

Electrodeposition of Highly Crystalline Silicon Using Liquid Metal Electrodes in Molten Salts

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2025

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Chapter 1

General Introduction

1.1 Current Status and Trends in Solar Photovoltaic Power

Global warming has become a severe global concern, giving rise to an urgent need to reduce emissions of greenhouse gases—particularly carbon dioxide (CO_2)—to mitigate its impact. This has led the international community to set a target of net zero carbon emissions (carbon neutrality) by 2050. In its report “Climate Change 2021,” the Intergovernmental Panel on Climate Change (IPCC) emphasized that it is essential to achieve net-zero CO_2 emissions globally by 2050 or sooner, in order to avoid the most severe impacts of climate change [1].

Renewable energy is essential for achieving net zero emissions. Fig. 1-1 shows the trend in global primary energy consumption from 1800 to 2023 for different energy sources [2]. It is

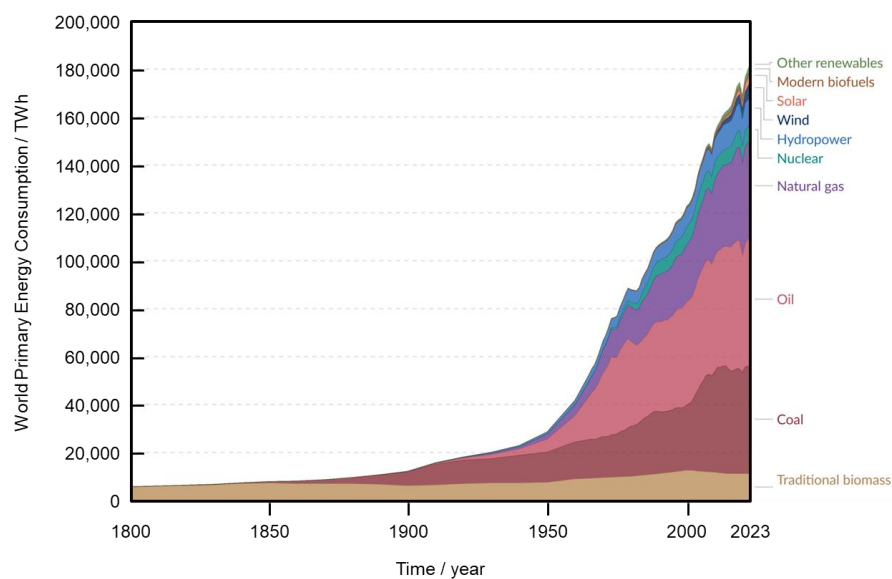


Fig. 1-1 World primary energy consumption from 1800 to 2023 by power sources (TWh) [2].

observed that society still relies strongly on fossil fuels, such as coal, oil, and natural gas. Unfortunately, fossil fuels emit very high amounts of CO₂ per kWh of electricity generated. Thus, if fossil fuels continue to be used as the primary energy source, their impact on climate change is expected to become even more severe. In addition to emitting large amounts of CO₂, combustion of fossil fuels also generates harmful gases, such as SO_x and NO_x, which contribute to air pollution. Furthermore, fossil fuels are finite resources that may become depleted.

Solar power generation is one of the most promising solutions for addressing the issues of global warming, air pollution and resource depletion associated with fossil fuels. Most importantly, solar power generation does not generate CO₂. As shown in Table 1-1, solar energy generation has an extremely low CO₂ emissions cost throughout its life cycle, including both power generation and the manufacturing, installation, and disposal of solar panels [3]. By contrast, biomass has very high CO₂ emissions per kWh⁻¹ of electricity generated. While nuclear power is also considered to be a low-carbon power source, it poses significant safety risks. Multiple large-scale accidents involving nuclear power plants have occurred since the introduction of nuclear power, and such accidents can cause significant long-term damage. In addition, the disposal of radioactive waste, which requires long-term management, is an unresolved issue, posing challenges to sustainability. Furthermore, solar power generation offers several advantages and in particular, allows relatively easy expansion of power generation capacity and flexible scaling of facilities, eliminating the need to concentrate power generation in large-scale plants. This enables solar energy to serve as a distributed power source for residential and small-scale facilities and allows for construction on any scale to meet the energy demand.

According to the International Energy Agency (IEA) report “Sustainable Recovery,” solar photovoltaic (PV) and wind power are rapidly becoming the most popular power generation technologies worldwide [4]. In 2019, capital spending on solar and wind power accounted for nearly half of all power plant investment [4]. Fig. 1-2 shows the growth of global photovoltaic (PV) and wind power generation capacities from 2019 to 2030 [5]. In the main-case forecast, global

annual renewable capacity additions rise from 666 GW in 2024 to almost 935 GW in 2030. Solar PV and wind are forecast to account for 95% of all renewable capacity additions through 2030, with PV growing at more than three times the rate of wind power. As compared to wind power, solar PV technology is advantageous in addressing issues such as noise pollution and regional disparities. Furthermore, the IEA predicts in its “Renewables 2024” report that, under current policies, solar PV capacity would increase by a factor of 4.2 and that it would increase by a factor of 4.8 under accelerated policies [5]. Nevertheless, further cost reduction is essential for the

Table 1-1 Lifecycle CO₂ emissions by electricity supply technologies (gCO₂-eq kWh⁻¹) [3].

Technology	Lifecycle CO ₂ emissions		
	Min.	Median	Max.
Currently commercially available technologies			
Coal–pulverized coal	740	820	910
Gas–combined cycle	410	490	650
Biomass–cofiring with coal	620	740	890
Biomass–dedicated	130	230	420
Solar PV–rooftop	26	41	60
Solar PV–utility scale	18	48	180
Concentrated solar power	9	27	63
Wind offshore	8	12	35
Geothermal	6	38	79
Hydropower	1	24	2200
Nuclear	4	12	110
Pre-commercial technologies			
CCS *–Coal–pulverized coal	190	220	250
CCS–Coal–integrated gasification combined cycle	170	200	230
CCS–Coal–oxyfuel	100	160	200
CCS–Gas–combined cycle	94	170	340
Ocean (tidal and wave)	6	17	28

* CCS is the abbreviation of “Carbon dioxide Capture and Storage”.

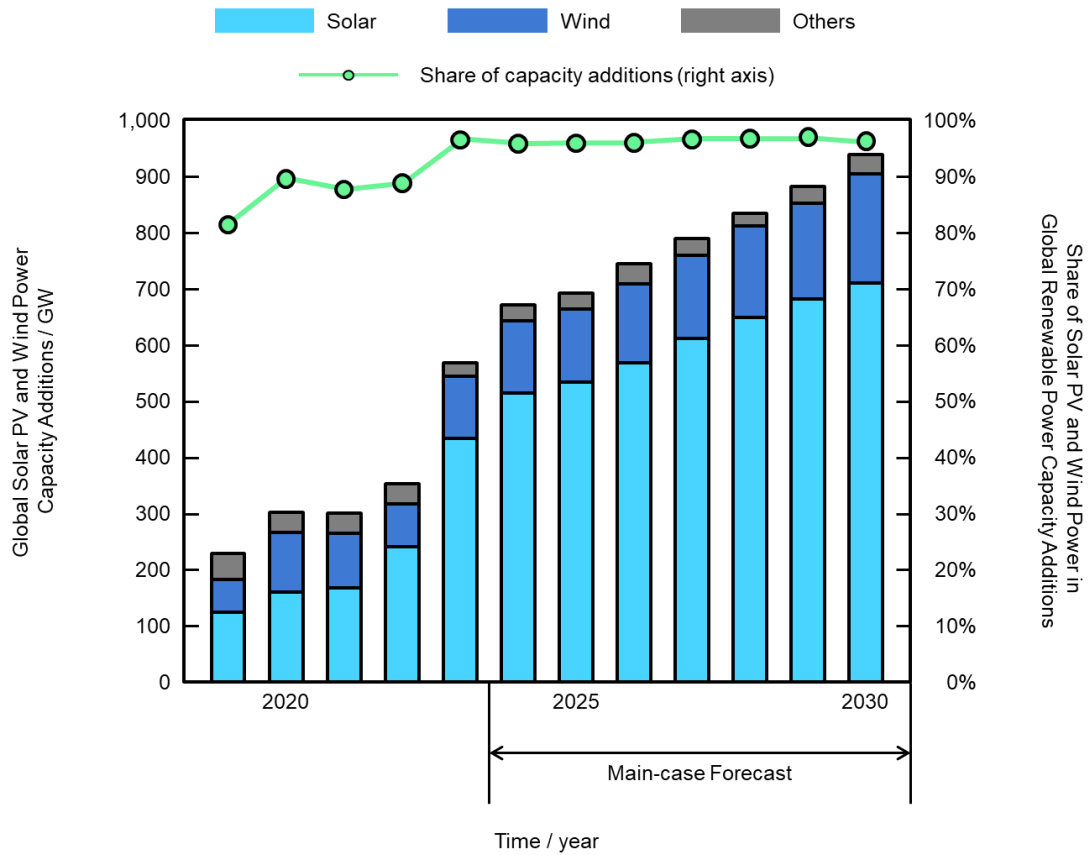


Fig. 1-2 Global solar PV and wind power capacity additions from 2019 to 2023 [5].

widespread use of solar power generation to replace fossil fuel combustion.

1.2 Solar Photovoltaic Power Generation

Solar cells are generally classified into three main types based on the substrate materials and their structures. Table 1-2 summarizes the classification, maximum conversion efficiency [6], and characteristics [7] of each technology. Crystalline Si solar cells are expected to play a key role in the renewable energy market. Si is the primary material used in crystalline solar cells. It is non-toxic, has a low environmental impact, and is abundant in the Earth's crust, accounting for 27.2% of its weight [8], eliminating concerns regarding resource depletion. According to the “Photovoltaic Market 2024” report by RTS Corporation, crystalline Si solar cells account for 98% of the global solar cell production in 2023 and are expected to maintain their position as the leading technology in the future (Fig. 1-3) [9]. Therefore, the global demand for Si substrates in solar cells is expected to grow steadily.

Alternative solar cell technologies, such as compound semiconductors (CdTe and CIGS) and organic materials, face challenges such as high costs, which require them to be used for specialized applications. This hinders their development into stable market products [7].

Table 1-2 Highest conversion efficiencies and features of solar photovoltaic cell technologies [6, 7].

Technology	Highest efficiency / %	Features	
		Advantage	Disadvantage
Single-crystalline Si	27.6	High conversion efficiency High durability	High cost
Polycrystalline Si	23.3	Lower cost than single-crystalline Si cell	Lower efficiency than single-crystalline Si cell
GaAs III–V	30.8	Highest efficiency Less loss at high temperature	High cost Use of toxic element
CIGS	23.6	Less material use	Use of In with low reserves
CdTe	23.1	Less material use	Use of toxic Cd
Organic (perovskite)	27.0	Less material use High flexibility	Low durability

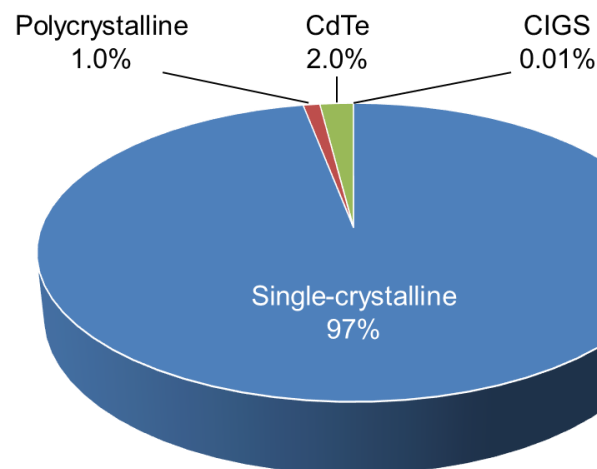


Fig. 1-3 Ratio of solar photovoltaic cells production by type of cells in 2023 [9].

1.3 Current Production Process of Crystalline Si Solar Cell

The manufacture of crystalline Si solar cells, which are currently in widespread use, involves the following multistep process [10]; steps (1)–(6) are illustrated in Fig. 1-4(a).

- (1) Production of metallurgical-grade Si (MG-Si, 2N purity) from SiO_2 via carbothermal reduction
- (2) Synthesis of SiHCl_3 via hydrochlorination of MG-Si with the SiCl_4 byproduct
- (3) Purification of SiHCl_3 via distillation
- (4) Production of high-purity polycrystalline Si via chemical vapor deposition (CVD) using SiHCl_3
- (5) Production of single-crystalline Si ingots via the Czochralski (CZ) method [11] or of polycrystalline Si ingots via the casting method
- (6) Production of Si wafers via slicing of Si ingots
- (7) Production of p–n junctions via either thermal diffusion or ion implantation
- (8) Cell fabrication by connecting electrical contacts and depositing an anti-reflective film coating
- (9) Module fabrication via cell encapsulation in resin and assembly into a frame with a back sheet, glass, or plastic cover

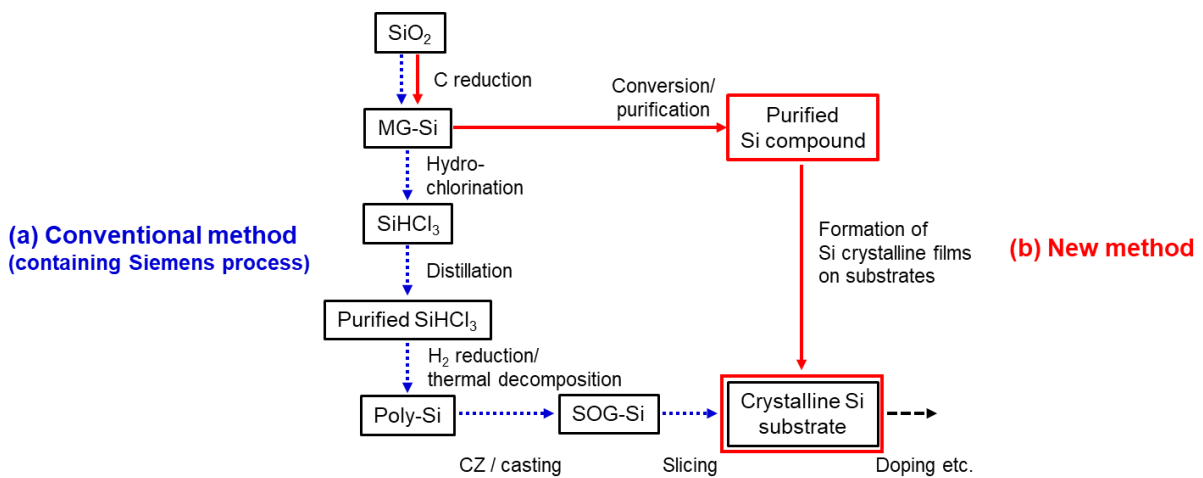


Fig. 1-4 Process flowcharts of manufacturing Si solar cells for (a) the conventional method using Siemens process and (b) the new method.

To manufacture polycrystalline Si from MG-Si, a manufacturing method based on the Siemens method has been used in steps (2)–(4) [12–14]. The Siemens method has also been used to manufacture semiconductor-grade Si (SEG-Si, purity 11N or higher). Owing to the rapid development of the solar cell industry in the late 2000s, the improved Siemens method, which simplifies the distillation process for purifying SiHCl_3 , has replaced the Siemens method as the manufacturing method for solar-cell-grade Si (SOG-Si) and has been adopted as the dedicated manufacturing method for SOG-Si. Although such methods ensure product purity, they entail energy-intensive processes given their basis in the Siemens method. Additionally, the multistep process inevitably involves the cutting of bulk Si, resulting in cutting losses. In summary, conventional manufacturing methods are associated with processes that are energy-intensive and those generating cutting losses. Therefore, new and efficient processes must be developed to mitigate the aforementioned challenges posed by the application of conventional methods for manufacturing polycrystalline Si. One such approach involves the direct formation of crystalline Si films on substrates from high-purity Si compounds, as shown in Fig. 1-4(b). This method differs from the Siemens method in that it does not require the manufacture or cutting of bulk Si and would therefore achieve higher energy efficiency and yield.

1.4 Electrochemical Process for Si Electrodeposition

1.4.1 Electrodeposition Method

Electrolysis can be used to directly deposit crystalline Si onto a substrate. Furthermore, electrolysis offers the capability to control the thickness and structure of the deposited film by varying the electrochemical parameters. It can also be adapted to substrates with complex shapes, making it suitable not only for manufacturing flat panels but also for applications such as columnar solar cells. Various electrolytes have been used in previous studies of Si electrodeposition, including organic solvents [15–22], ionic liquids [23–32], and high-temperature molten salts. In particular, electrodeposition in high-temperature molten salts has been shown to be a promising

approach for the production of highly crystalline Si films and has been extensively investigated. This section discusses electrodeposition using solid electrodes, and Section 1.5 concerns electrodeposition using liquid electrodes.

1.4.2 Si Electrodeposition in High-temperature Molten Salts

1.4.2.1 Molten Chloride Electrolytes

To date, several studies on Si electrodeposition using molten chloride salts, such as NaCl–KCl and LiCl–KCl, have been reported. Table 1-3 summarizes relevant previous studies [33-40]. In many cases, it was difficult to obtain smooth and flat Si films. This is attributable to the low concentration of Si ions in the molten chloride salts. The solubility of SiCl₄ introduced into molten LiCl–KCl molten salts at 723 K was quite low [34]. For the SiO₂ added as a Si ion source, the use of CaCl₂-or BaCl₂-based chloride melts, which dissolves oxides well, is considered to be promising. However, smooth and dense Si films were not obtained even by using these melts [35, 40].

The use of CaCl₂–CaO-based molten salts has been investigated to increase the solubility of SiO₂ in molten salts. Recently, Bard et al. successfully electroplated dense and smooth Si films

Table 1-3 Previous studies on the electrodeposition of Si in chloride melts.

Molten salt	Si source	Si ion conc.	Temperature / K	Current density or potential	Authors	Year	Ref.
NaCl–KCl	K ₂ SiF ₆	20 wt%	973–1123	2.8–3.9 V (voltage)	Stern <i>et al.</i>	1959	[33]
LiCl–KCl	SiCl ₄	—	723	–1.5 V vs. Ag ⁺ /Ag	Matsuda <i>et al.</i>	1996	[34]
CaCl ₂ –NaCl–CaO	SiCl ₄	3.7 mol%	1173	150 mA cm ^{–2}	Kongstein <i>et al.</i>	2007	[35]
BaCl ₂ –CaCl ₂ –NaCl	SiO ₂	1 mol%	923	–1.2 to –1.7 V vs. Ag ⁺ /Ag	Sakanaka <i>et al.</i>	2017	[36]
CaCl ₂ –CaO	SiO ₂	3.9 mol%	1123	10–20 mA cm ^{–2}	Yang <i>et al.</i>	2017	[37]
CaCl ₂ –CaO	CaSiO ₃ –SiO ₂	3.9 mol%	1123	10–20 mA cm ^{–2}	Zou <i>et al.</i>	2017	[38]
CaCl ₂ –CaO	CaSiO ₃ –SiO ₂	3.9 mol%	1123	10–20 mA cm ^{–2}	Zou <i>et al.</i>	2019	[39]
NaCl–CaCl ₂	SiO ₂	Saturated	1073	0.3 V vs Ca ²⁺ /Ca	Weng <i>et al.</i>	2019	[40]

using this method [37-39]. However, even though they have not reported detailed current density, it was quite low, and a long time was required to obtain sufficiently thick films. The film thickness was limited to approximately 60% of the theoretical value, with the remaining 40% reported to have deposited as powder [38]. The existence of Si ions as silicate ions is considered to be one of the causes of the insufficient diffusion of the O^{2-} ions into the bath during reduction at the cathode which limits the supply of Si ions to the cathode.

1.4.2.2 Molten Fluoride Electrolytes

The electrodeposition of Si using fluoride molten salts, such as LiF–KF and LiF–NaF–KF, has also been extensively reported with the representative studies summarized in Table 1-4 [41-60]. Smoother films were obtained when molten fluoride salts were used compared to those formed using molten chloride salts. Elwell et al. reported the formation of a Si film on a graphite substrate at a current density of up to 60 mA cm^{-2} [42-44, 46, 47, 49, 52]. In contrast to chloride molten salts, Si(IV) ions exist as stable ion species (SiF_6^{2-}) in fluoride molten salts. The high solubility of this ion at high concentrations likely enables electrodeposition of Si films at relatively high current densities.

Additionally, electrodeposition using baths containing SiO_2 as the Si ion source or baths containing K_2SiF_6 and SiO_2 has been reported. Elwell et al. reported that only a film was recovered on a graphite substrate from a NaF– CaF_2 melt, while only trace amounts of Si were recovered from the MgF_2 –NaF, KF– BaF_2 , KF– CaF_2 and KF– MgF_2 melts. In a unique study, fabrication of a dense Si film on a Mo substrate in a BaF_2 – CaF_2 – SiO_2 melt via electrolysis at 1573 K has been reported; however, this was attributed to the formation of intermetallic compounds [58]. Furthermore, the change in the coordination state of Si ions due to the addition of Li_2O was analyzed; however, the current efficiency of Si electrodeposition from LiF–NaF–KF containing SiO_2 was only 10% at 873 K [59, 60]. These reports suggest that the presence of oxide ions in molten salts inhibits the formation of Si films. Other issues with the use of molten fluoride salts include high corrosion and

difficulty in the removal of the salts.

Table 1-4 Previous studies on the electrodeposition of Si in fluoride melts.

