1) is close to the top surface layer, where the sputtering time is limited to 1 min, region (2) is an intermediate area with a substantially uniform concentration profile through the Si film, and region (3) is the zone close to the Au substrate, which corresponds to 3 to 4 min of sputtering time. Region (1) is characterized by an increasing Si profile and the resulting decrease in the O and C profiles along its depth. When the electrodeposited sample is characterized, its surface is always rinsed by dimethyl carbonate, which contains oxygen atoms. Moreover, the film may be instantaneously exposed to a slightly oxidizing atmosphere when it is placed in the XPS instrument, even if a transfer vessel is employed. Thus, region (2) may represent compositions characterized primarily by the electrodeposition conditions. Table 1 demonstrates the averaged mass concentration of each element in region (2). The Si mass concentration is 57%, 65%, and 53% at -2.0, -2.5, and -3.0 V_{vs. Pt QRE}, respectively, in region (2).

The concentration level of Cl is quite low compared with that of Si in the film. Thus, SiCl₄ molecules are electrochemically reduced to Si, leaving Cl⁻ ions in the electrolyte. Note that the C content increases and the O content decreases with the shift toward negative potential. The potential dependence of the other element is, however, not clearly observed. These data may suggest that the SiCl₄ reduction reaction partially

accompanies cation decomposition.

Figure 7 (a) shows the frequency change measured by the EQCM during potentiostatic electrodeposition. The mass change calculated from the frequency change in Fig. 7 (a) is multiplied by the Si mass concentrations obtained from the XPS depth profiles. That is, the mass of Si accumulated on the substrate due to SiCl_4 reduction is obtained, as illustrated in Fig. 7 (b) as a function of the charge density. The straight line expressing the relationship between the mass of Si and the charge density is drawn using Faraday's law assuming a four-electron transfer reaction. The measured data follow this straight line during the initial stage and start to deviate slightly above 400 mC cm^{-2} at -2.0 and -2.5 $V_{\text{vs. Pt QRE}}$. The agreement with Faraday's law is maintained to 150 mC cm^{-2} at -3.0 $V_{\text{vs. Pt QRE}}$. The deviation from this straight line may be caused by enhanced surface roughness of the Si thin films [19]. SEM images of Si thin films with rough surface morphology electrodeposited at all potentials at a charge density of 500 mC cm^{-2} are shown in Fig. 5.

By comparing the mass change due to SiCl_4 reduction with Faraday's law at 400 mC cm^{-2} , the current efficiency of SiCl_4 reduction was calculated to be 94.6%, 93.4%, and 73.2% at -2.0, -2.5, and -3.0 $V_{\text{vs. Pt QRE}}$, respectively. Thus, Si may apparently be electrodeposited by four-electron electroreduction. The poorer efficiency is probably

caused by the difficulty of converting the frequency data to the mass gain in the film with a rough surface at $-3.0 \text{ V}_{\text{vs. Pt QRE}}$.

3.3 Characterization of Electrodeposited Si Films

The Si binding energy of the topmost surface of the deposits at each potential are shown in Fig. 8. These data were analyzed using MultiPak to obtain detailed peak fitting information. The black lines show the original data measured by XPS, and the red and blue lines show the analyzed data. The jagged red lines are the background spectrum. At all the potentials, Si–Si and Si–O_x bonding were observed at the topmost surface. The ratio of the Si–Si bonding peak intensity to that for SiO_x is increased as the potential is decreased from -2.0 to $-2.5 \text{ V}_{\text{vs. Pt QRE}}$. It is almost saturated at $-3.0 \text{ V}_{\text{vs. Pt QRE}}$. This behavior is also expected from the depth profile measurement shown in Fig. 6, where the O concentration is highest near the topmost surface (until 1 min of Ar sputter time).

Raman spectra are shown in Fig. 9. A peak around 480 cm^{-1} was observed in the Si thin films electrodeposited at all the potentials. This peak was analyzed using Origin [Fig. 9 (d)]. The pink dots show the original data measured by Raman spectroscopy, and the continuous lines show fitting results. This analysis confirms the existence of a peak

around 480 cm^{-1} . The peak at around 480 cm^{-1} generally originates from amorphous Si (a-Si) inside Si thin films. The other peaks in Fig. 9 are thought to be derived from ionic liquids. For example, the peak around 770 cm^{-1} probably indicates S=O bonding, and that around 300 cm^{-1} indicates C–C–C bonding. CH₃ bonding appears around 2950 cm^{-1} . It becomes sharper as the electrode potential is shifted in the negative direction. This may suggest that cations including CH₃ bonding may participate in the cathodic reduction process. These peaks due to such chemical bonding may be caused by adsorption of the fragment ion in ionic liquids.

Another concern is the high content of C and O in the electrodeposited a-Si film. It is likely that even after rinsing with dimethyl carbonate, some ionic liquid remains on the surface of the deposits. Then, the as-deposited Si film was annealed at $700\text{ }^{\circ}\text{C}$ in a 99.8% Ar gas stream.