Molten salt	Si source	Si ion conc.	Temperature / K	Current density or potential	Authors	Year	Ref.
LiF–KF and LiF–NaF–KF	K ₂ SiF ₆	1–10 mol%	873–1123	0.1–100 mA cm ⁻²	Cohen <i>et al.</i>	1976	[41]
LiF–KF and LiF–NaF–KF	K ₂ SiF ₆	0.5–2.5 mol%	1018–1023	–0.40 to –0.86 V vs Pt, 10–60 mA cm ⁻²	Rao <i>et al.</i>	1980	[42]
LiF–KF	K ₂ SiF ₆	12 mol%	1023	25 mA cm ⁻²	Rao <i>et al.</i>	1981	[43]
LiF–KF	K ₂ SiF ₆	8–14 mol%	1018	–0.75 V vs Pt	Rao <i>et al.</i>	1981	[44]
NaF–CaF ₂	SiO ₂	13.8 mol%	1423	1.02 V (voltage)	Elwell	1981	[45]
LiF–NaF–KF	K ₂ SiF ₆	15 mol%	1018	–	Elwell <i>et al.</i>	1982	[46]
LiF–KF and LiF–NaF–KF	K ₂ SiF ₆	0.5–2.5 mol%	1018–1023	–0.40 to –0.86 V vs Pt, 10–60 mA cm ⁻²	Rao <i>et al.</i>	1982	[47]
NaF–KF	K ₂ SiF ₆ –SiO ₂	39.5 mol%	983–1053	300–3000 mA cm ⁻²	Boiko <i>et al.</i>	1982	[48]
LiF–KF	K ₂ SiF ₆	0.5–2.5 mol%	1018–1023	–0.80 to –0.65 V vs Pt	Elwell <i>et al.</i>	1983	[49]
LiF–KF	K ₂ SiF ₆	8 mol%	1023	40–70 mA cm ⁻²	Carleton <i>et al.</i>	1983	[50]
LiF–KF and LiF–NaF–KF	K ₂ SiF ₆ and Na ₂ SiF ₆	0.05–5 mol%	1023	5–40 mA cm ⁻² (pulse)	Bouteillon <i>et al.</i>	1983	[51]
LiF–KF	K ₂ SiF ₆	8–14 mol%	1023	20–50 mA cm ⁻²	Elwell <i>et al.</i>	1984	[52]
LiF–NaF–KF	K ₂ SiF ₆	10 wt%	1023–1043	–0.7 to –1.3 V vs Pt	Stern <i>et al.</i>	1985	[53]
LiF–KF	K ₂ SiF ₆	10 wt%	1023–1123	10–150 mA cm ⁻² , 0.3 V (voltage)	Moore <i>et al.</i>	1997	[54]
Na ₃ AlF ₆	SiO ₂	5 wt%	973–1573	2.2 A	Oishi <i>et al.</i>	2007	[55]
LiF–KF	K ₂ SiF ₆	5 mol%	823–1073	21–41 mA cm ⁻²	Osen <i>et al.</i>	2010	[56]
LiF–KF and LiF–NaF–KF	K ₂ SiF ₆	5–20 mol%	823–1073	40–100 mA cm ⁻²	Haarberg <i>et al.</i>	2013	[57]
BaF ₂ –CaF ₂	SiO ₂	1.06 × 10 ⁻⁴ to 2.05 × 10 ⁻³ mol cm ⁻³	1573	118 mA cm ⁻²	Hu <i>et al.</i>	2013	[58]
LiF–NaF–KF	SiO ₂	0.2–0.5 mol%	873	0.2–0.7 V vs K ⁺ /K	Sakanaka <i>et al.</i>	2015	[59]
LiF–NaF–KF	SiO ₂	0.5 mol%	873	0.2–0.4 V vs K ⁺ /K	Suzuki <i>et al.</i>	2019	[60]

1.4.2.3 Molten Fluoride–Chloride Electrolytes

Si electrodeposition using fluoride–chloride mixed molten salts has also been reported, as summarized in Table 1-5 [61-73]. Deposits in film form have been mostly obtained using baths with fluoride concentrations of 40 mol% or higher. Zaykov et al. investigated the diffusion coefficient of Si(IV) ions and the nucleation modes in a bath containing the KF–KCl molten salt with added K₂SiF₆ and obtained smooth Si films [62]. Nohira et al. reported the temperature dependence of crystal size using a bath containing the KF–KCl molten salt with added K₂SiF₆ [63, 64, 69, 72]. Cross-sectional and electron backscatter diffraction (EBSD) images of the electrolytically deposited Si films are shown in Fig. 1-5 [69]. At 923 K in molten KF–KCl, the film thickness was approximately 50 nm, while at the higher temperature of 1073 K, it was limited to a maximum of approximately 20 μm [69].

Yasuda et al. proposed a Si electrodeposition method using KF–KCl molten salt and SiCl₄ as the Si source [67]. Fig. 1-6 shows a schematic diagram of the overall reaction [63]. When SiCl₄ is introduced as the Si source and electrodeposition is performed, the reaction proceeds through the SiF₆²⁻ generation reaction (reaction 1-1), the Si generation reaction at the cathode (reaction 1-2), and the Cl₂ gas generation reaction at the anode (reaction 1-3).



In this case, closed-cycle operation can be achieved by reusing the Cl₂ generated at the anode for SiCl₄ production.

Similar to reports on molten fluoride salts, it has been reported that the addition of oxygen-containing substances causes Si deposits to change from a continuous planar structure to a fibrous and powdery structure, accompanied by a decrease in the average grain size. Additionally, Norikawa et al. reported the influence of cation species on Si electrodeposition in molten AF–ACl

(A = Li, Na, K, or Cs) with a single cation [73]. In Si electrodeposition on a Ag substrate at 1073 K, smooth films were not obtained in the Li and Na systems, whereas dense and smooth Si films were obtained in the K and Cs systems [73].

Table 1-5 Previous studies on the electrodeposition of Si in fluoride–chloride melts.

Molten salt	Si source	Si ion conc.	Temperature / K	Current density or potential	Authors	Year	Ref.
NaCl–KCl–NaF	K ₂ SiF ₆	$1.5\text{--}3.3 \times 10^{-4}$ mol cm ⁻³	1023	–0.75 to –1.2 V vs C	Kuznetsova <i>et al.</i>	2009	[61]
KF–KCl	K ₂ SiF ₆ and SiO ₂	0.5–13 mol%	923–1073	2–4 V (voltage)	Zaykov <i>et al.</i>	2014	[62]
KF–KCl	K ₂ SiF ₆	0.5–5 mol%	923	60 mA cm ⁻²	Maeda <i>et al.</i>	2015	[63]
KF–KCl	K ₂ SiF ₆	0.5–5 mol%	923	10–500 mA cm ⁻²	Yasuda <i>et al.</i>	2016	[64]
KF–KCl	K ₂ SiF ₆ and SiO ₂	10 mol%	1023	20–1500 mA cm ⁻²	Zhuk <i>et al.</i>	2017	[65]
KF–KCl	K ₂ SiF ₆	10 mol%	943–1103	10–150 mA cm ⁻²	Zhuk <i>et al.</i>	2017	[66]
KF–KCl	SiCl ₄	2.3 mol%	923	155 mA cm ⁻²	Yasuda <i>et al.</i>	2017	[67]
KF–KCl	K ₂ SiF ₆	1.0 mol%	923	5–20 mA cm ⁻²	Peng <i>et al.</i>	2017	[68]
KF–KCl	K ₂ SiF ₆	2.0–3.5 mol%	923–1073	100–300 mA cm ⁻²	Yasuda <i>et al.</i>	2018	[69]
KF–KCl–KI	K ₂ SiF ₆	0.075–0.5 mol%	973–1023	20–200 mA cm ⁻²	Laptev <i>et al.</i>	2020	[70]
KF–KCl–KI	K ₂ SiF ₆	0.5 mol%	993	100 mA cm ⁻²	Isakov <i>et al.</i>	2020	[71]
KF–KCl	K ₂ SiF ₆	2.0–5.0 mol%	1073	50–100 mA cm ⁻²	Yasuda <i>et al.</i>	2021	[72]
AF–ACl, (A=Li, Na, K, Cs)	A ₂ SiF ₆ , (A=Li, Na, K, Cs)	0.7 mol L ⁻¹	1073	50–200 mA cm ⁻²	Norikawa <i>et al.</i>	2022	[73]

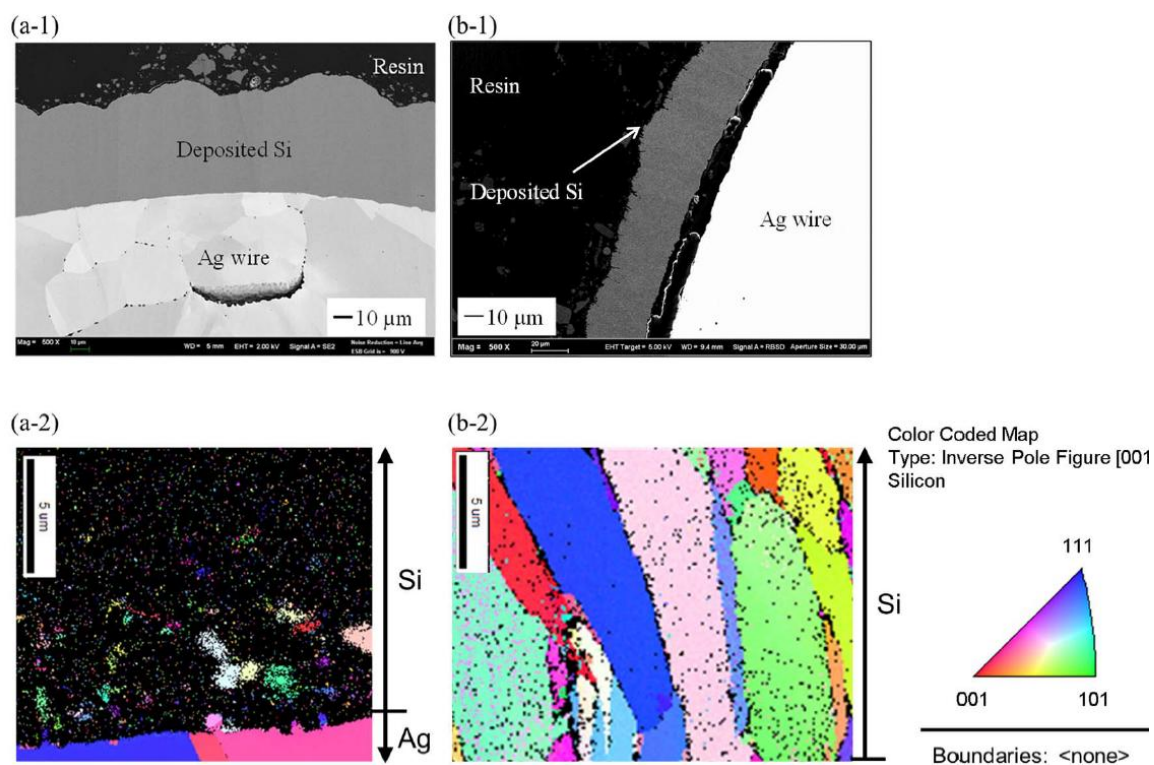


Fig. 1-5 (a-1)(b-1) Cross-sectional FE-SEM images and (a-2)(b-2) crystal grain maps from EBSD analysis of the Si deposit. The deposits were obtained by galvanostatic electrolysis on Ag wire electrodes at 155 mA cm^{-2} for 20 min in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at (a-1)(a-2) 923 K and (b-1)(b-2) 1073 K [69].

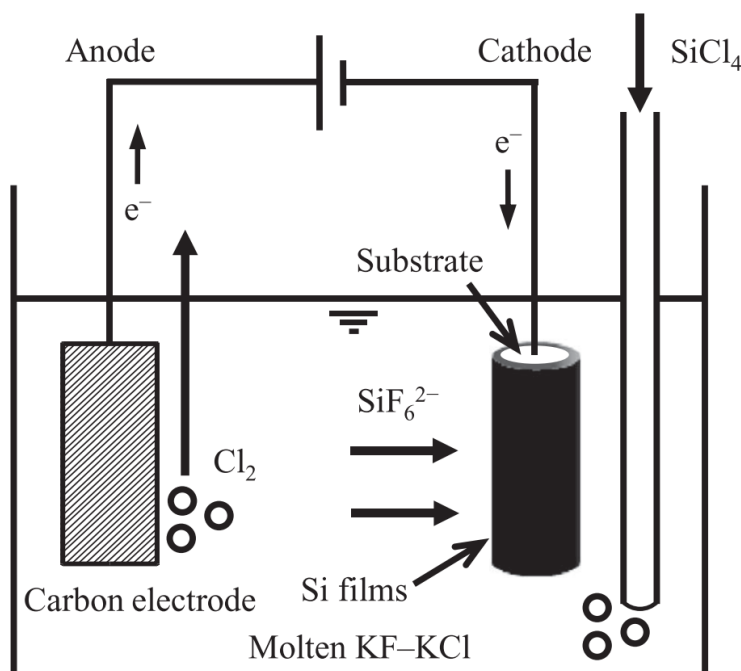


Fig. 1-6 A schematic illustration for the principle of electroplating process of Si in KF-KCl molten salt [63].

1.5 Background and Purpose of This Study

1.5.1 KF–KCl Mixed Molten Salt

Based on the above-discussed reports, molten salts containing no oxides and rich in fluorides are considered to be suitable electrolyte baths for electrodepositing Si films. The use of easily water-soluble fluoride–chloride mixed molten salts is important for addressing the issues associated with fluoride molten salts, namely difficulty in removal of adhered salt. Therefore, in this study, a KF–KCl mixed molten salt is used as the electrolyte. The solubilities of representative alkali and alkaline earth metal halides in water at 298 K are listed in Table 1-6 [74]. While many fluoride salts, including LiF and CaF₂, are poorly soluble in water, KF is highly soluble in water and KCl which has the same cation also has a relatively high solubility in water. Therefore, compared to fluoride molten salts, the KF–KCl mixed molten salts are more soluble in water, facilitating the removal of adhered salt from the surface of the deposit. Fig. 1-7 shows the dissolution of LiF–NaF–KF and KF–KCl molten salts in warm water [75]. The KF–KCl molten salt pellets dissolved rapidly in warm water at 333 K and disappeared completely after 30 min [75]. Fig. 1-8 shows the binary phase diagram of the KF–KCl system [76]. By using the eutectic composition, electrodeposition can be carried out at a relatively low temperature of approximately

Table 1-6 Solubilities in water at 298 K for representative alkali halides and alkaline earth halides [74].

Alkali fluoride Alkaline earth fluoride	Solubility / g (100g-H ₂ O) ⁻¹	Alkali chloride Alkaline earth chloride	Solubility / g (100g-H ₂ O) ⁻¹
LiF	0.134	LiCl	84.54
NaF	4.13	NaCl	35.96
KF	101.7	KCl	35.54
RbF	300	RbCl	93.87
CsF	573	CsCl	191.0
MgF ₂	0.013	MgCl ₂	56.0
CaF ₂	0.0016	CaCl ₂	81.26

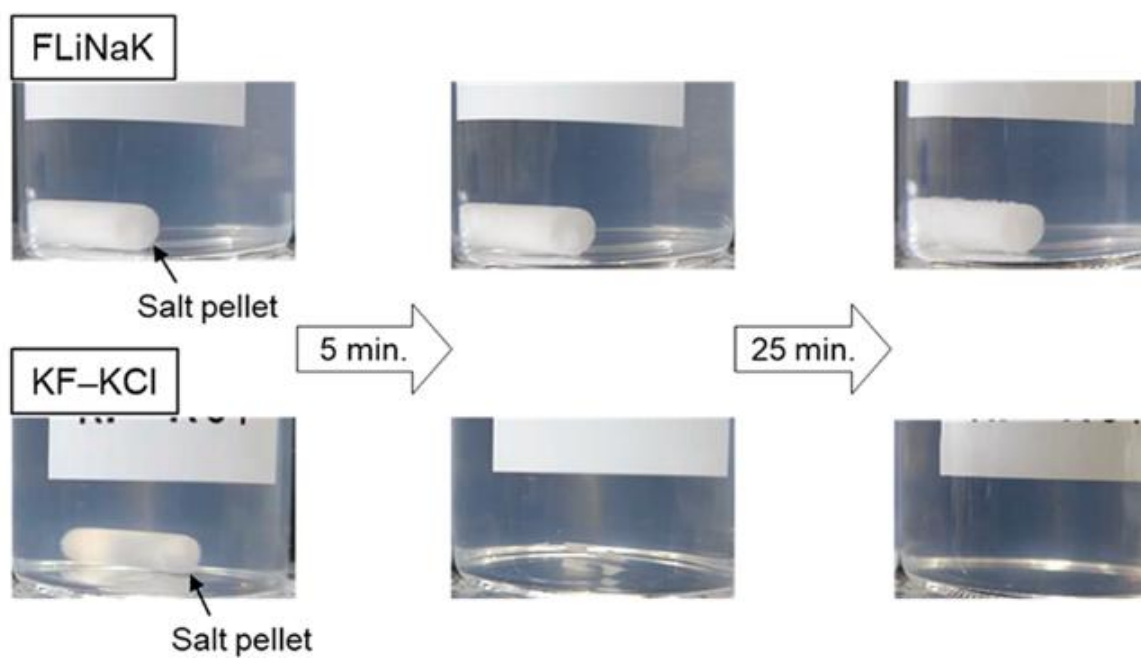


Fig. 1-7 Comparison of solubility to hot water (333 K) for LiF–NaF–KF and KF–KCl pellets [75].

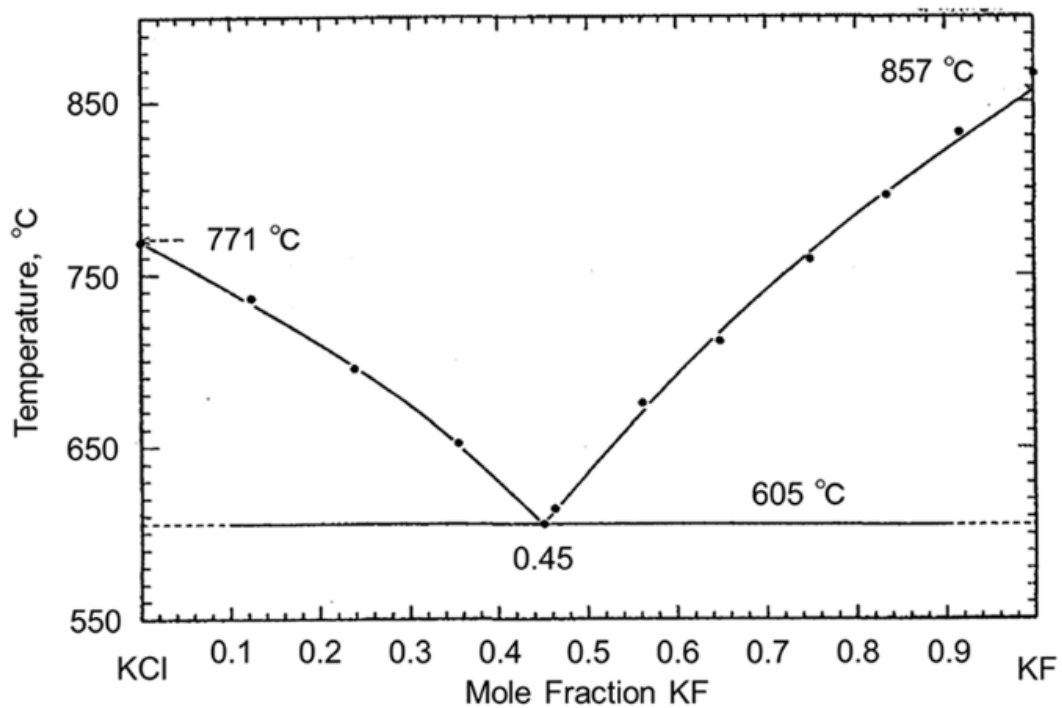


Fig. 1-8 Phase diagram of the KF–KCl system [76].

923 K. Notably, similar to the KF–KCl mixed molten salts, RbF–RbCl mixed molten salts or CsF–CsCl mixed molten salts are also highly soluble in water; however, they are much more expensive than the KF–KCl mixed molten salts. Therefore, the KF–KCl molten salts are advantageous from the perspective of practical use.

1.5.2 Liquid Metal Electrodes in Si Electrodeposition and the ec-LLS Method

The crystal size required for Si in polycrystalline Si solar cell substrates is 500 μm or more [77]. Thus, the small size of Si crystals in crystalline Si films is one of the challenges that must be overcome for practical implementation of an electrodeposition-based method for high-quality Si fabrication. The sizes of the Si crystals obtained using the method described in Section 1.4, which employs solid electrodes, are all significantly smaller than the required size. Therefore in this study, in order to electrolytically deposit Si with larger crystal sizes, liquid metal electrodes are used instead of conventional solid electrodes, such as Ag or graphite.

The main studies on Si electrodeposition using liquid metal electrodes are summarized in Table 1-7 [78-81]. Using organic solvents and a liquid Ga electrode, Gu et al. successfully deposited crystalline Si powder with a crystal size of 200 nm at 353 K [78]. Using ionic liquids together with a liquid Ga electrode, Zhang et al. successfully deposited crystalline Si powder at 373 K; however, the purity of the powder was low [80]. In other studies using solid cathodes in organic solvents and ionic liquids near room temperature, the deposition of crystalline Si has not been reported. Therefore, the use of liquid metal electrodes is expected to promote crystal growth. As regards studies using high-temperature molten salts, in which crystalline Si deposition on solid electrodes was confirmed, Haarberg et al. successfully deposited granular crystalline Si at 923 K using a liquid Ga electrode [81]. The grain size of the obtained Si was larger than that of the Si obtained using the solid Ag electrode in the same electrolyte bath at the same temperature. These results suggest that further crystal growth can be expected by using liquid metal electrodes in high-temperature molten salts. The promotion of crystal growth using liquid metal electrodes has been explained

based on the electrochemical liquid–liquid–solid (ec-LLS) crystal growth method proposed by Maldonado et al. [78]. The ec-LLS method promotes crystal growth by forming a liquid–liquid–solid three-phase boundary between the electrolyte, the liquid metal electrode, and solid product. The liquid metal not only serves as an electrode but also functions as a solvent intermediate that dissolves the product during crystal growth. As shown in Fig. 1-9, this method proceeds through the following four stages [78]: (1) electrochemical reduction of the unreduced precursor dissolved in the solvent on the surface of a liquid metal electrode, (2) dissolution of the reduced product into the liquid metal electrode, (3) nucleation of the product after reaching a certain degree of supersaturation, and (4) crystal growth. Previous studies using this method have reported the electrodeposition of various semiconductor materials, including cases wherein a liquid metal electrode served as a co-reagent for polycrystalline synthesis [82-93].

Maldonado et al. used the same principle to prepare nano-droplets on a solid substrate in an organic solvent as electrodes and electrodeposited crystalline nanowires [79]. As shown schematically in Fig. 1-10(a), the nanowires grew from a solid substrate. This growth is reported to occur because the Si dissolved in the metal nano-droplets deposits onto the solid substrate, as shown in the microscopic schematic diagram in Fig. 1-10(b). By applying this mechanism,

Table 1-7 Previous studies on electrodeposition of Si using liquid metal electrodes.

Electrolyte	Si source	Si ion conc.	Temperature / K	Cathode	Authors	Year	Ref.
PC–TBAC	SiCl ₄	0.5 M	353–373	Ga	Gu et al.	2013	[78]
PC–TBAC	SiCl ₄	0.5 M	373	Ga nano-droplet	Ma et al.	2015	[79]
[TBMA][TFSA]	SiCl ₄	0.25 M	373	Ga	Zhang et al.	2016	[80]
KF–KCl	K ₂ SiF ₆	2.0 mol%	923	Ga	Haaberg et al.	2019	[81]

PC: propylene carbonate

TBAC: tetrabutylammonium chloride

TBMA: tributyl(methyl)ammonium

TFSA: bis(trifluoromethylsulfonyl)amide

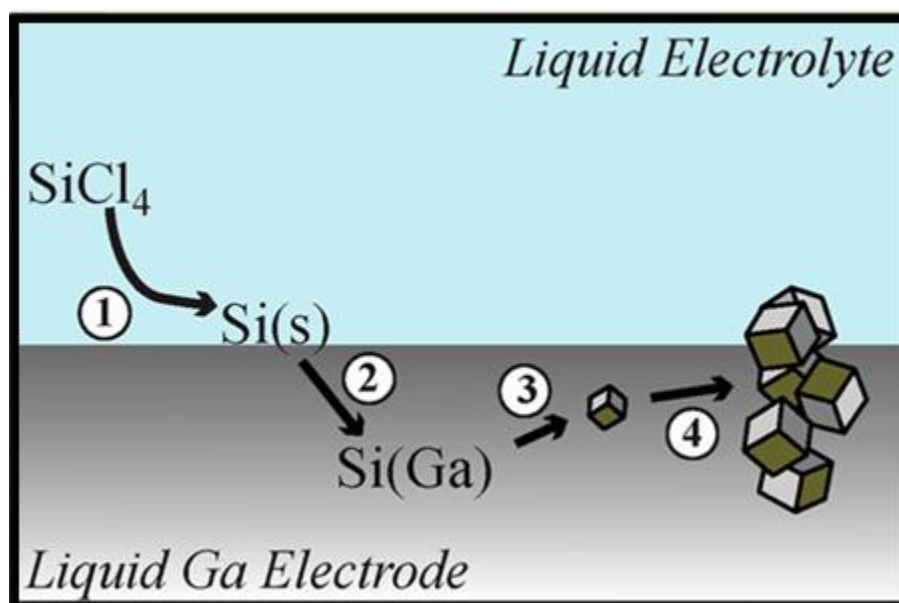


Fig. 1-9 A schematic depiction (not drawn to scale) of an electrochemical liquid–liquid–solid (ec-LLS) process yielding crystalline Si with a liquid Ga electrode [78].

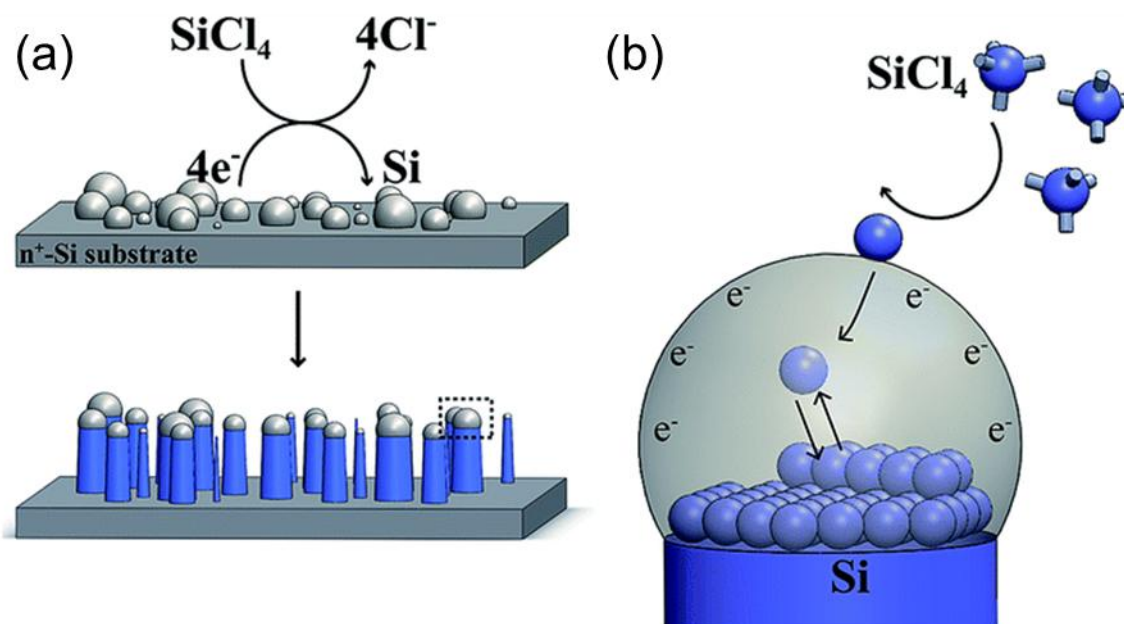


Fig. 1-10 (a) A pictorial representation of the Si ec-LLS nanowire deposition process, where the electrochemical reduction of SiCl_4 seeded the growth of Si nanowires only at liquid metal nano-droplets. (b) A microscopic illustration of the elementary steps in the Si nanowire ec-LLS process (not drawn to scale) [79].

electrodeposits in film form can be obtained on a solid substrate via electrodeposition using the liquid metal as an electrode with a solid boundary and a planar surface.

Even when liquid metal electrodes are used in high-temperature molten salts, crystal growth is expected to be promoted by the same mechanism as that in the ec-LLS method described above. However, to date, no reports on the mechanism of Si growth for systems with liquid metal electrodes and high-temperature molten salts have been published.

1.5.3 Selection of Liquid Metal Electrodes

The liquid metal electrode used in Si electrodeposition must satisfy the following two conditions: (a) it must exist in the liquid form at the temperature for Si electrodeposition, and (b) it must not form intermetallic compounds with Si. Both of these conditions are satisfied by Zn. Regarding condition (a), the melting point of Zn is 693 K and its boiling point is 1180 K; thus, its liquid phase matches the typical range of the temperature for Si electrodeposition [94]. Regarding condition (b), as observed from the Si–Zn binary phase diagram presented in Fig. 1-11 [95], Zn does not form intermetallic compounds with Si at room temperature and only forms a liquid alloy, even at the temperature for Si electrodeposition. Moreover, the liquid metal electrodes remaining on the surface of the electrolytic product must be removed in subsequent processes. Zn is used in a previous method developed by DuPont for manufacturing high-purity Si for semiconductors, and the manufacturing process included a Zn removal step that exploited the high vapor pressure of Zn. Therefore, Zn can be removed in principle. Furthermore, Yasuda et al. investigated the evaporation of liquid Zn at a higher temperature of 1123 K in a molten salt and reported that despite its high vapor pressure, the evaporation rate of Zn is sufficiently low to allow its use as a liquid electrode [96]. This is due to the presence of molten salt above Zn.

Ga is another metal that satisfies conditions (a) and (b). Regarding condition (a), the melting point of Ga is 303 K and its boiling point is 2676 K. Compared to other metals, its low melting point is expected to facilitate physical separation of the liquid product from solid Si. In addition, it

has a high boiling point and low vapor pressure. As a result, it is easy to handle as a liquid metal electrode, which is another advantage. Regarding condition (b), as observed from the Si–Ga binary phase diagram presented in Fig. 1-12 [97], Ga does not form intermetallic compounds with Si at room temperature and only forms a liquid alloy at the temperature for Si electrodeposition.

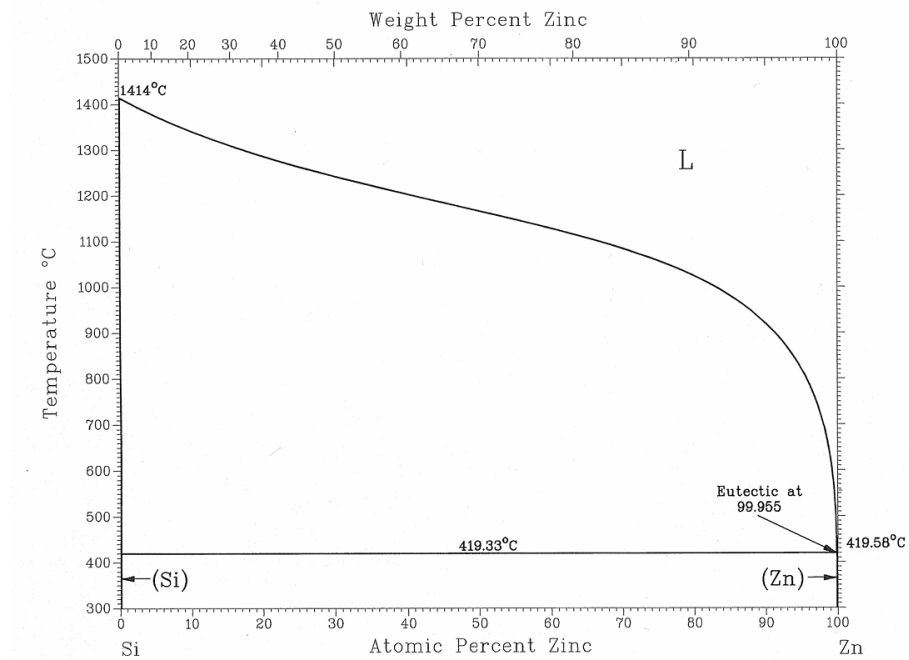


Fig. 1-11 Si–Zn binary phase diagram [95].

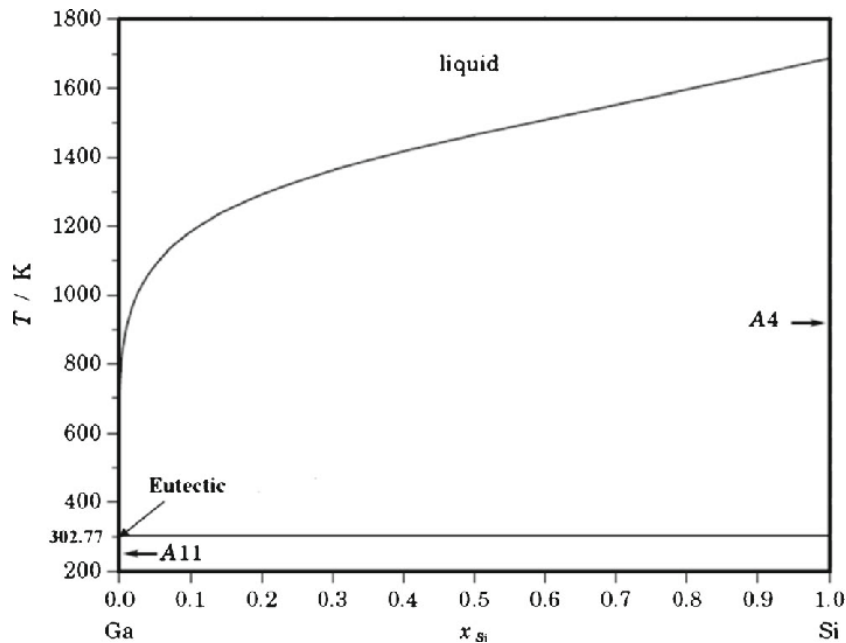


Fig. 1-12 Si–Ga binary phase diagram [97].

1.5.4 Electrodeposition of Crystalline Si Film Using Liquid Zn Electrode

As mentioned in Section 1.4, various methods have been investigated for electrodepositing crystalline Si films onto substrates. However, no reports have been published on the electrodeposition of crystalline Si films using liquid metal electrodes. Therefore, this study aimed to develop a method for electrodepositing Si films onto solid substrates using a liquid metal electrode. Here, Zn is used as a liquid metal electrode for description. Two methods for electrodeposition of Si films have been proposed, and are described in Sections 1.5.4.2 and 1.5.4.3, respectively.

1.5.4.1 Selection of Solid Substrates

It is preferable to use a material that does not form compounds with liquid Zn as a substrate for forming a Si film. Therefore, both W and graphite are used in this study. These materials do not form compounds with Zn, making them suitable for retaining liquid Zn in film form on solid substrates.

1.5.4.2 Electrodeposition of Si Films Using a Thin Film of Liquid Zn

To obtain a crystalline Si film with large grain size on a solid substrate, electrodeposition is performed using the mechanism illustrated in the schematic diagram presented in Fig. 1-13. First, a thin film of liquid Zn is prepared on a solid substrate as the electrode (a). When Si ions are reduced by electrodeposition, Si and Zn form a liquid alloy according to reaction (1-4), and the thin film of liquid Zn becomes a thin film of liquid Si–Zn (b).



After the liquid Si–Zn thin film becomes saturated with Si, solid Si begins to deposit on the solid substrate. After that, by continuing the electrolysis, a crystalline Si film composed of large Si grains is obtained on the solid substrate (d). After cooling, Zn is removed by post-treatment (e). In

the actual process, it is considered preferable to reuse the liquid Si–Zn alloy before cooling and then remove any remaining Zn by vacuum evaporation. In the laboratory-scale experiments of this study, acid treatment is conducted after cooling.

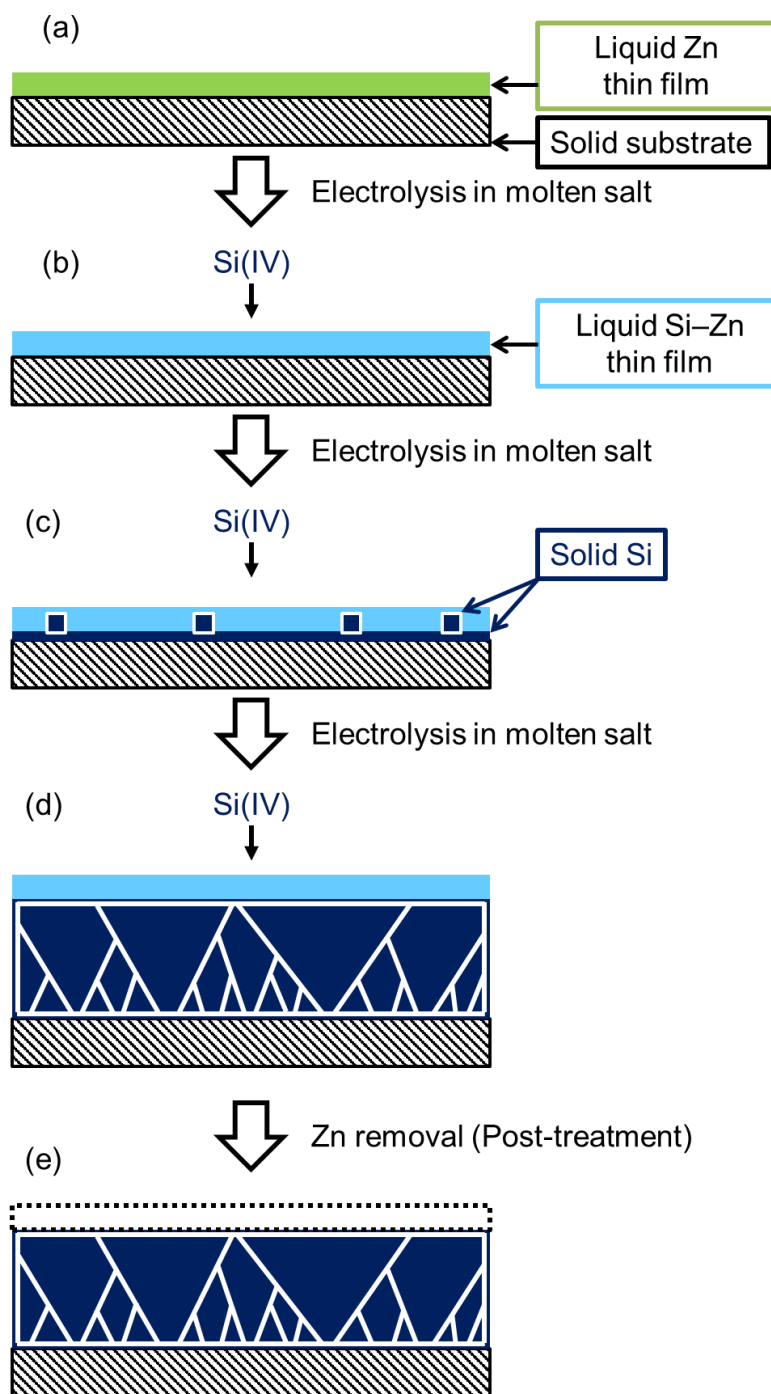


Fig. 1-13 A schematic of the proposed mechanism of Si deposition using liquid Zn thin-film electrode.

1.5.4.3 Electrodeposition of Si Films via Co-deposition of Si and Zn

When materials such as graphite are used as solid substrate materials, wettability with liquid Zn is poor, which may prevent liquid Zn from forming a film. Unless liquid Zn forms a film, Si with large crystal sizes cannot be electrodeposited in a film. Therefore, instead of retaining liquid Zn as an electrode, a method of supplying it by electrochemical reduction is used. Although liquid Zn is considered to have poor wettability with graphite, this may not be the case for liquid Si–Zn alloys. To deposit the liquid Si–Zn alloys, co-deposition of Si and Zn is conducted. A schematic of the proposed method is shown in Fig. 1-14. First, a solid substrate is used as the electrode (a). Upon the reduction of Si ions by electrolysis, a liquid Si–Zn thin film forms on the solid substrate according to reactions (1-4) and (1-5) (b).



As shown in the phase diagram, the concentration of soluble Si is low (1 at%) [95], and the liquid Si–Zn alloy quickly becomes saturated with Si, leading to the initiation of the deposition of solid Si on the solid substrate (c). Liquid Zn continues to be generated during electrolysis, but solid Si deposition continues to occur on the solid substrate, forming a crystalline Si film composed of large Si grains (d). Finally, Zn is removed as described in Section 1.5.3.2.

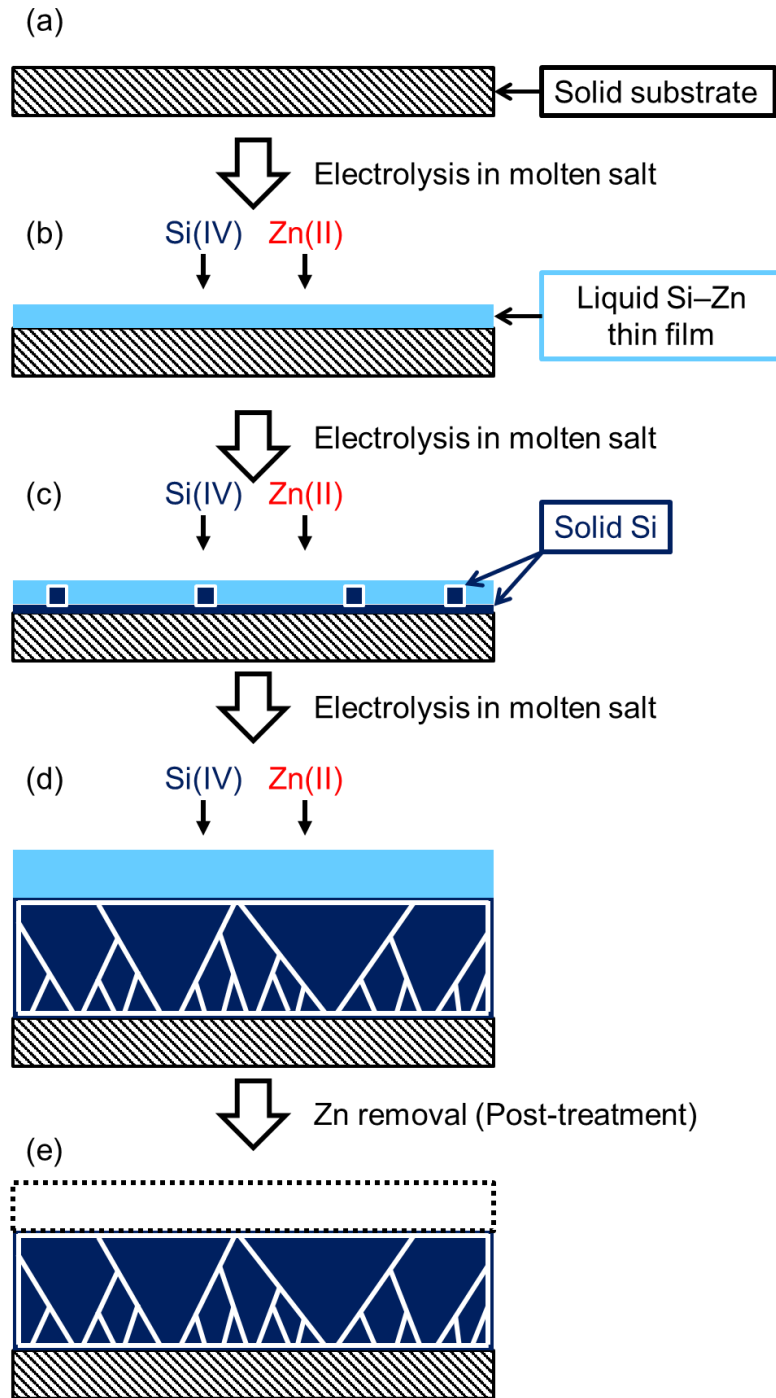


Fig. 1-14 A schematic of the proposed mechanism of Si deposition via co-deposition of Si and Zn.