Raman spectra of the Si thin films electrodeposited at $-2.5\text{ V}_{\text{vs. Pt QRE}}$ before and after annealing are shown in Fig. 10 (a). A broad peak detected at around 480 cm^{-1} changed to a sharp peak at 520 cm^{-1} after annealing. The sharper peak suggests that Si in the deposited films is crystallized by annealing. This spectrum was also analyzed using Origin [Fig. 10 (b)]. The pink line shows the original data measured by Raman spectroscopy, and the black and red lines show the existence of peaks in the measured

spectrum. Further, the blue line shows the fitting results. This analysis confirms the existence of the peak around 520 cm^{-1} . The composition of each thin film was measured by XPS depth profiling before and after annealing, as shown in Fig. 11. The carbon content was significantly decreased by annealing, suggesting that there are no covalent bonds between carbon and silicon. The increase in the oxygen content after annealing is due to the exposure to air in the annealing treatment during sample transfer to the annealing apparatus.

To further improve the purity of Si thin films, three methods can be considered to improve the purity or reduce the impurities in the films. First, an annealing treatment is thought to be useful, although the annealing procedure must be further refined. Second, an electrolyte with lower viscosity is desired. The addition of some organic solvents into ionic liquids may be helpful. Increasing the temperature is another method of decreasing the viscosity. When the viscosity becomes lower, the mass transfer rate of SiCl_4 to the cathode surface is enhanced. Third, pulse electrodeposition may also provide a useful methodology.

4. Conclusion

Si electrodeposition was conducted in TMHATFSI with SiCl_4 . For application to solar cells, it is critical to produce a high-purity deposit. To achieve high-purity Si thin films, it is important to understand the Si electrodeposition reaction mechanism and the conditions that produce high-quality Si thin films. A combination of EQCM and XPS measurements suggested apparent Si electrodeposition with a net four-electron reduction from SiCl_4 . We also confirmed that Si thin films electrodeposited in TMHATFSI with SiCl_4 are primarily amorphous Si with Si–Si bonding, and crystalline Si thin films were obtained after an annealing treatment.

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Figures

Fig. 1 Cyclic voltammogram (scan rate = 10 mV s⁻¹) in TMHATFSI with 1.0 M Fc⁺/Fc at 40 °C

Fig. 2 (a) Cyclic voltammogram (scan rate = 10 mV s^{-1}) (b) Mass change calculated from EQCM

measurement during CV in TMHATFSI with (continuous line) and without (dotted line) 0.5 M SiCl_4

at 40°C

Arrows show the path of voltammogram.

Fig. 3 The mean of uncommon parameters in EQCM analysis

Fig. 4 Current density (continuous line) and charge density (dotted line) during potentiostatic

electrodeposition in TMHATFSI with 0.5 M SiCl_4 at 40 °C at each potential

Charge limited to 1000 mC cm^{-2} .

Fig. 5 SEM images of the Si thin films electrodeposited at 40 °C at 500 mC cm⁻² at each potential:

(a) -2.0 V_{vs. Pt QRE} (b) -2.5 V_{vs. Pt QRE} (c) -3.0 V_{vs. Pt QRE}

Fig. 6 XPS depth profiles of the Si thin films electrodeposited at 40 °C at each potential: (a) -2.0 V_{vs.}

Pt QRE (b) -2.5 V_{vs.} Pt QRE, (c) -3.0 V_{vs.} Pt QRE

Table 1

	-2.0 V _{vs. Pt QRE}	-2.5 V _{vs. Pt QRE}	-3.0 V _{vs. Pt QRE}
N	1	1	1
S	2	1	2
O	18	14	7
C	17	14	31
F	3	1	2
Cl	2	4	4
Si	57	65	53

Table 1 Average % of mass concentration of each element in region (2) in Fig. 6

Fig. 7 (a) Frequency change measured by EQCM during potentiostatic electrodeposition at each potential (b) Accumulation of mass of Si on the films estimated from average % Si determined by XPS and the total mass change calculated from frequency change in (a)

Fig.8 Si 2p binding energy of the top most surface of the thin films electrodeposited at 40 °C at each

potential: (a) -2.0 V_{vs. Pt QRE} (b) -2.5 V_{vs. Pt QRE}, (c) -3.0 V_{vs. Pt QRE}

Fig. 9 Raman spectra, with possible weak Si peaks (wavenumbers indicated in the figures), of thin films electrodeposited at 40 °C at each potential: (a) -2.0 V_{vs. Pt QRE} (b) -2.5 V_{vs. Pt QRE} (c) -3.0 V_{vs. Pt QRE} (d) analyzed result of the peak around 480 cm⁻¹

Fig. 10 (a) Raman spectra of the Si thin films electrodeposited at -2.5 V_{vs. Pt QRE} before and after annealing (at 700 °C for 1 h) (b) Analyzed result of the peak around 520 cm⁻¹

Fig. 11 XPS depth profiles of the thin films electrodeposited -2.5 V_{vs. Pt QRE} (a) before and (b) after

annealing (at 700 °C for 1 h)