1.6 Outline of This Study

For the establishment of the production process of crystalline Si substrate for solar cells using a liquid Zn electrode in molten salts, the electrochemical study using liquid Zn electrode is investigated in fluoride–chloride mixed molten salts in this study.

Chapter 2 presents the first study that confirmed that large-grain crystalline Si can be obtained using a liquid Zn electrode. Si electrodeposition is performed using a liquid Zn electrode in the KF–KCl molten salt at 923 K. The reaction during Si electrodeposition on the liquid Zn electrode is investigated using cyclic voltammetry (CV). The grain size distributions of the samples obtained under various electrical conditions is compared, and the mechanism of solid Si crystal deposition using a liquid Zn electrode is investigated. The cross-section of the Zn electrode solidified after electrodeposition and the electrodeposited Si is observed by scanning electron microscopy (SEM) and analyzed by energy-dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD). The grain size distribution is investigated by weight sieving.

In Chapter 3, to compare the results obtained using a liquid Zn electrode with those obtained using other liquid metals, Si electrodeposition is performed using a liquid Ga electrode in a KF–KCl molten salt at 923 K. The reaction during Si electrodeposition on the liquid Ga electrode is investigated using cyclic voltammetry, and Si electrodeposition is performed using a liquid Ga electrode. The grain size distribution of the electrolytically deposited Si is investigated under various electrical conditions. The results are compared with those obtained using a liquid Zn electrode and the causes of these differences are examined.

Chapter 4 describes Si electrodeposition performed using thin liquid Zn deposited on a substrate as an electrode in a KF–KCl molten salt at 923 K, with the aim of obtaining crystalline Si in film form using a liquid Zn electrode. A thin film of liquid Zn is prepared via electrolysis using graphite and W as substrates in a KF–KCl molten salt solution of at 923 K and in a sulfuric acid solution at 313 K. The conditions under which liquid Zn could be maintained in film form in the molten salt solution at the temperature used for Si electrodeposition are determined, and the

surface and cross-sectional structures of the samples electrodeposited using the thin film of liquid Zn under these conditions are analyzed by SEM/EDX and XRD.

In Chapter 5, to deposit crystalline Si films with large grain sizes on graphite substrates that show poor wettability with liquid Zn, electrodeposition co-deposition of Si and Zn is conducted in molten $\text{KF-KCl-K}_2\text{SiF}_6\text{-ZnCl}_2$ systems at 923 K. The electrochemical behavior of Si(IV) and Zn(II) ions is investigated using cyclic voltammetry. Electrodeposition is performed at various current densities and Zn ion concentrations, and the surfaces and cross-sections of the deposited films are analyzed via SEM/EDX to determine the optimal conditions.

Finally, Chapter 6 summarizes the preceding chapters. In particular, the author discusses the deposition mechanism of crystalline Si films containing large Si grains.

References

1. *Climate Change 2021: The Physical Science Basis*, Intergovernmental Panel on Climate Change (IPCC) (2021).
2. Global Change Data Lab from University of Oxford, Energy Production and Consumption, <https://ourworldindata.org/energy-production-consumption#primary-energy-consumption> (05/18/2025 accessed).
3. *Climate Change 2014-Mitigation of Climate Change, Annex III: Technology-Specific Cost and Performance Parameters*, Intergovernmental Panel on Climate Change (IPCC) Working Group III (2014).
4. *Sustainable Recovery: World Energy Outlook 2020 Special Report*, International Energy Agency (IEA) (2020).
5. *Renewables 2024*, International Energy Agency (IEA) (2024).
6. National Renewable Energy Laboratory transforming ENERGY, Best Research-Cell Efficiency Chart, <https://www.nrel.gov/pv/cell-efficiency.html> (05/18/2025 accessed).
7. *Trends 2018 in Photovoltaic Applications*, International Energy Agency Photovoltaic Power

System Programme (IEA PVPS) (2018).

8. *Kagaku Binran Kisohen, 5th ed.*, Maruzen Co., Ltd. (2004). [in Japanese]
9. *Photovoltaic Market 2024*, RTS Corp. (2024).
10. T. Abe, *Advanced Electronics I-5, Si-Crystal Growth and Wafer Manufacturing*, Baifukan Co., Ltd. (1994). [in Japanese]
11. J. Czochralski, *Z. Phys. Chem.*, **92**, 219 (1918). [in German]
12. C. Bye and B. Ceccaroli, *Sol. Energy Mater. Sol. Cells*, **130**, 634 (2014).
13. H. Schweickert, K. Reusche, and H. Gutsche, U.S. Patent 3011877 (1961).
14. H. Gutsche, U.S. Patent 3011877 (1962).
15. A. K. Agrawal and A. E. Austin, *J. Electrochem. Soc.*, **128**, 2292 (1981).
16. M. Bechelany, J. Elias, P. Brodard, J. Michler, and L. Philippe, *Thin Solid Films*, **520**, 1895 (2012).
17. A. K. Cendrowska, L. Marot, M. Strawski, R. Steiner, and E. Mayer, *J. Electrochem. Soc.*, **163**, D100 (2016).
18. Q. P. Ma, W. Liu, B. C. Wang, and Q. S. Meng, *Adv. Mater. Res.*, **79–82**, 1635 (2009).
19. Y. Takeda, R. Kanno, and O. Yamamoto, *J. Electrochem. Soc.*, **128**, 1221 (1981).
20. O. Yamamoto and Y. Takeda, *Kinzoku Hyomen Gijutsu*, **37**, 262 (1986). [in Japanese]
21. T. Munisamy and A. J. Bard, *Electrochim. Acta*, **55**, 3797 (2010).
22. C. Vichery, V. Le Nader, C. Frantz, Y. Zhang, J. Michler, and L. Philippe, *Phys. Chem. Chem. Phys.*, **16**, 22222 (2014).
23. N. Borisenko, S. Z. E. Abedin, and F. Endres, *J. Phys. Chem. B.*, **110**, 6250 (2006).
24. A. M. Martinez, K. S. Osen, O. E. Kongstein, E. Sheridan, A. Ulyashin, and G. M. Haarberg, *ECS Trans.*, **25**, 107 (2010).
25. J. Park, C. K. Lee, K. Kwon, and H. Kim, *Int. J. Electrochem. Sci.*, **8**, 4206 (2013).
26. N. K. Shah, R. K. Pati, and A. R. Mukhopadhyay, *Langmuir*, **33**, 1599 (2017).
27. S. Thomas, D. Kowalski, M. Molinari, and J. Mallet, *Electrochim. Acta*, **265**, 166 (2018).

28. Y. Tsuyuki, T. A. P. Huynh, J. Komajina, Y. Fukunaka, and T. Homma, *Electrochim. Acta*, **183**, 49 (2015).
29. Y. Tsuyuki, H. Takai, Y. Fukunaka, and T. Homma, *Jpn. J. Appl. Phys.*, **57**, 08RB11 (2018).
30. S. Zein El Abedin, N. Borissenko, and F. Endres, *Electrochem. Commun.*, **6**, 510 (2004).
31. Y. Nishimura, Y. Fukunaka, T. Nishida, T. Nohira, and R. Hagiwara, *Electrochemical and Solid State Letters*, **11**, D75 (2008).
32. G. Pulletikurthi, A. Lahiri, T. Carstens, N. Borisenko, S. Z. El Abedin, and F. Endres, *J. Solid State Electrochem.*, **17**, 2823 (2013).
33. D. R. Stern and Q. H. McKenna, US Patent 2892763 (1959).
34. T. Matsuda, S. Nakamura, K. Ide, K. Nyudo, S. Yae, and Y. Nakato, *Chem. Lett.*, **25**, 569 (1996).
35. O. E. Kongstein, C. Wollan, S. Sultana, and G. M. Haarberg, *ECS Trans.*, **3**, 357 (2007).
36. Y. Sakanaka, A. Murata, T. Goto, and K. Hachiya, *Journal of Alloys and Compounds*, **695**, 2131 (2017).
37. X. Yang, L. Ji, X. Zou, T. Lim, J. Zhao, E. T. Yu, and A. J. Bard, *Angew. Chem. Int. Ed.*, **56**, 15078 (2017).
38. X. Zou, L. Ji, X. Yang, T. Lim, E. T. Yu, and A. J. Bard, *J. Am. Chem. Soc.*, **139**, 16060 (2017).
39. X. Zou, L. Ji, J. Ge, D. R. Sadoway, E. T. Yu, and A. J. Bard, *Nat Commun*, **10**, 5772 (2019).
40. W. Weng and W. Xiao, *ACS Applied Energy Materials*, **2**, 804 (2019).
41. U. Cohen and R. A. Huggins, *J. Electrochem. Soc.*, **123**, 381 (1976).
42. G. M. Rao, D. Elwell, and R. S. Feigelson, *J. Electrochem. Soc.*, **127**, 1940 (1980).
43. G. M. Rao, D. Elwell, and R. S. Feigelson, *Surface Technology*, **13**, 331 (1981).
44. G. M. Rao, D. Elwell, and R. S. Feigelson, *J. Electrochem. Soc.*, **128**, 1708 (1981).
45. D. Elwell, *Solar Energy Materials*, **5**, 205 (1981).
46. D. Elwell and G. M. Rao, *Electrochim Acta*, **27**, 673 (1982).
47. G. M. Rao, D. Elwell, and R. S. Feigelson, *Solar Energy Materials*, **7**, 15 (1982).
48. O. I. Boiko, Y. K. Delimarskii, and R. V. Chernov, *Soviet Powder Metallurgy and Metal*

Ceramics, **21**, 425 (1982).

49. D. Elwell, R. S. Feigelson, and G. M. Rao, *J. Electrochem. Soc.*, **130**, 1021 (1983).
50. K. L. Carleton, J. M. Olson, and A. Kibbler, *J. Electrochem. Soc.*, **130**, 782 (1983).
51. R. Boen and J. Bouteillon, *J. Appl. Electrochem.*, **13**, 277 (1983).
52. D. Elwell and G. M. Rao, *Surface Technology*, **23**, 67 (1984).
53. K. H. Stern and M. E. McCollum, *Thin Solid Films*, **124**, 129 (1985).
54. J. T. Moore, T. H. Wang, M. J. Heben, K. Douglas, and T. F. Ciszek, in *Conference Record of the Twenty Sixth IEEE Photovoltaic Specialists Conference - 1997*, p. 775 (1997).
55. T. Oishi, M. Watanabe, K. Koyama, M. Tanaka, and K. Saegusa, *J. Electrochem. Soc.*, **158**, E93 (2011).
56. K. S. Osen, A. M. Martinez, S. Rolseth, H. Gudbrandsen, M. Juel, and G. M. Haarberg, *ECS Trans.*, **33**, 429 (2010).
57. G. M. Haarberg, L. Famiyeh, A. M. Martinez, and K. S. Osen, *Electrochim. Acta*, **100**, 226 (2013).
58. Y. Hu, X. Wang, J. Xiao, J. Hou, S. Jiao, and H. Zhu, *J. Electrochem. Soc.*, **160**, D81 (2013).
59. Y. Sakanaka and T. Goto, *Electrochim. Acta*, **164**, 139 (2015).
60. Y. Suzuki, Y. Inoue, M. Yokota, and T. Goto, *J. Electrochem. Soc.*, **166**, D564 (2019).
61. S. V. Kuznetsova, V. S. Dolmatov, and S. A. Kuznetsov, *Russ. J. Electrochem.*, **45**, 742 (2009).
62. Y. Zaikov, A. Isakov, A. Apisarov, and O. Chemezov, *Non-ferrous Metals*, 33 (2014).
63. K. Maeda, K. Yasuda, T. Nohira, R. Hagiwara, and T. Homma, *J. Electrochem. Soc.*, **162**, D444 (2015).
64. K. Yasuda, K. Maeda, T. Nohira, R. Hagiwara, and T. Homma, *J. Electrochem. Soc.*, **163**, D95 (2016).
65. S. I. Zhuk, V. A. Isaev, O. V. Grishenkova, A. V. Isakov, A. P. Apisarov, and Y. P. Zaikov, *J. Serb. Chem. Soc.*, **82**, 51 (2017).
66. S. I. Zhuk, A. V. Isakov, A. P. Apisarov, O. V. Grishenkova, V. A. Isaev, E. G. Vovkotrub, and

- Y. P. Zaykov, *J. Electrochem. Soc.*, **164**, H5135 (2017).
67. K. Yasuda, K. Maeda, R. Hagiwara, T. Homma, and T. Nohira, *J. Electrochem. Soc.*, **164**, D67 (2016).
68. J. Peng, H. Yin, J. Zhao, X. Yang, A. J. Bard, and D. R. Sadoway, *Adv. Funct. Mater.*, **28**, 1703551 (2018).
69. K. Yasuda, K. Saeki, T. Kato, R. Hagiwara, and T. Nohira, *J. Electrochem. Soc.*, **165**, D825 (2018).
70. M. V. Laptev, A. V. Isakov, O. V. Grishenkova, A. S. Vorob'ev, A. O. Khudorozhkova, L. A. Akashev, and Y. P. Zaikov, *J Electrochem Soc*, **167**, 042506 (2020).
71. A. Isakov, S. Khvostov, E. Kinev, M. Laptev, A. Khudorozhkova, O. Grishenkova, V. Rychkov, and Y. Zaikov, *J. Electrochem. Soc.*, **167**, 082515 (2020).
72. K. Yasuda, T. Kato, Y. Norikawa, and T. Nohira, *J. Electrochem. Soc.*, **168**, 112502 (2021).
73. Y. Norikawa, A. Kondo, K. Yasuda, and T. Nohira, *Electrochim. Acta*, **434**, 141255 (2022).
74. J. R. Rumble, *CRC Handbook of Chemistry and Physics, 99th Edition*, CRC Press, Boca Raton (2018).
75. Y. Norikawa and T. Nohira, *Acc. Chem. Res.*, **56**, 1698 (2023).
76. L. P. Cook and H. F. M. (Eds.), *Phase Diagrams for Ceramists vol. VII, The American Ceramic Society, Columbus* (1989).
77. A. K. Ghosh, C. Fishman, and T. Feng, *J. Appl. Phys.*, **51**, 446 (1980).
78. J. Gu, E. Fahrenkrug, and S. Maldonado, *J. Am. Chem. Soc.*, **135**, 1684 (2013).
79. L. Y. Ma, S. Lee, J. DeMuth, and S. Maldonado, *Rsc Advances*, **6**, 78818 (2016).
80. J. Zhang, S. M. Chen, H. T. Zhang, S. J. Zhang, X. Yao, and Z. H. Shi, *Rsc Advances*, **6**, 12061 (2016).
81. G. M. Haarberg, T. Kato, Y. Norikawa, and T. Nohira, *ECS Trans.*, **89**, 29 (2019).
82. J. P. Hazelnis, T. T. Nguyen, H. Wu, and S. Maldonado, *ACS Applied Materials & Interfaces*, **17**, 12415 (2025).

83. H. Wu, J. P. Hazelnis, and S. Maldonado, *ChemElectroChem*, **11**, e202400229 (2024).
84. H. Wu, J. P. Hazelnis, and S. Maldonado, *Acc. Chem. Res.*, **56**, 846 (2023).
85. J. P. Hazelnis and S. Maldonado, *J. Am. Chem. Soc.*, **145**, 27616 (2023).
86. Q. Cheek, E. Fahrenkrug, S. Hlynchuk, D. H. Alsem, N. J. Salmon, and S. Maldonado, *ACS Nano*, **14**, 2869 (2020).
87. J. Demuth, E. Fahrenkrug, L. Ma, T. Shodiya, J. I. Deitz, T. J. Grassman, and S. Maldonado, *J. Am. Chem. Soc.*, **139**, 6960 (2017).
88. E. Fahrenkrug, J. Biehl, and S. Maldonado, *Chem. Mater.*, **27**, 3389 (2015).
89. E. Fahrenkrug, J. Gu, S. Jeon, P. A. Veneman, R. S. Goldman, and S. Maldonado, *Nano Lett.*, **14**, 847 (2014).
90. E. Fahrenkrug, J. Gu, and S. Maldonado, *J. Am. Chem. Soc.*, **135**, 330 (2013).
91. J. Gu, S. M. Collins, A. I. Carim, X. Hao, B. M. Bartlett, and S. Maldonado, *Nano Lett.*, **12**, 4617 (2012).
92. A. I. Carim, J. Gu, and S. Maldonado, *ACS Nano*, **5**, 1818 (2011).
93. A. I. Carim, S. M. Collins, J. M. Foley, and S. Maldonado, *J. Am. Chem. Soc.*, **133**, 13292 (2011).
94. M. W. Chase, *NIST-JANAF Thermochemical Tables, 4th ed., Part I Al-Co*, American Chemical Society, and the American Institute of Physics for the National Institute of Standards and Technology (1998).
95. T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak, *Binary Alloy Phase Diagrams* (2nd ed.), ASM International, Materials Park, Ohio (1990), CD-ROM version 1.0.
96. K. Yasuda, T. Shimao, R. Hagiwara, T. Homma, and T. Nohira, *J. Electrochem. Soc.*, **164**, H5049 (2017).
97. R. W. Olesinski, N. Kanani, and G. J. Abbaschian, *Bull. Alloy Phase Diagrams*, **6**, 362 (1985).

Chapter 2

Electrodeposition of Crystalline Si Using a Liquid Zn Electrode in Molten KF–KCl–K₂SiF₆

2.1 Introduction

In this chapter, in order to confirm that crystalline Si with large grain sizes is electrodeposited using a liquid Zn electrode, the electrochemical study was conducted in a KF–KCl molten salt at 923 K. First, the reduction reaction of Si(IV) ions on the surface of the liquid Zn electrode was investigated using cyclic voltammetry. Second, electrodeposition of Si via a liquid Si–Zn alloy was carried out using potentiostatic electrolysis. Third, the grain size distribution of the samples obtained by galvanostatic electrolysis under various charge conditions was compared. Finally, the mechanism of solid Si crystal deposition in the liquid Si–Zn electrode was discussed.

2.2 Experimental

Fig. 2-1(a) shows a schematic illustration of the experimental apparatus. Reagent grade KF (FUJIFILM Wako Pure Chemical Corp., purity >99.0%) and KCl (FUJIFILM Wako Pure Chemical Corp., purity >99.5%) were mixed in a eutectic composition (KF: KCl = 45:55 mol%, melting point = 873 K, weight = 400–500 g) and loaded into a graphite crucible (SANKO Co., Ltd., IG-110 grade, o.d. 100 mm × i.d. 90 mm × height 120 mm). The mixture in the crucible was first dried under vacuum at 453 K for more than 72 h. The crucible was placed at the bottom of a stainless-steel vessel in an airtight Kanthal container and further dried under vacuum at 773 K for 24 h.

Electrochemical measurements were conducted at 923 K in a glove box (Yamato Co., Ltd., pure box system with an electric furnace, ZYS 16-0057) with an Ar atmosphere at conditions of O₂ and H₂O below 1 ppm. After blank measurements in KF–KCl, K₂SiF₆ (Junsei Chemical Co., Ltd., purity >99.0%) was added to the melt to obtain a concentration of 0.5 or 2.0 mol%.

Electrochemical measurements and galvanostatic electrolysis were conducted using the three-electrode method with an electrochemical measurement system (Meiden Hokuto Corp., HZ-7000). The working electrodes were liquid Zn (Kojundo Chemical Lab. Co., Ltd., 7 or 13 g, purity = 99.99%) held in a small boron nitride (BN) crucible (Fig. 2-1 (b)) and an Ag flag (Nilaco Corp., thickness = 0.1 mm, diameter = 3 mm, purity >99%). A W wire (Nilaco Corp., diameter = 1.0 mm, purity = 99.98%) was used as the lead wire for the Zn electrode. The structure of the Ag flag electrode is described in detail in a previous study [1]. Si (Furuichi Chemical Corp., diameter = 73 mm, purity = 10N) or carbon rods (SANKO Co., Ltd., diameter 7 mm × length 520 mm) were used as counter electrodes. A Pt wire (Tanaka Precious Metal Technologies Co. Ltd., diameter = 1 mm, purity >99.98%) was used as a quasi-reference electrode for blank measurements, and a Si rod was used as the reference electrode after adding K₂SiF₆. The potential of the reference electrode was calibrated with respect to the K⁺/K potential estimated using cyclic voltammetry on a Ag wire (Nilaco Corp., diameter = 1 mm, purity = 99.99%).

After the electrolysis, the Zn electrodes were immediately removed from the furnace and cooled in a glove box. Before the solidification of liquid Zn, the Mo wire hanging on the BN crucible was cut, and the lead wire and BN protection tube were removed from liquid Zn. The small BN crucible was immersed in stirring water to dissolve and eliminate the solidified salt at room temperature. Subsequently, the Zn samples were collected from the bottom of the crucible and further immersed and washed in distilled water at room temperature for 2 h to eliminate the adhered salts.

The samples were characterized using energy-dispersive X-ray spectroscopy (EDX; Thermo Fisher Scientific K. K., SE1200-8001) and X-ray diffraction (XRD; Rigaku Holdings Corp., Ultima

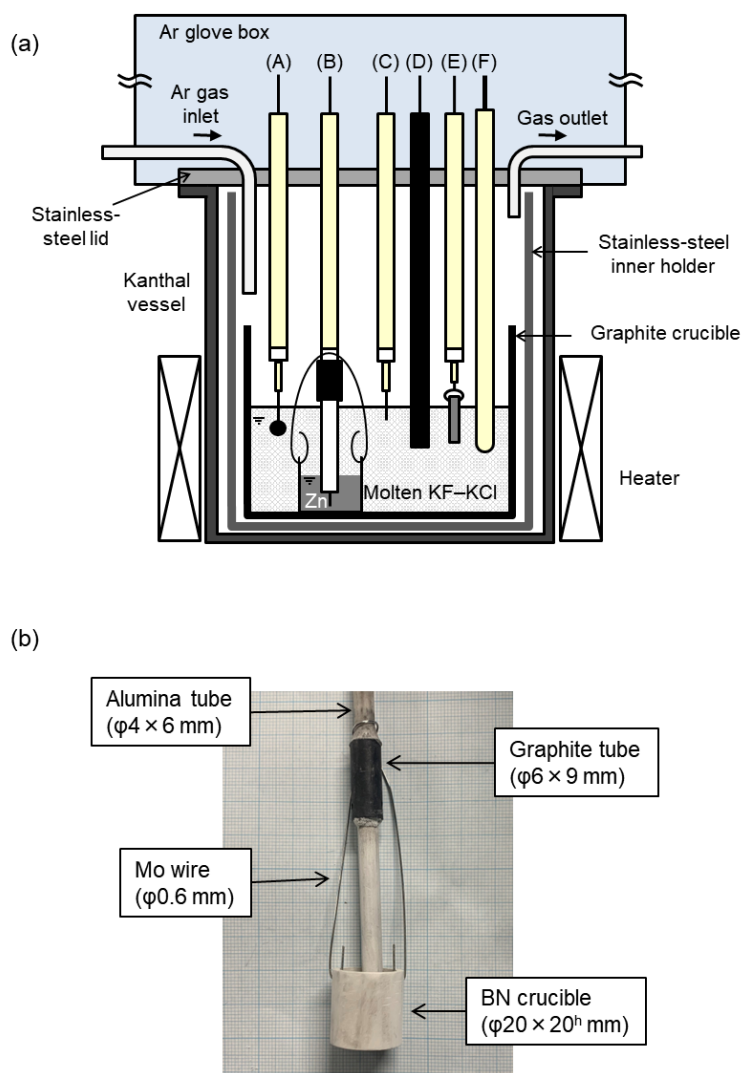


Fig. 2-1 (a) A schematic illustration of the entire experimental apparatus. (A) Ag flag electrode, (B) liquid Zn electrode, (C) Pt wire electrode, (D) carbon rod electrode, (E) Si rod electrode, and (F) thermocouple. (b) Photograph of the liquid Zn electrode.

IV, Cu-K α line) analyses. The surface of the samples was analyzed using optical microscopy (Thanko, inc., DinoLite Premier S). The surface and cross-section of the samples were analyzed using scanning electron microscopy (SEM; Keyence Corp., VE-8800 or Thermo Fisher Scientific K. K., Phenom Pro Generation 5). The Zn metal lumps were dissolved in 500 mL of HCl solution (20 wt%) to recover the deposited Si granules. After being filtered off, the resulting deposited Si was collected separately based on the grain size using stainless-steel sieves (AS ONE Corp., sieve opening = 0.1 mm, 0.212 mm, 0.5 mm, and 1 mm). The grain size distribution was examined from

the weight of the deposited Si in each grain size range.

2.3 Results and Discussion

2.3.1 Reduction Behavior of Si(IV) Ions Using Cyclic Voltammetry

First, cyclic voltammetry was conducted to investigate the reduction of Si(IV) ions, and the resulting cyclic voltammograms at the liquid Zn electrode in molten KF–KCl before and after the addition of K₂SiF₆ (0.5 mol%) at 923 K are shown in Fig. 2-2. Before adding K₂SiF₆, a rise in reduction current was observed at approximately 0.8 V, which was attributed to the formation of the liquid K–Zn alloy that exists at 923 K [2].



After adding K₂SiF₆, a rise in reduction current, which was not present before, was observed at approximately 1.0 V. The reduction current continued to increase, and at 0.75 V, its value reached about six times larger than before the addition. In a previous work in the same condition, the electrochemical behavior of Si(IV) on solid Ag electrode has been studied, in which the

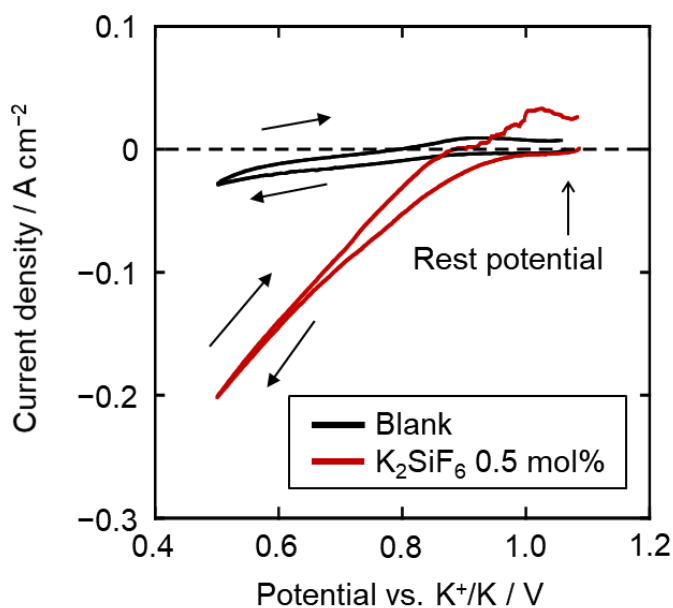


Fig. 2-2 Cyclic voltammograms at a liquid Zn electrode in molten KF–KCl at 923 K before and after adding K₂SiF₆ (0.5 mol%). Scan rate: 0.20 V s⁻¹.

electrodeposition of solid Si occurs at potentials more negative than 0.75 V [1]. Since only liquid Si–Zn alloy exists in the Si–Zn binary phase diagram at 923 K [3], the reduction currents at 0.75–1.0 V were attributed to the formation of the liquid Si–Zn alloy.



2.3.2 Deposition of Si Using Potentiostatic Electrolysis

To confirm the electrodeposition of Si via the formation of liquid Si–Zn alloy, potentiostatic electrolysis was conducted at 0.75 V for 48 h in molten KF–KCl–K₂SiF₆ (2.0 mol%) using a liquid Zn electrode. The charge on the electrode was 3312 C. Theoretically, reducing Si(IV) ions using all the charge on the electrode could result in the formation of a liquid Si–Zn alloy with 4.3 at% Si. However, per the phase diagram, the solubility of Si is 1 at% at 923 K [3], suggesting that Si was saturated during the electrolysis.

Fig. 2-3(a) shows a surface photograph of the Zn electrode removed from the BN small crucible. Large grains with metallic luster were observed at the boundary of the BN crucible and not of the molten salt. EDX analysis of these grains revealed that those large grains were 100 at% Si, indicating Si deposits on the boundary of the BN crucible and not of the molten salt. The Si deposits would have been observed at the boundary of the molten salt only if the solid Si was directly electrodeposited on the liquid Zn electrode. These results confirm that Si was electrodeposited via Si–Zn alloying inside the liquid Zn electrode.

The site on the Zn electrode where Si was deposited via liquid Si–Zn alloying was investigated in detail by analyzing the cross section of the Zn electrode using SEM. As shown in Fig. 2-3(b), small Si particles were detected inside the Zn electrode, suggesting that Si in the liquid Si–Zn alloy on the surface of the Zn electrode diffused into the interior of the electrode. A Si grain of size 200 μm was detected at the interface between the Zn electrode and BN crucible, indicating preferential deposition of Si at the BN crucible boundary. Figs. 2-4(a), (b), and (c) show the

photographs and an SEM image of Si deposits after hydrochloric acid treatment of the sample. The photograph in Fig. 2-4(a) shows Si deposits of various sizes, some of which were in powder form. The photograph and the SEM image in Figs. 2-4(b) and (c) of a large Si grain separated from Zn reveal the maximum size of the deposited Si to be approximately 2 mm. This size was much larger than 50 nm, the crystal size of Si obtained on solid electrodes in $\text{KF-KCl-K}_2\text{SiF}_6$ melt at 923 K [4]. Fig. 2-4(d) shows an XRD pattern of the separated large Si, which was lightly crushed in a

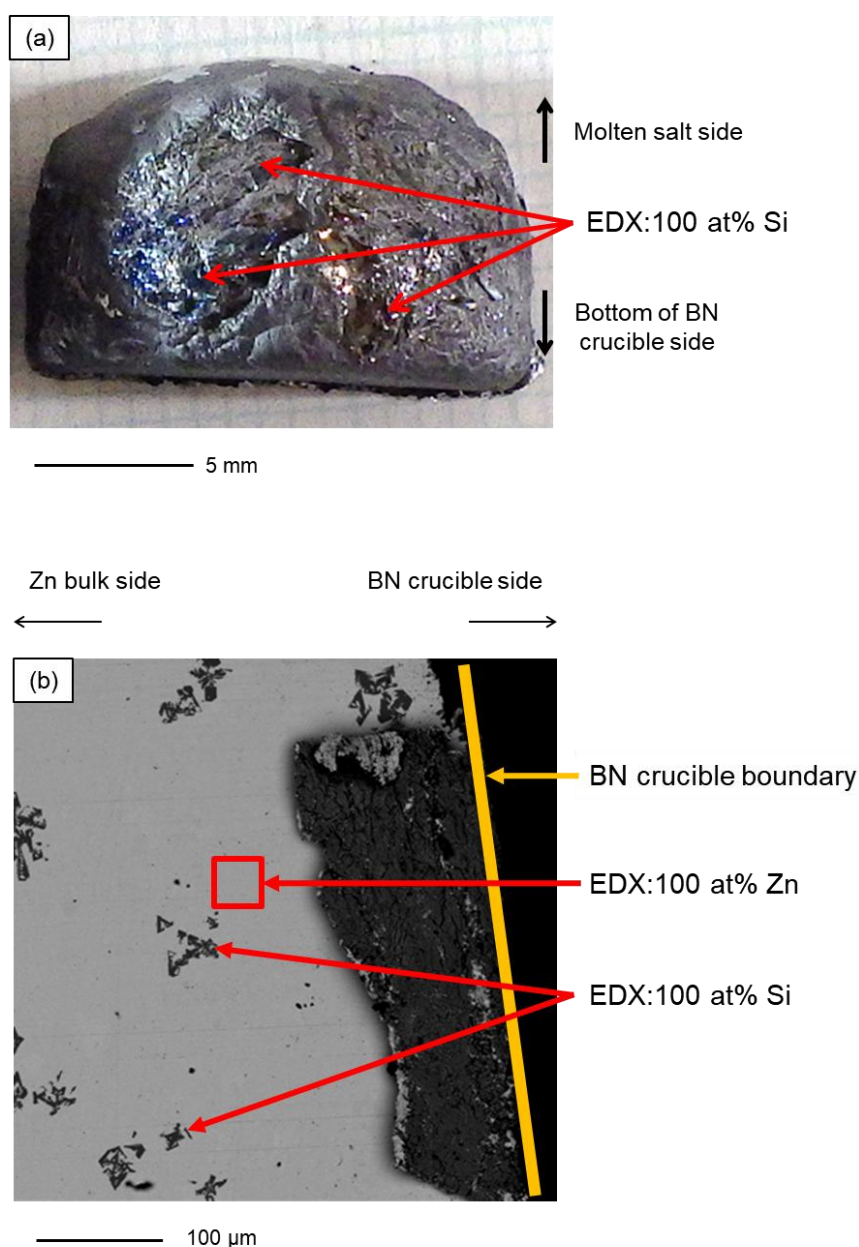


Fig. 2-3 (a) A photograph and (b) a cross-sectional SEM image of the Zn electrode sample obtained from potentiostatic electrolysis at 0.75 V for 48 h in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K. Charge: 3312 C.

mortar. The sharp peaks corresponding to the 111 and 511 diffraction peaks of Si were observed, confirming the crystalline form of the electrodeposited Si. The absence of other diffraction peaks was assumed owing to the preferential orientations.

Herein, the deposition mechanism of crystalline Si is discussed in terms of crystal size. Previous reports on Si precipitation showed that the size of Si particles precipitating during the cooling of liquid Si–Zn alloys decreases as the cooling rate increases [5]. Even at the temperature-decreasing rate of 20 K h^{-1} , only Si grains smaller than 1 mm were obtained [5]. In the present study, the liquid Si–Zn alloy was cooled through natural cooling, and the temperature-decreasing

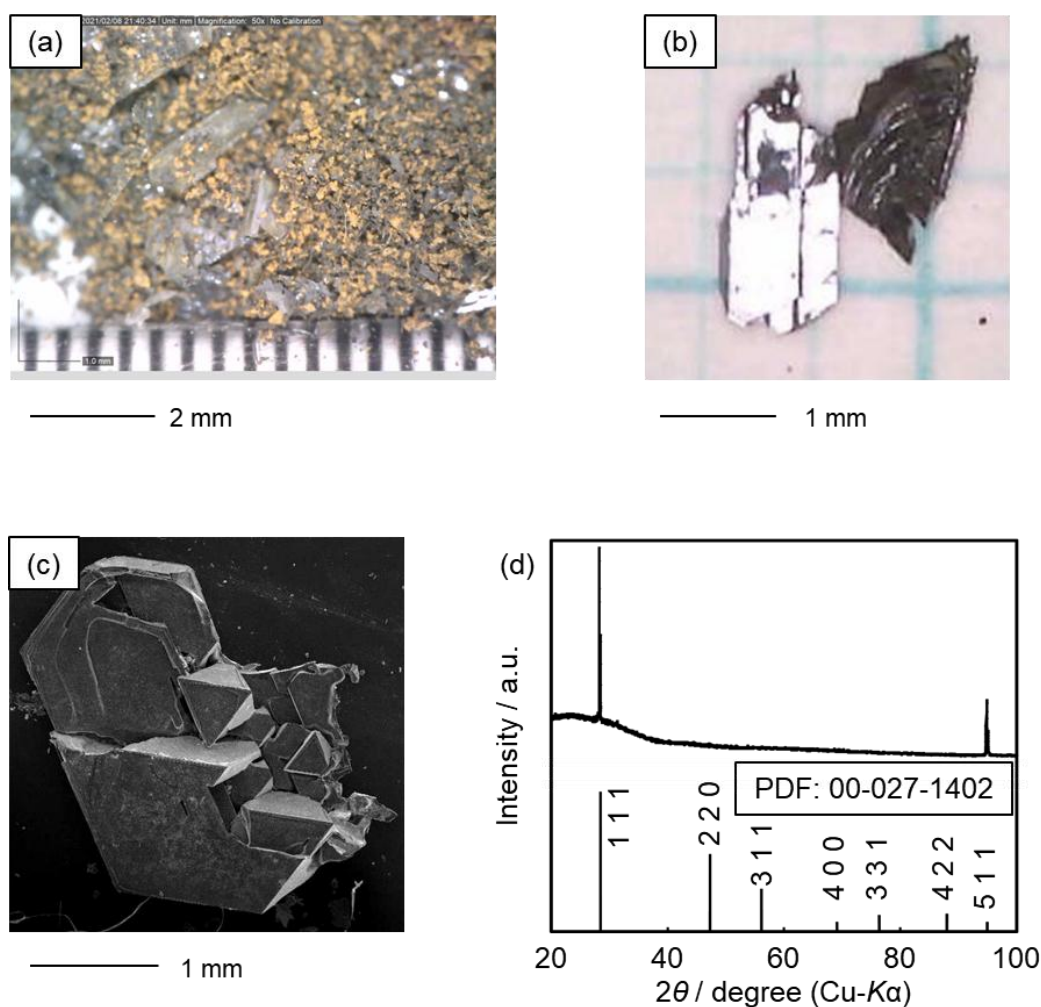


Fig. 2-4 (a) A photograph of deposited Si obtained by potentiostatic electrolysis at 0.75 V for 48 h in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K. (b) Optical microscopy and (c) SEM images of a separated large Si grain. (d) An XRD pattern of the separated large Si grain after lightly crushed in a mortar.

rate was extremely high (approximately 230 K s^{-1}). Therefore, Si powders with small grain sizes could have been deposited during the natural cooling.

2.3.3 Crystal Growth of Deposited Si by Increasing Electrolysis Charge

To investigate the Si crystal growth during galvanostatic electrolysis, the amount of Si supplied to the liquid Zn electrode was varied by changing the charge on the electrode from 417 C (corresponding to the Si saturation of the Zn electrode) to 4173 C (corresponding to ten times the Si saturation of the Zn electrode) at a current density of 20 mA cm^{-2} . The obtained samples were treated with hydrochloric acid to dissolve Zn. The grains of the deposited Si were separated based on the grain size using sieves. Figs. 2-5(a) to (e) show photographs of Si grains of varying grain sizes ranging from less than 0.1 mm to more than 1 mm. As seen in the photographs, all Si grains exhibited a metallic luster.

Figs. 2-6(a) to (e) show the grain size distributions of Si deposited through galvanostatic electrolysis at different charges ranging from 417 to 4173 C. When the amount of charge corresponded to the Si saturation (417 C, Fig. 2-6(a)), the weight ratio of Si grains larger than 0.5 mm was very small, less than 5%. The weight ratio of Si grains larger than 0.5 mm increased with increasing the charge, and Si grains larger than 1 mm were also observed at larger amounts of charges.

The weight ratio of Si larger than 1 mm was maximum when the amount of charge was 4173 C and accounted for over 80% of the Si obtained from the sample. Furthermore, the weight ratio of Si grains smaller than 0.5 mm decreased with increasing charge. These results suggest that the growth of Si grains proceeds with increasing charge. Note that the current efficiency was 80.0% at 4173 C.

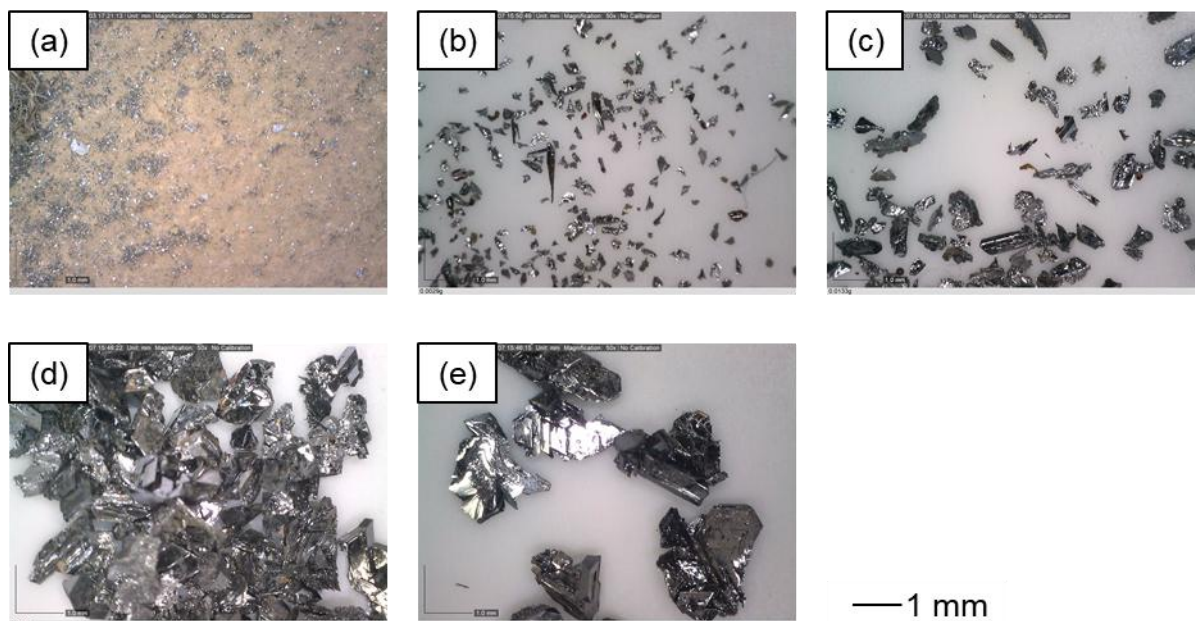


Fig. 2-5 Photographs of Si obtained through galvanostatic electrolysis of a liquid Zn electrode at 20 mA cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K. Charge on the electrode: 2087 C. The grain sizes of Si are (a) $< 0.1 \text{ mm}$, (b) $0.1\text{--}0.212 \text{ mm}$, (c) $0.212\text{--}0.5 \text{ mm}$, (d) $0.5\text{--}1 \text{ mm}$, and (e) $> 1 \text{ mm}$.

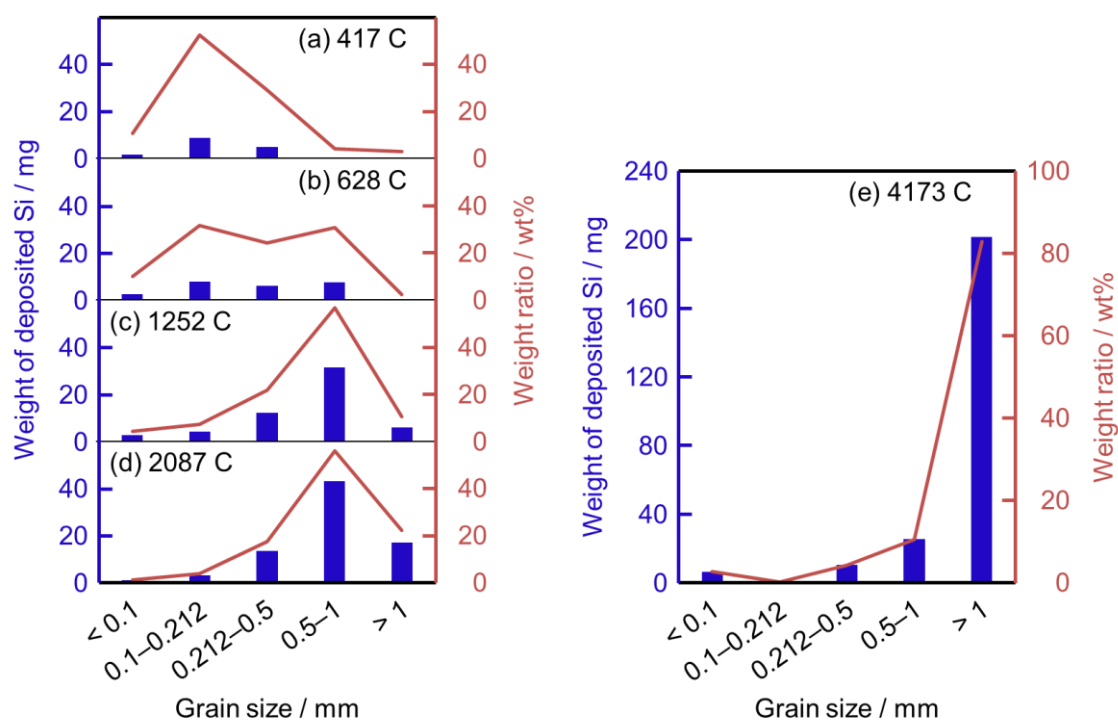


Fig. 2-6 Grain size distributions of the deposited Si obtained via galvanostatic electrolysis at charges of (a) 417 C, (b) 628 C, (c) 1252 C, (d) 2087 C, and (e) 4173 C.

2.3.4 Mechanism of Electrodeposition of Crystalline Si via Si–Zn Alloying

Fig. 2-7 shows a schematic illustration of the proposed process of crystalline Si deposition through electrolysis using a liquid Zn electrode. First, as shown in Fig. 2-7(a), Si(IV) ions are electrochemically reduced to Si at the surface of the liquid Zn electrode, followed by liquid Si–Zn alloy formation by the reduced Si. As the electrolysis proceeds (Fig. 2-7(b)), the Si concentration on the surface of the Zn electrode increases, and Si begins to diffuse on the surface of the electrode. As the charge increases and the Si concentration in the liquid Zn electrode saturates, solid Si deposits inside the liquid Zn electrode. As shown in Fig. 2-3, crystalline Si is deposited preferentially at the interface between liquid Zn and the BN crucible (Fig. 2-7(c)). As discussed earlier, the crystallite size increases with the increasing charge on the electrode. This suggests that almost no new nucleation occurred, and the existing crystallites continued to grow. Thus, electrodepositing Si using a liquid Zn electrode can produce crystalline Si with a larger grain size than conventional electrodeposition using a solid electrode.

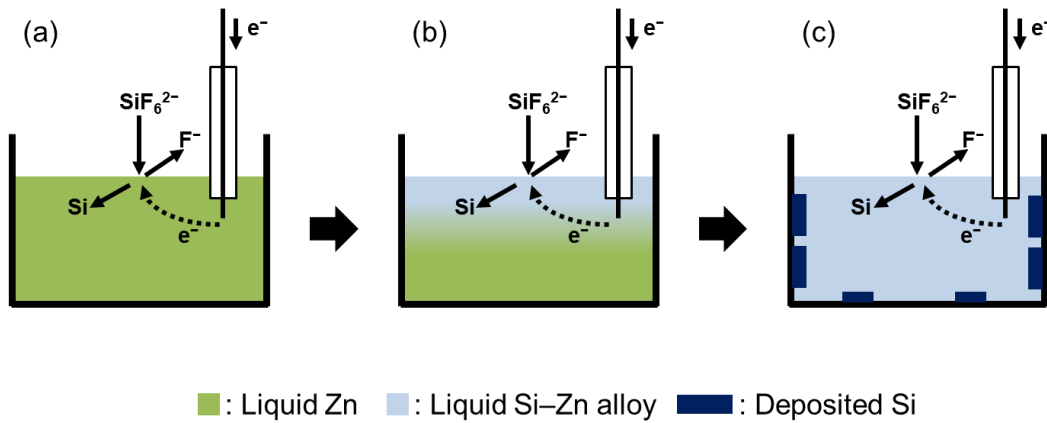


Fig. 2-7 A schematic illustration of crystalline Si deposition through electrolysis using a liquid Zn electrode.

2.4 Conclusion

Crystalline Si was electrodeposited using a liquid Zn electrode in a $\text{KF-KCl-K}_2\text{SiF}_6$ melt at 923 K. Cyclic voltammetry showed that Si(IV) ions reduced to form a liquid Si–Zn alloy, which did not occur when using a solid electrode. In potentiostatic electrolysis at 0.75 V vs. K^+/K , crystalline Si with a maximum grain size of approximately 2 mm was deposited inside the liquid Zn electrode. Large Si grains were obtained via the formation of liquid Si–Zn alloy. In galvanostatic electrolysis at 20 mA cm^{-2} , increasing the charge resulted in the deposition of crystalline Si with a larger grain size. Moreover, the weight ratio of Si grains larger than 1 mm was over 80%, with a maximum of 4173 C. The mechanism of Si deposition on a liquid Zn electrode was described in three steps: the formation of liquid Si–Zn alloy at the surface of the Zn electrode, the increase of Si concentration in the Zn electrode, and the deposition of solid Si inside the Zn electrode. By this mechanism, the electrodeposition of Si using a liquid Zn electrode can produce crystalline Si with a larger grain size than conventional electrodeposition using a solid electrode.

References

1. K. Maeda, K. Yasuda, T. Nohira, R. Hagiwara, and T. Homma, *J. Electrochem. Soc.*, **162**, D444 (2015).
2. A. D. Pelton, *Bull. Alloy Phase Diagrams*, **8**, 548 (1987).
3. T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak, *Binary Alloy Phase Diagrams* (2nd ed.), ASM International, Materials Park, Ohio (1990), CD-ROM version 1.0.
4. K. Yasuda, K. Saeki, T. Kato, R. Hagiwara, and T. Nohira, *J. Electrochem. Soc.*, **165**, D825 (2018).
5. Y. Ma, K. Yasuda, A. Ido, T. Shimao, M. Zhong, R. Hagiwara, and T. Nohira, *Mater. Trans.*, **62**, 403 (2021).

Chapter 3

Electrodeposition of Crystalline Si Using a Liquid Ga Electrode in Molten $\text{KF-KCl-K}_2\text{SiF}_6$

3.1 Introduction

In the previous chapter, crystalline Si with large grain size was electrodeposited using a liquid Zn electrode in a KF-KCl molten salt. The mechanism of electrodeposition of such large Si was also discussed. In this chapter, in order to compare the results of using a liquid Zn electrode with those of using other liquid metal electrodes, electrochemical study using a liquid Ga electrode was carried out. First, the reduction reaction of Si(IV) ions on the surface of the liquid Ga electrode was investigated using cyclic voltammetry. Second, electrodeposition of Si via the formation of liquid Si-Ga alloy was conducted using potentiostatic electrolysis. Third, the grain size distribution was compared between the samples obtained by potentiostatic electrolysis under various charge conditions was compared. Finally, the grain size distributions of the electrodeposits were compared with those obtained using the liquid Zn electrode, and the causes of the difference were discussed.

3.2 Experimental

A preparation method of KF-KCl molten salt, an experimental apparatus, and analysis methods are almost the same as Chapter 2. Important and/or different points are described below.

The working electrodes were liquid Ga (Kojundo Chemical Lab. Co., Ltd., 7 or 15 g, purity = 99.99%) held in a small crucible and an Ag flag (Nilaco Corp., thickness = 0.1 mm, diameter =

3 mm, purity >99%). The crucibles were composed of boron nitride (BN) or alumina. The detailed structure of the liquid Ga electrode using a BN crucible is described in the previous chapter, whereas that using an alumina crucible is shown in Fig. 3-1. A W wire (Nilaco Corp., diameter = 1.0 mm, purity = 99.98%) was used as the lead wire for the Ga electrode. Si (Furuuchi Chemical Corp., diameter = 73 mm, purity = 10N) or glassy carbon (Tokai Carbon Co., Ltd., diameter = 3.0 mm, purity >99.999998%) rods were used as counter electrodes. After the electrolysis, the Ga electrodes were immediately removed from the furnace and allowed to cool naturally in a glove box. The Mo wire hanging on the crucible was cut, and the lead wire and BN or alumina protective tube were removed from the liquid Ga. The crucible was immersed in stirring water to dissolve and eliminate the solidified salt at room temperature. The sample was then collected from the bottom of the crucible, immersed, and washed in distilled water for 2 h at room temperature to remove any remaining salts.

The sample surfaces were analyzed using optical microscopy (KEYENCE Corp., VHX-7100). After physically separating the Si sample from the liquid Ga, the sample was immersed in 500 mL of a HNO₃ solution (30 wt%) to dissolve the adhered Ga.

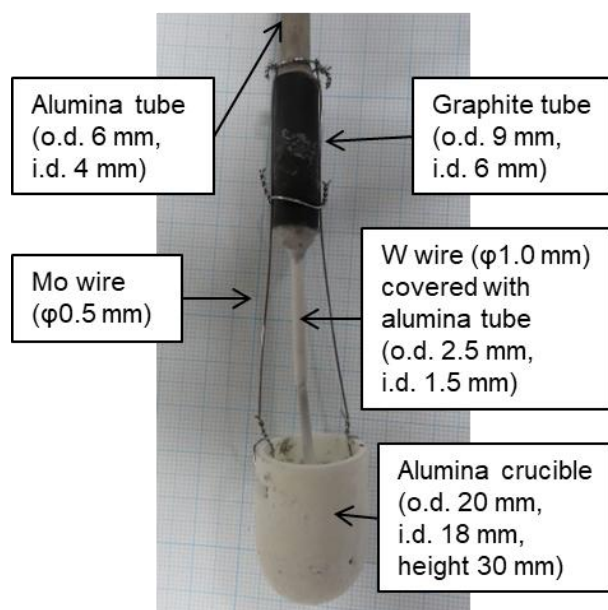


Fig. 3-1 A photograph of the liquid Ga electrode.

3.3 Results and Discussion

3.3.1 Reduction Behavior of Si(IV) Ions Using Cyclic Voltammetry

First, cyclic voltammetry was performed to investigate the reduction of Si(IV) ions. Fig. 3-2 shows the cyclic voltammograms of the liquid Ga and Ag flag electrodes in the molten KF–KCl–K₂SiF₆ at 923 K. The broken red curve indicates the cyclic voltammogram of the Ga liquid electrode before adding 0.5 mol% K₂SiF₆. The reduction current around 0.5 V is attributed to the formation of the K–Ga liquid alloy at 923 K [1].



The solid red curve indicates the cyclic voltammogram of the Ga liquid electrode after adding 0.5 mol% K₂SiF₆. An increase in the reduction current was observed at approximately 0.9 V, which was not observed before adding the K₂SiF₆. The reduction current continued to increase as the potential became more negative. For comparison, the solid blue curve represents the cyclic voltammogram of the solid Ag electrode. As the electrodeposition of solid Si occurs at potentials

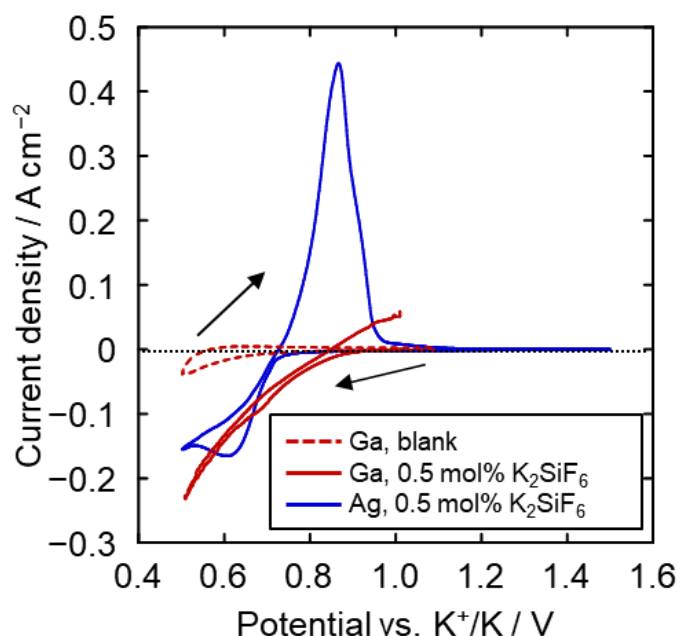


Fig. 3-2 Cyclic voltammograms at a liquid Ga electrode and an Ag flag electrode in molten KF–KCl–K₂SiF₆ (blank and 0.5 mol%) at 923 K. Scan rate: 0.10 V s⁻¹.

that are more negative than 0.75 V [2] and the Si–Ga liquid alloy exists at 923 K [3], the reduction currents at 0.6–0.9 V are attributed to the formation of the Si–Ga liquid alloy.



3.3.2 Deposition of Si Using Potentiostatic Electrolysis

To confirm the electrodeposition of Si via the formation of the Si–Ga liquid alloy, potentiostatic electrolysis was performed at 0.80 V for 24 h in molten KF–KCl–K₂SiF₆ (2.0 mol%) using a liquid Ga electrode. The weight of the liquid Ga in the electrode was 15 g. The theoretical amount of Si that dissolves in this amount of Ga was calculated to be 73.4 mg at 923 K [3], and the charge on the electrode was 4143 C. Assuming that this charge was used to reduce the Si(IV) ions, 301.6 mg of solid Si would be produced, approximately 4.1 times the theoretical amount of Si soluble in the Ga electrode. This suggests that the Ga electrode was saturated with Si during electrolysis.

Fig. 3-3(a) shows a photograph of the deposits after the removal of adhered Ga. Grains with a metallic luster, ranging from 0.1 mm to several millimeters, were observed, mainly at the boundaries of the Ga and the crucible. Fig. 3-3(b) presents particularly large grains obtained from the sample shown in Fig. 3-3(a). The maximum grain size was approximately 6 mm, significantly larger than those obtained using a liquid Zn electrode (maximum ca. 2 mm) as shown in the previous chapter. Fig. 3-3(c) shows an XRD pattern of the deposits, with peaks assigned to Si.

The mechanism of crystalline Si deposition via liquid Si–Ga alloy by electrolysis using a liquid Ga electrode is expected to be the same as described in Fig. 2-7 in the previous chapter using liquid Zn electrodes. Therefore, Si crystals are expected to grow larger by increasing the Si supply to the electrode.

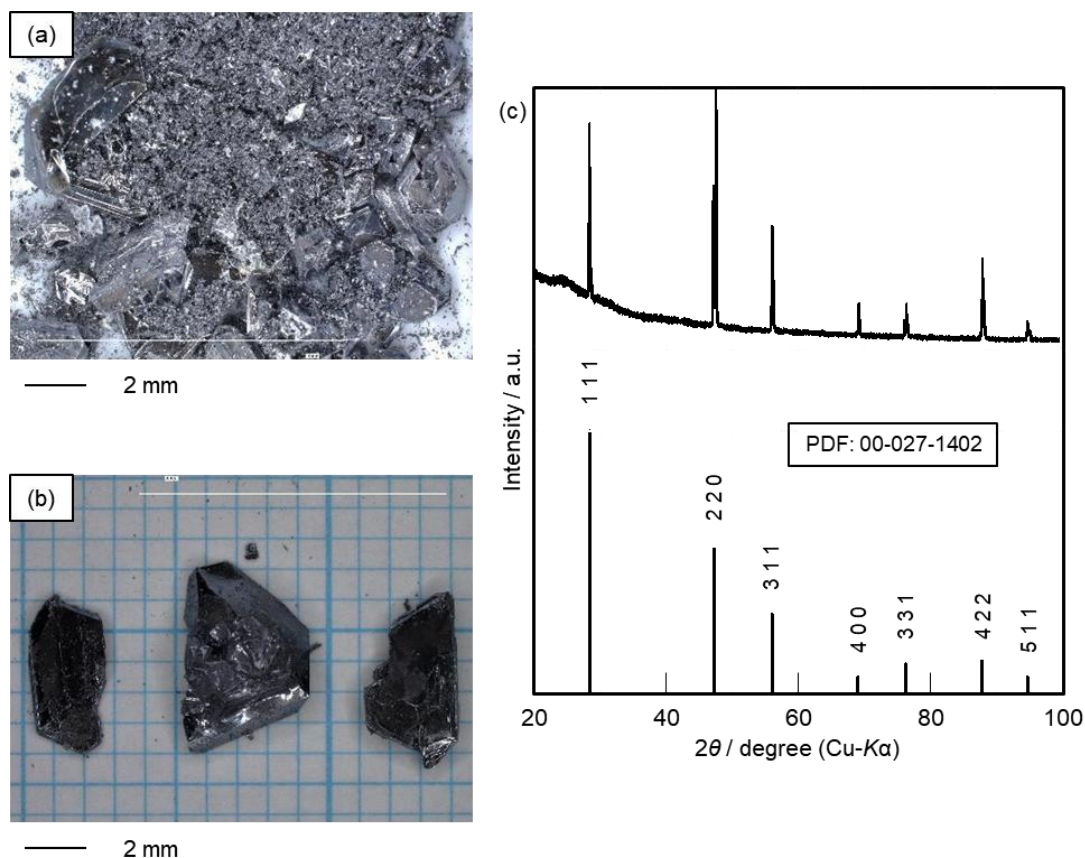


Fig. 3-3 (a) A photograph of the deposits obtained via potentiostatic electrolysis at 0.80 V for 24 h in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K. (b) A photograph of the separated large grains. (c) An XRD pattern of the deposits.

3.3.3 Crystal Growth of Deposited Si by Increasing Electrolysis Charge

To investigate the crystal growth of solid Si during potentiostatic electrolysis, the amount of Si supplied to the liquid Ga electrode was varied according to the charge: (i) 471 C, (ii) 706 C, (iii) 1412 C, and (iv) 2354 C. Potentiostatic electrolysis was performed at a potential of 0.80 V vs K^+/K using 7 g of the Ga electrode. The theoretical amount of Si in the Si-saturated Ga electrode ($w_{\text{Si, sat.}}^{\text{Ga}}$) is 34.3 mg, and the charge required to electrodeposit this amount of Si is 471 C. Table 3-1 lists the theoretical amount of Si electrodeposited for each charge ($w_{\text{Si, e.d.}}^{\text{Ga}}$) and the ratio $r_{\text{e.d./sat.}}^{\text{Ga}} = w_{\text{Si, e.d.}}^{\text{Ga}} / w_{\text{Si, sat.}}^{\text{Ga}}$. Charges (i) 471 C, (ii) 706 C, (iii) 1412 C, and (iv) 2354 C correspond to the ratios $r_{\text{e.d./sat.}}^{\text{Ga}} =$ (i) 1, (ii) 1.5, (iii) 3, and (iv) 5.

Table 3-1 Charge conditions; the number of times the amount of Si electrodeposited by each charge is the theoretical amount of Si soluble in the liquid metal electrode.

Electrode, M	Theoretical amount of Si existing in the Si saturated M electrode, $w_{\text{Si, sat.}}^{\text{M}} / \text{mg}$	Charge, Q / C	Si electrodeposited, $w_{\text{Si, e.d.}}^{\text{M}} / \text{mg}$	Ratio, $r_{\text{e.d./sat.}}^{\text{M}}$
Ga (7 g)	34.3	(i) 471	34.3	1
		(ii) 706	51.4	1.5
		(iii) 1412	102.8	3
		(iv) 2354	171.4	5
Zn (7 g)	30.4	(i) 417	30.4	1
		(ii) 628	45.6	1.5
		(iii) 1252	91.1	3
		(iv) 2087	151.9	5

$$w_{\text{Si, e.d.}}^{\text{M}} = \frac{Q}{4F} \times M_{\text{Si}}, \quad M_{\text{Si}}: \text{molar weight of Si, } F: \text{Faraday constant, } r_{\text{e.d./sat.}}^{\text{M}} = \frac{w_{\text{Si, e.d.}}^{\text{M}}}{w_{\text{Si, sat.}}^{\text{M}}}$$

Figs. 3-4(a)–(d) show photographs of Si obtained via electrolysis using a liquid Ga electrode. The grain size of the crystalline Si increased with increasing charge. Under the condition of the smallest charge (Fig. 3-4(a)), many small grains were observed, with none larger than 1 mm. A 1.5-fold increase in charge (Fig. 3-4(b)) resulted in larger grains, with a few exceeding 1 mm. As the charge increased further (Fig. 3-4(c)), grains similar in size to the largest grains observed under the previous condition appeared in greater numbers. In the condition of the largest charge (Fig. 3-4(d)), the grains were particularly large, with most exceeding 1 mm.

The distributions of the Si grain size based on weight ratio were subsequently examined. As shown in Fig. 3-5(a), the percentage of Si with a large grain size increased as the charge increased. Under the condition of the smallest charge ($r_{\text{e.d./sat.}}^{\text{Ga}} = 1$), most of the Si crystals were less than 1 mm in size, with the majority of the grain size distribution being within 0.1–0.5 mm. As the

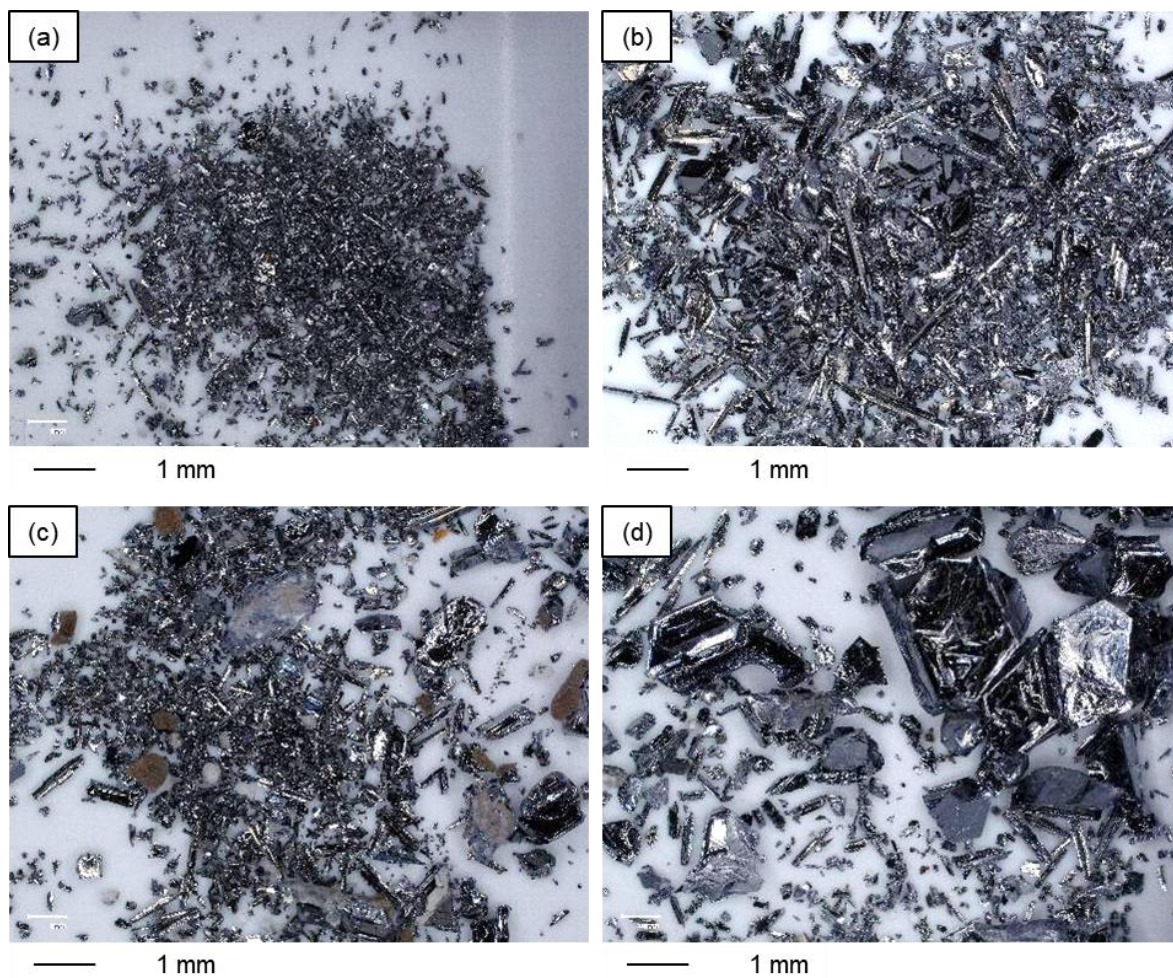


Fig. 3-4 Photographs of the Si obtained by the potentiostatic electrolysis of a liquid Ga electrode at 0.80 V in molten KF–KCl–K₂SiF₆ (2.0 mol%) at 923 K with charges of (a) 471 C, (b) 706 C, (c) 1412 C, and (d) 2354 C.

charge increased ($r_{\text{e.d./sat.}}^{\text{Ga}} = 1.5$), approximately half of the grains became larger than 0.5 mm, and grains larger than 1 mm began to appear. As the charge further increased ($r_{\text{e.d./sat.}}^{\text{Ga}} = 3$), the percentage of grains larger than 1 mm increased to approximately 50%. Under the condition with the largest charge of 2354 C, that is, $r_{\text{e.d./sat.}}^{\text{Ga}} = 5$, grains larger than 1 mm in diameter accounted for 79.3% of the total grains.

For comparison, the grain size distributions of the crystalline Si obtained with the liquid Zn electrode are shown in Fig. 3-5(b). In the previous chapter, 7 g of liquid Zn electrode was used, in which the theoretical amount of Si ($w_{\text{Si, sat.}}^{\text{Zn}}$) is 30.4 mg, and the charge required to deposit this amount of Si is 417 C. Table 3-1 lists the charge of each sample, amount of Si electrodeposited by

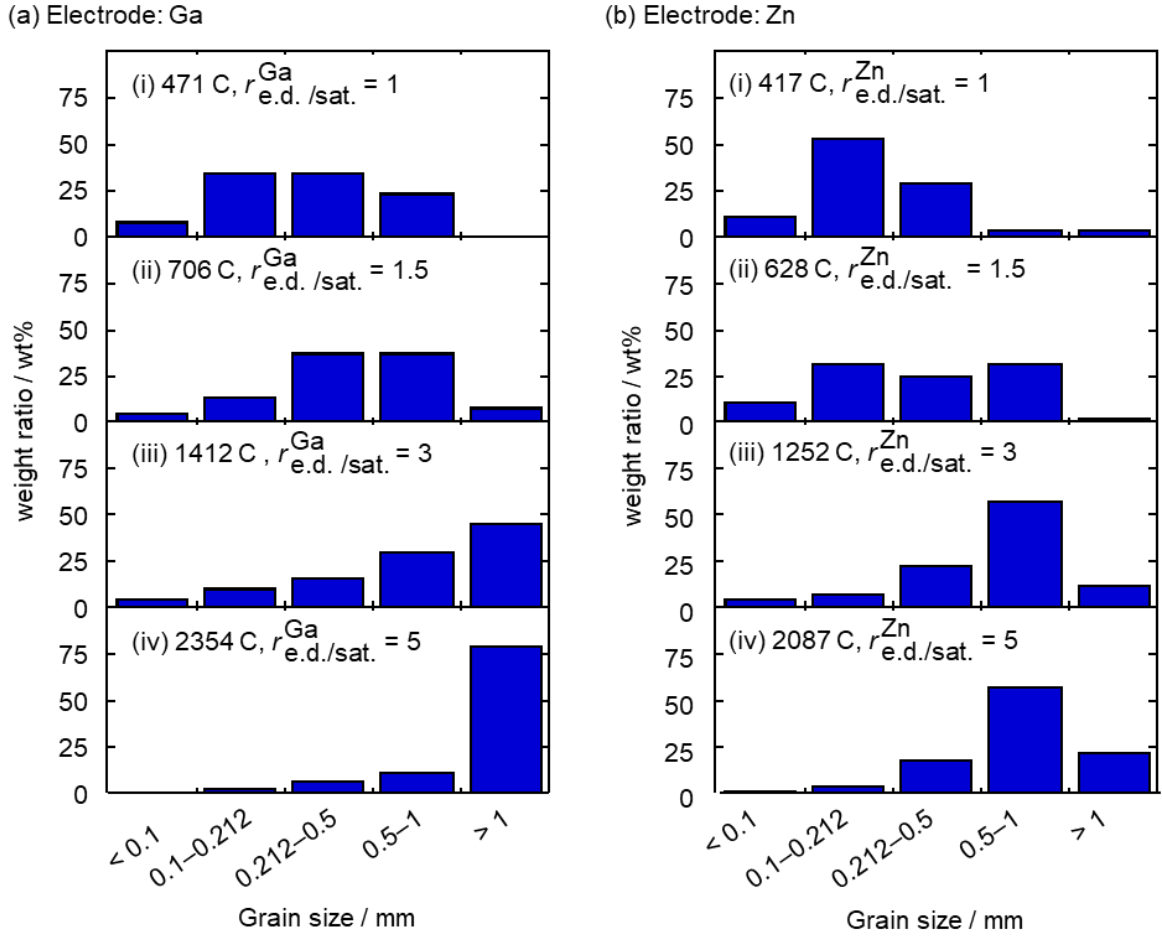


Fig. 3-5 (a) Grain size distributions of the deposited Si obtained via potentiostatic electrolysis of a liquid Ga electrode at charges of (i) 471 C, (ii) 706 C, (iii) 1412 C, and (iv) 2354 C. (b) Grain size distributions of the deposited Si obtained via galvanostatic electrolysis of a liquid Zn electrode at charges of (i) 417 C, (ii) 628 C, (iii) 1252 C, and (iv) 2087 C.

each charge ($w_{\text{Si, e.d.}}^{\text{Zn}}$), and the ratio $r_{\text{e.d./sat.}}^{\text{Zn}} = w_{\text{Si, e.d.}}^{\text{Zn}} / w_{\text{Si, sat.}}^{\text{Zn}}$. Charges (i) 417 C, (ii) 628 C, (iii) 1252 C, and (iv) 2087 C correspond to the ratios $r_{\text{e.d./sat.}}^{\text{Zn}} =$ (i) 1, (ii) 1.5, (iii) 3, and (iv) 5, respectively. Comparing Figs. 3-5(a) and (b), in all cases of $r_{\text{e.d./sat.}}^{\text{M}} =$ (i) 1, (ii) 1.5, (iii) 3, and (iv) 5, the liquid Ga electrode gave Si with a larger grain size. Under the conditions of $r_{\text{e.d./sat.}}^{\text{M}} = 5$, for example, the percentage of > 1 mm grains was as high as 79.3% for Ga and as low as 22.1% for Zn.

Here, the cause of the larger grain size obtained with the liquid Ga electrode compared to that obtained with the Zn electrode is discussed. The mechanism of solid Si growth during electrolysis using liquid metal electrodes is described in the previous chapter, and two factors are

considered to affect the crystal growth rate: the mass transport rate of Si in the Si–M liquid alloy and the surface incorporation rate during Si deposition from the Si–M liquid alloy.

First, the mass transport rate of Si in a Si–M liquid alloy is discussed. Previous studies have reported Si–M binary phase diagrams [3, 4] in which these liquid alloys can be treated as regular solutions based on their properties in the liquid state [5]. A regular solution can be considered to have the same properties as a Newtonian fluid for the particles in it, where Si dissolved in the liquid metal electrode is considered a solute particle. The diffusion coefficient of dissolved Si in the liquid metal can be expressed by the Stokes-Einstein equation:

$$D = \frac{k_b T}{6\pi\eta a} \quad (3-3)$$

where D is the diffusion coefficient, k_b is Boltzmann's constant, T is the temperature, a is the radius of the particle, and η is the viscosity of the fluid. In this study, as the solubilities of Si in Zn and Ga at 923 K are as low as 1 and 1.2 at%, respectively, the viscosity of the Si–M liquid alloy is assumed to be the same as that of M. The viscosity of M can be estimated using the Arrhenius behavior of the flow:

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right) \quad (3-4)$$

where E is the activation energy of the viscous flow, η_0 is the pre-exponential viscosity, and R is the gas constant. The calculated viscosities and literature values of the data required for the calculations are summarized in Table 3-2 [6]. Because the viscosity of Ga is approximately 1/3 that of Zn, the viscosity of the Si–Ga liquid alloy is approximately 1/3 that of the Si–Zn liquid alloy. Equation (3-3) indicates that the diffusion coefficient of Si in the Si–Ga liquid alloy is approximately three times larger than that in the Si–Zn liquid alloy. A larger diffusion coefficient

Table 3-2 **Viscosity of liquid Zn and Ga.**

Element	T_m / K	$\eta_0 / \text{mPa s [6]}$	$E / \text{kJ mol}^{-1} \text{ [6]}$	$\eta (923 \text{ K}) / \text{mPa s}$
Ga	303	0.436	4.0	0.7
Zn	693	0.413	12.7	2.16

E : the activation energy of the viscous flow, η_0 : the pre-exponential viscosity

resulted in a faster mass transport of the dissolved Si onto the already deposited solid Si, which is thought to have led to a larger growth of Si crystals when a liquid Ga electrode was used.

Regarding the surface incorporation rate during Si deposition from the Si–M liquid alloys, there are currently no reports on the differences between $M = \text{Ga}$ and $M = \text{Zn}$, which remains a topic for future study.

3.4 Conclusion

Crystalline Si was electrodeposited using a liquid Ga electrode in a $\text{KF–KCl–K}_2\text{SiF}_6$ melt at 923 K. Cyclic voltammetry demonstrated that Si(IV) ions were reduced to form a Si–Ga liquid alloy. During potentiostatic electrolysis at 0.80 V vs K^+/K , crystalline Si with a maximum grain size of approximately 6 mm was deposited within the liquid Ga electrode. When potentiostatic electrolysis was performed at various charges, the weight ratio of Si with larger grain sizes increased as the charge increased. Specifically, the weight ratio of Si grains larger than 1 mm reached 79.3% at a charge of 2354 C. The grain sizes of Si obtained with the liquid Ga electrode were significantly larger than those obtained with a liquid Zn electrode. The difference in the mass transport rate of Si atoms in the liquid metal electrode is considered a primary reason for the difference in crystal growth rates.

References

1. A. D. Pelton and S. Larose, *Bull. Alloy Phase Diagrams*, **11**, 343 (1990).
2. K. Maeda, K. Yasuda, T. Nohira, R. Hagiwara, and T. Homma, *J. Electrochem. Soc.*, **162**, D444 (2015).
3. R. W. Olesinski, N. Kanani, and G. J. Abbaschian, *Bull. Alloy Phase Diagrams*, **6**, 362 (1985).
4. R. W. Olesinski and G. J. Abbaschian, *Bull. Alloy Phase Diagrams*, **6**, 545 (1985).
5. F. A. Trumbore, *Bell. Syst. Tech. J.*, **39**, 205 (1960).
6. E. A. Brandes, *Smithells Metals Reference Book* (7th ed.), Butterworths, London (1992).

Chapter 4

Electrochemical Formation of Highly Crystalline Si Film Using Thin Liquid Zn on Substrate in Molten KF–KCl–K₂SiF₆

4.1 Introduction

In Chapters 2 and 3, Si electrodeposition was performed using liquid Zn and Ga electrodes held in small crucibles and showed that the Si grain size was larger than that obtained using solid electrodes. However, the morphology of the electrodeposited Si was granular instead of the desired film form. In addition, regardless of whether Zn or Ga was used, the difficulty of removing the liquid metal electrode itself remained an issue. Therefore, a method using Zn, which is expected to be removable in the post-process by vacuum evaporation, was considered promising.

In this chapter, in order to obtain crystalline Si films with large grain sizes, the electrodeposition was conducted using an electrode on which liquid Zn was maintained as a thin film in a KF–KCl–K₂SiF₆ molten salt. As shown in Fig. 4-1, highly crystalline Si films are expected to be deposited via a two-step electrolysis process using two types of electrolytic baths. In the first step, a thin film of Zn is formed on the substrate via electrolysis. In the second step, using the samples obtained in the first step as electrodes, Si is electrodeposited in a KF–KCl–K₂SiF₆ melt at 923 K. The electrodeposited Si samples were analyzed by surface and cross-sectional SEM, EDX, and XRD.

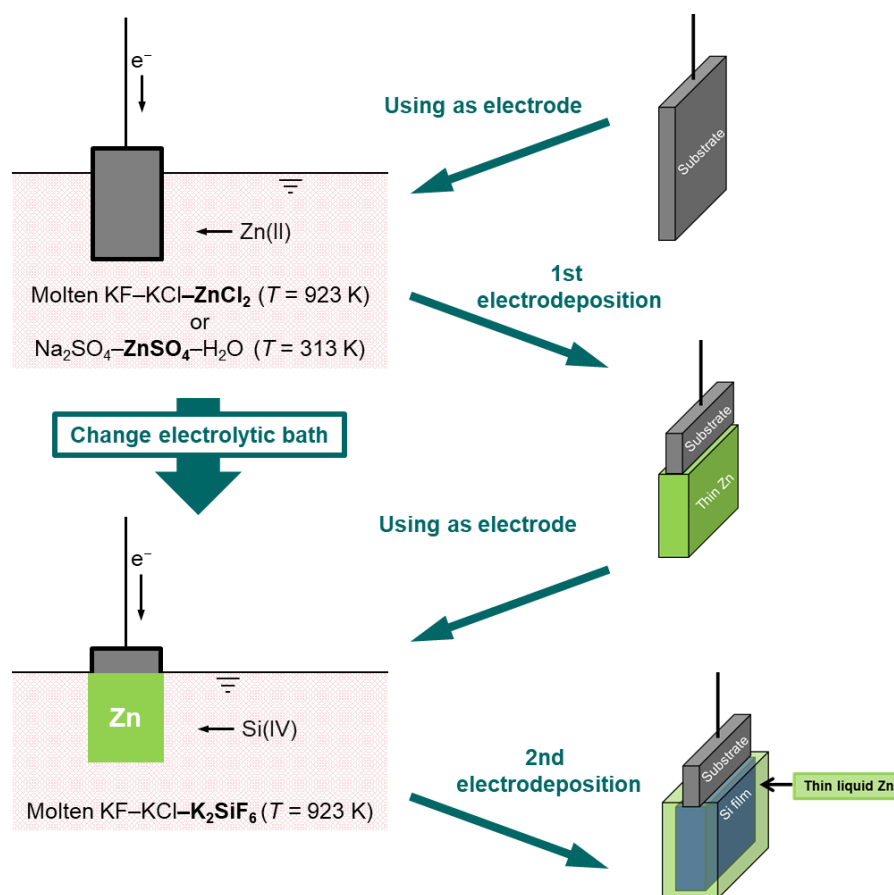


Fig. 4-1 A schematic of the proposed method of Si film formation using thin liquid Zn.

4.2 Experimental

4.2.1 First-step Electrodeposition: Preparation of Zn Thin Films

Zn electrodeposition on graphite substrates was conducted in a KF-KCl molten salt at 923 K. KF-KCl was mixed in a eutectic composition of KF:KCl = 45:55, and ZnCl₂ was added at a concentration of 1.0 mol%. The preparation methods for KF and KCl and the apparatus for the electrolysis experiment using this molten salt were the same as those described in the previous Chapters 2 and 3. ZnCl₂ (FUJIFILM Wako Pure Chemical Corp., purity >98.0%) was vacuum-dried in an alumina crucible at 453 K for 72 h and at 523 K for 24 h. The electrodeposition was conducted using a graphite plate (Toyo Tanso Co., Ltd., IG-15, width: 10.0 mm, thickness: 1.0 mm) as the working electrode and GC rods (Tokai Fine Carbon Co., Ltd., >99.9998%, diameter = 3.0

mm) as the counter electrodes, with a current density of 150 mA cm^{-2} and charge density of 90 C cm^{-2} .

Zn electrodeposition on W substrates was conducted in a stirred sulfuric acid solution containing $1.2 \text{ mol L}^{-1} \text{ ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (FUJIFILM Wako Pure Chemical Corp., purity >99.5%) and $0.56 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ (FUJIFILM Wako Pure Chemical Corp., purity >99.0%) at pH 1.8 and 313 K. The stirring speed was set to 400 rpm, and galvanostatic electrolysis was performed at a current density of 150 mA cm^{-2} and charge density of 10 C cm^{-2} . Electrolysis was conducted using a two-electrode system with a W plate (Nilaco Corp., width: 10.0 mm, thickness: 0.1 mm, purity = 99.95%) as the working electrode and a Pt plate (Nilaco Corp., thickness: 0.1 mm, purity = 99.95%) as the counter electrode.

Since the Zn electrodeposited on the W substrate was in a solid state, the possibility of maintaining it in a film form was confirmed after it was melted into a liquid state. The samples were immersed in $\text{KF-KCl-K}_2\text{SiF}_6$ molten salt at 923 K for 30 min without electrolysis, the weight change was measured, and the surface after immersion was observed.

4.2.2 Second-step Electrodeposition: Formation of Si Films

The apparatus, preparation of the molten salt, and sample analysis methods were similar to those described in the previous chapters. A schematic of the experimental apparatus is shown in Fig. 4-2. The Zn thin film electrodeposited by the method described in the previous section was used as the working electrode, a Si rod was used as the reference electrode, and two Si rods were used as counter electrodes, which were arranged symmetrically with respect to the working electrode. The liquid Zn thin-film electrode was then immersed vertically. Galvanostatic electrolysis was conducted at a current density of 50 mA cm^{-2} and charge density of 90 C cm^{-2} .

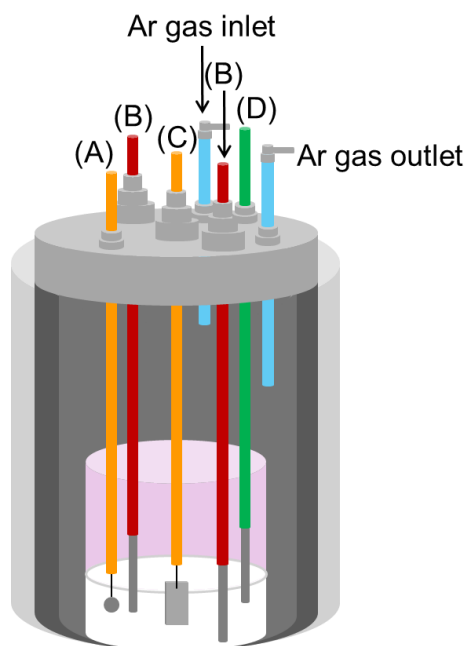


Fig. 4-2 A schematic drawing of the experimental apparatus for the electrochemical measurements in molten $\text{KF-KCl-K}_2\text{SiF}_6$ at 923 K: (A) Ag flag electrode (WE), (B) Si rod electrodes (CE), (C) W plate electrode (WE), (D) Si rod electrode (RE). WE: working electrode, CE: counter electrode, RE: reference electrode.

4.2.3 Analysis of Samples

The compositional images and topographic images were obtained using the backscattered electron (BSE) mode of SEM (Thermo Fisher Scientific K. K., Phenom Pro Generation 5). Secondary electron (SE) images were also obtained using SEM. For cross-sectional SEM observation, the samples were embedded in resin (Nissin ES Co., Ltd., room temperature curing epoxy resin NER-814, medium) and then polished using emery paper (#320, #600), abrasives (SANKEI Co., Ltd., polycrystalline diamond suspension (diameter = 9 and 3 μm), and high-purity alumina (diameter = 0.05 μm)) using a rotary polishing machine (Buehler Ltd., Ecomet III). After polishing, the samples were coated with Au using an ion-sputtering apparatus (Hitachi High-Tech Corp., E-101) to ensure conductivity. To analyze the surface morphology of the Si film, any residual Zn on the deposit was dissolved in 50 mL of an HCl solution (20 wt%). The other analyses were similar to those described in Chapters 2 and 3.

4.3 Results and Discussion

4.3.1 First-step Electrodeposition: Preparation of Zn Thin Films

Initially, Zn electrodeposition on a graphite substrate was conducted. Zn can be electrodeposited at low temperatures near room temperature using aqueous solutions. However, under these conditions, water tends to penetrate the graphite substrate. When the resulting electrode is immersed in a molten salt for the Si electrodeposition, the water retained in the graphite substrate may contaminate the molten salt. To avoid water contamination of the molten salt used for Si electrodeposition, Zn electrodeposition was conducted in a KF–KCl–ZnCl₂ melt at 923 K. The melting point of Zn is 693 K, which is lower than the temperature of the molten salt, so the electrodeposited Zn is in a liquid state. Optical and SEM images after galvanostatic electrolysis at a current density of 150 mA cm⁻² and charge density of 90 C cm⁻² are shown in Fig. 4-3. Almost no deposit remained on the substrate, and no metallic luster was observed in an optical image (Fig. 4-3(a)). In addition, the weight increase was extremely small. Spherical particles were observed in an SEM image in Fig. 4-3(b). EDX analysis confirmed that they were Zn. These observations confirmed that a uniform liquid Zn film was not formed on the graphite substrate. Because liquid

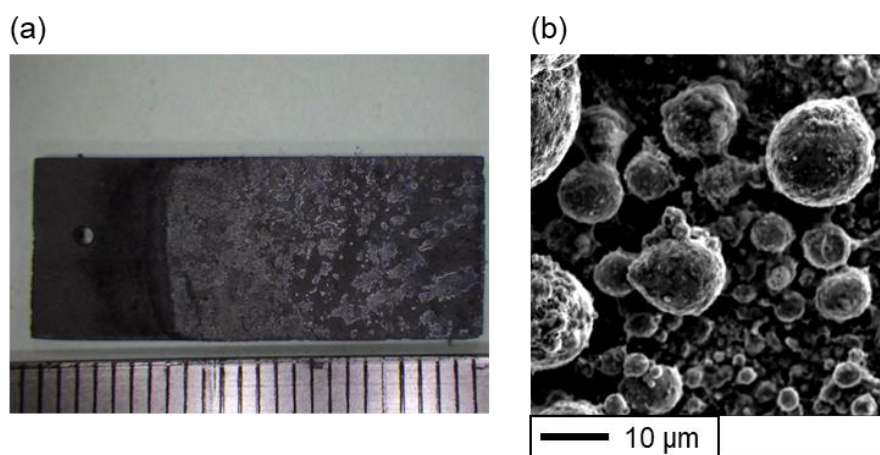


Fig. 4-3 (a) A photograph and (b) a surface SEM image of sample obtained by galvanostatic electrolysis of a graphite plate electrode at 150 mA cm⁻² for 90 C cm⁻² in molten KF–KCl–ZnCl₂ (1.0 mol%) at 923 K. The SEM image represents a backscattered electron (BSE) compositional image.

Zn did not wet the graphite well, only a small part of the Zn remained on the surface, and the shape was spherical.

Next, Zn electrodeposition on a W substrate was conducted. Fig. 4-4(a) shows an optical image of the sample after electrolysis in a sulfuric acid solution at a current density of 150 mA cm^{-2} and charge density of 10 C cm^{-2} . The parts immersed in the solution were covered with a silvery-white electrodeposit. An SEM image of the surface of the electrodeposit is presented in Fig. 4-4(b). A uniformly shaped electrodeposit covered the entire surface. An EDX spectrum in this area indicates only Zn, as shown in Fig. 4-4(c). Furthermore, a cross-sectional SEM image shown in

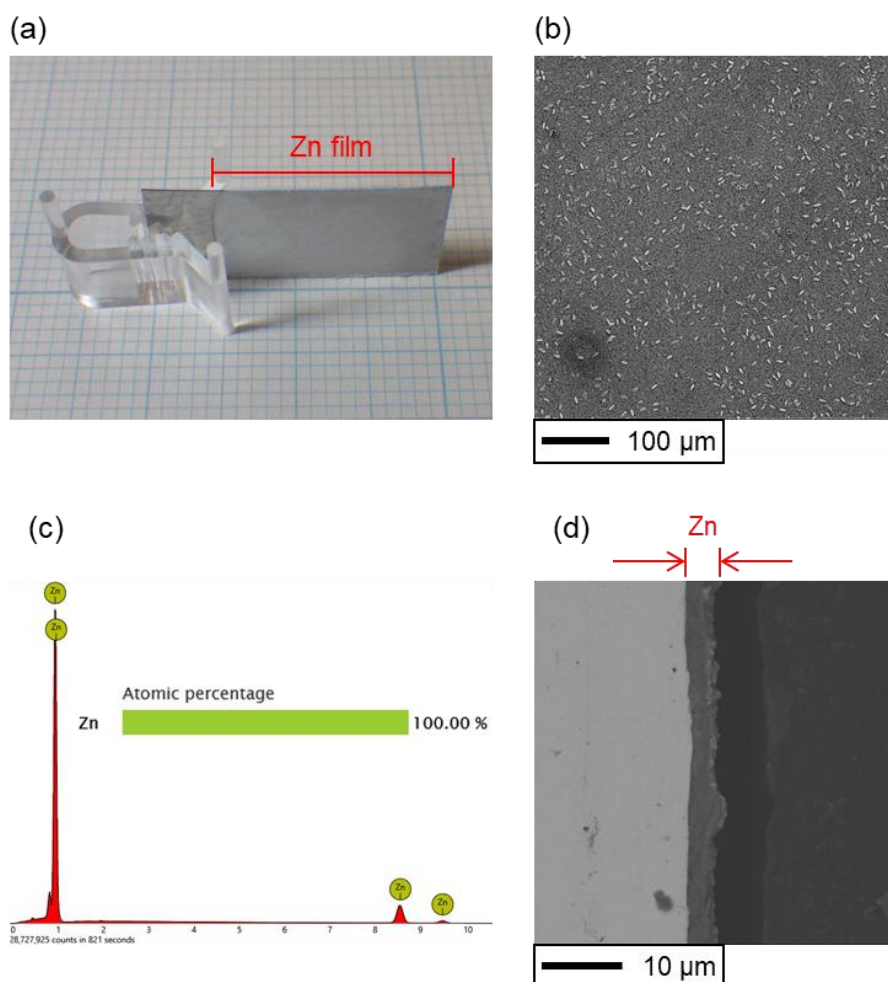


Fig. 4-4 (a) A photograph of sample obtained by galvanostatic electrolysis of a W substrate at 150 mA cm^{-2} for 10 C cm^{-2} in agitated sulfate solutions containing 1.2 mol L^{-1} of ZnSO_4 and 0.56 mol L^{-1} of Na_2SO_4 at pH 1.8 and 313 K. (b) An SEM image of the sample shown in (a). The SEM image represents a secondary electron (SE) image. (c) An EDX spectrum of the sample in (b) and atomic percentages of elements. (d) A cross-sectional SEM image of sample shown in (a). The SEM image represents a BSE compositional image.

Fig. 4-4(d) reveals that the entire surface is covered with a Zn film having a thickness of approximately 5 μm —almost the same as the theoretical thickness. Furthermore, the silver-white electrodeposit was confirmed to be Zn by an XRD patterns shown in Fig. 4-5. Peaks other than Zn were also observed in the XRD pattern; however, these were attributed to the W substrate. The peak for the W substrate is attributed to the exposed area of the substrate observed in the photograph (Fig. 4-4(a)).

The obtained samples were then immersed in a $\text{KF-KCl-K}_2\text{SiF}_6$ melt at 923 K for 30 min. Fig. 4-6 presents an optical image of sample after 30 min of immersion. The sample exhibited a Zn thin film in the areas immersed in the molten salt, indicating that it remained in film form even

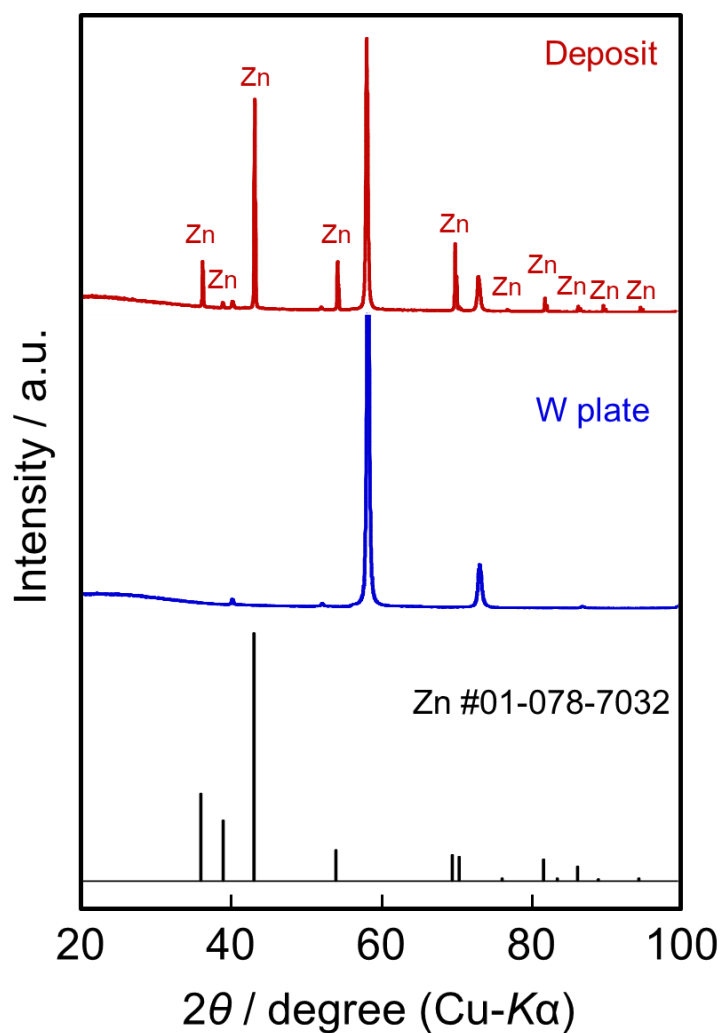


Fig. 4-5 An XRD pattern of the sample shown in Fig. 4-4. An XRD pattern of the W plate is also shown for comparison.

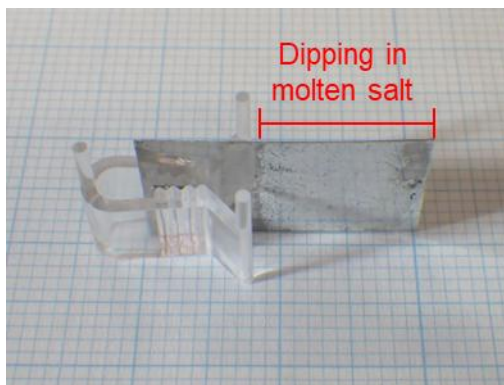


Fig. 4-6 A photograph of liquid thin Zn electrode after being immersed in molten $\text{KF-KCl-K}_2\text{SiF}_6$ at 923 K without electrolysis for 30 min.

after transforming into a liquid state. The weight of Zn after immersion was approximately 75% of that before immersion. Zn—equivalent to approximately 25% of the weight loss—is thought to have detached from the substrate and fell into the molten salt under the force of gravity. Nevertheless, Zn electrodeposited on the W substrate achieves the objective of remaining in liquid film form in molten salt during Si electrodeposition.

4.3.2 Second-step Electrodeposition: Formation of Si Films

Using the Zn thin film on the W substrate obtained in the previous section as an electrode, galvanostatic electrolysis was conducted in a $\text{KF-KCl-K}_2\text{SiF}_6$ melt at 923 K with a current density of 50 mA cm^{-2} and charge density of 90 C cm^{-2} . The potential during electrolysis was more positive than 0.8 V vs. K^+/K . As mentioned in Chapter 2, this potential is more positive than the solid Si deposition potential, suggesting that the reaction during electrolysis was the formation of a liquid Si–Zn alloy. Fig. 4-7(a) shows the optical image of the samples after Si electrodeposition. Areas where Zn remained in the visible small granules were confirmed. In other areas, the surface was a dark blue color owing to Si rather than the metallic luster of Zn. To confirm if Zn remains in these areas, SEM observations were conducted. Fig. 4-7(b) presents a SEM image of the area where granular Zn was not observed with naked eye. In the SEM image, Zn, shown in a brighter color, was observed on part of the surface, while most of the surface was Si, shown in a darker

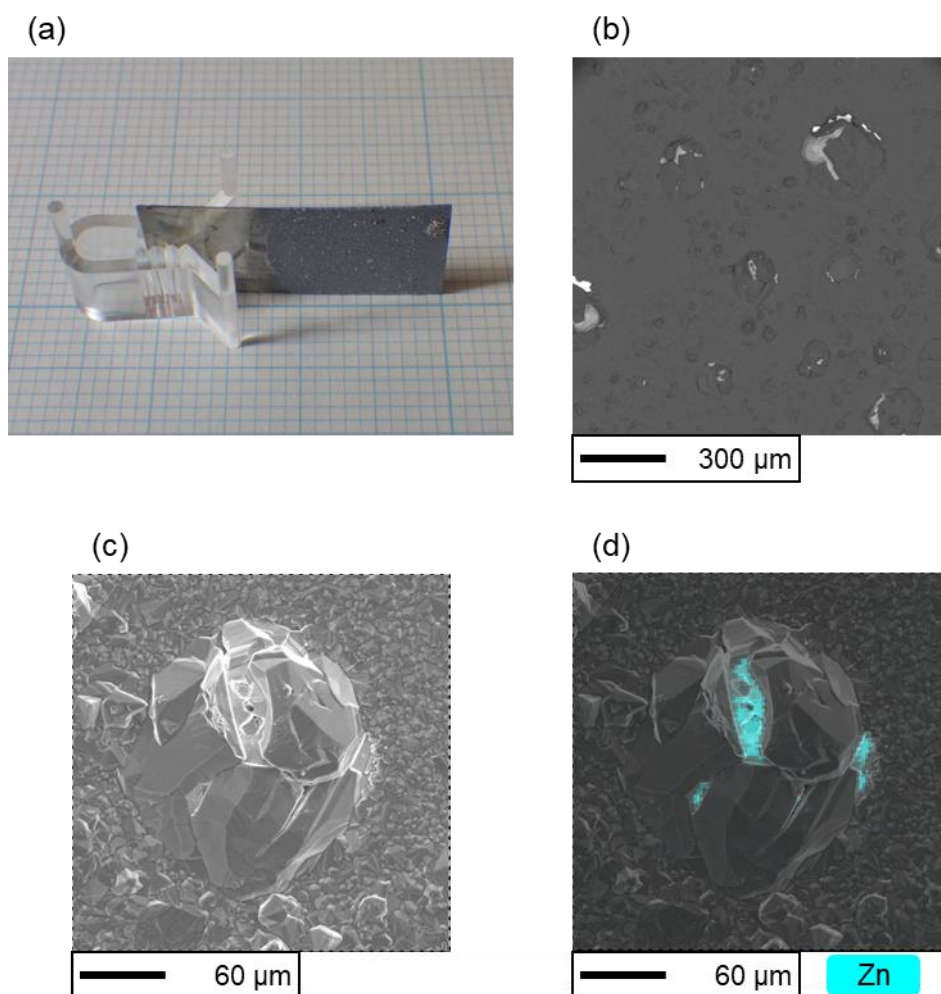


Fig. 4-7 (a) A photograph of sample obtained by galvanostatic electrolysis of thin liquid Zn electrode at 50 mA cm^{-2} for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K before HCl treatment. (b) A surface SEM image of sample shown in (a). The SEM image represents a BSE compositional image. (c) A higher magnification SEM image of (b). The SEM image represents an SE image. (d) An EDX mapping image of (c).

color. The area where Zn was observed in the SEM image was less than 50%. However, since the decrease in Zn weight is approximately 50% after electrolysis assuming 100% current efficiency in Si electrodeposition, more Zn should remain. The remaining Zn that has not been observed in these areas is thought to be concentrated in the granular Zn areas. As shown in a higher magnification SEM image (Fig. 4-7(c)) and a corresponding EDX mapping image (Fig. 4-7(d)), Zn is mainly observed in depressed areas of the Si deposit on the substrate. The movement of Zn from protruding areas to depressed areas due to the formation of roughness may lead to the

accumulation of Zn, causing liquid Zn to form larger particles. Larger liquid Zn particles are heavier and more prone to detachment. Therefore, Zn was observed only in the depressed areas of the Si deposited on the substrate.

Next, Zn was removed via hydrochloric acid treatment. The current efficiency calculated from the sample weight after hydrochloric acid treatment was 100%. Fig. 4-8(a) presents an optical image of the sample after Zn removal. The areas where Zn remained in granular form, as shown in Fig. 4-7(a), exposed the W substrate after Zn removal. There was almost no color change in the other areas compared to that before Zn removal. In a surface SEM image (Fig. 4-8(b)), crystals with a grain size of $\geq 20 \mu\text{m}$ were observed over the entire surface. The crystallite size was reported to be approximately 50 nm in Si electrodeposition on Ag substrates [2]. Thus, the presence of liquid Zn on the substrate promotes crystal growth. The promotion of crystal growth was attributed to the mechanism of solid Si electrodeposition via the liquid Si–Zn alloy proposed in the previous chapters. This result was exactly as expected. Fig. 4-8(c) shows a cross-sectional SEM image. The electrodeposited Si formed a film on the W substrate. The film thickness

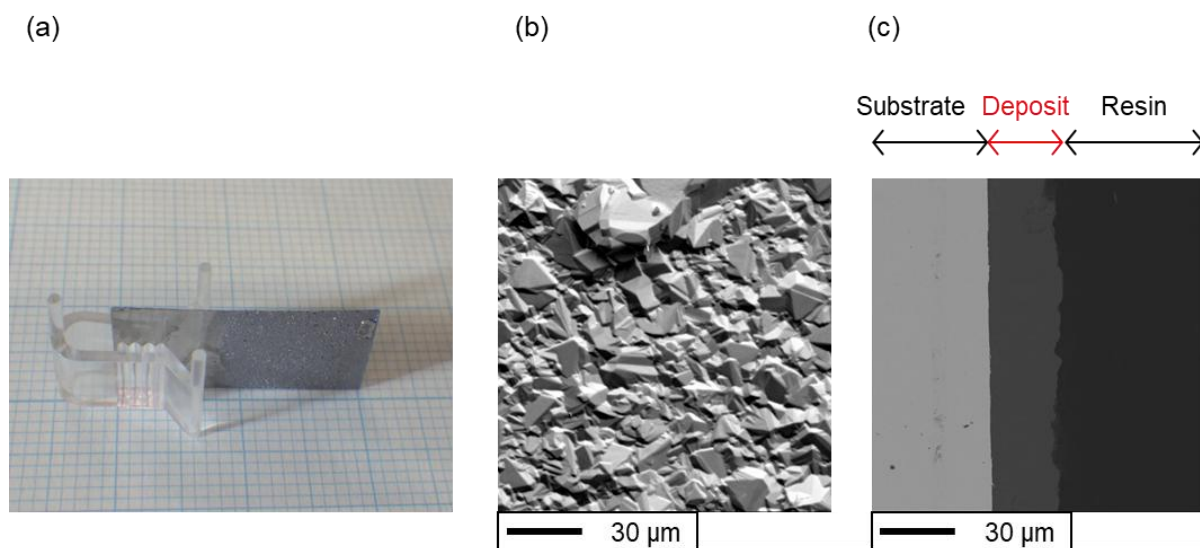


Fig. 4-8 (a) A photograph of sample obtained by galvanostatic electrolysis of thin liquid Zn electrode at 50 mA cm^{-2} for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K after HCl treatment. (b) A surface SEM image and (c) a cross-sectional SEM image of the sample shown in (a). (b) represents an SE image and (c) represents a BSE compositional image.

measured in this image was approximately 26 μm . The theoretical film thickness is 28 μm . Electrical charge is thought to have been concentrated in specific areas, resulting in unevenness in the Si film. Thus, the film thickness of the sample was considered to be slightly smaller than the theoretical film thickness.

Fig. 4-9 shows an XRD pattern of the sample surface. All the peaks were attributed to Si and the W substrate pattern. According to the Si–W binary phase diagram, the intermetallic compound WSi_2 was present [3]; however, no patterns attributable to WSi_2 were observed in the XRD pattern of the sample. This confirmed that WSi_2 was not formed, and only Si was deposited.

Areas with larger grain sizes were also observed in this sample. Fig. 4-10 shows an area (a)

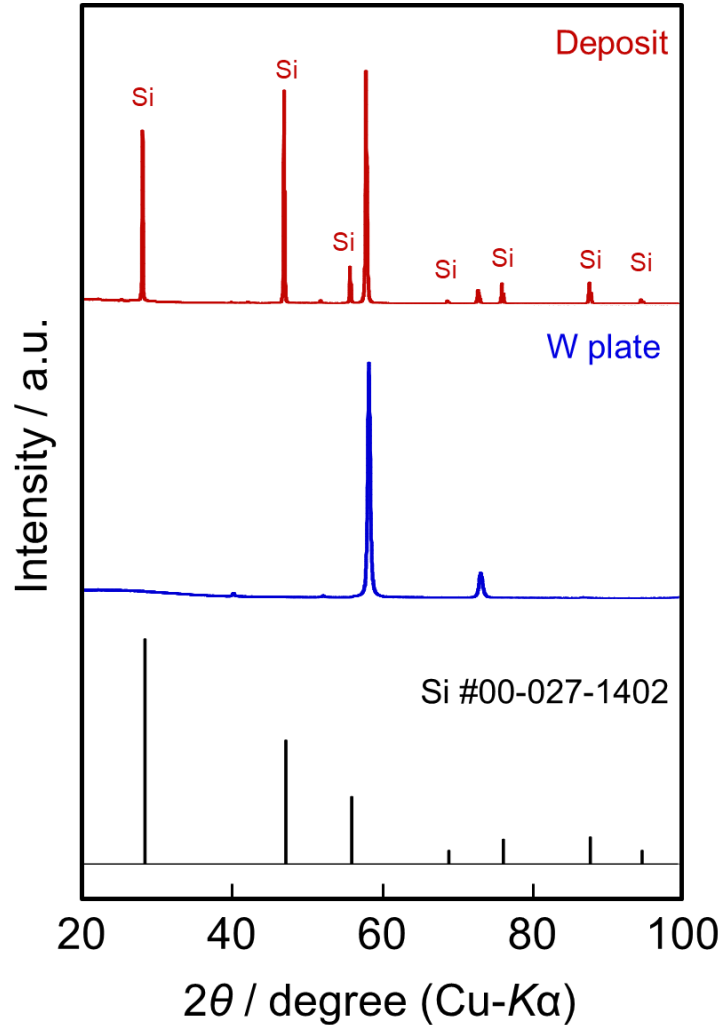


Fig. 4-9 XRD patterns of the sample shown in Fig. 4-8 and of the W plate with Si #00-027-1402.

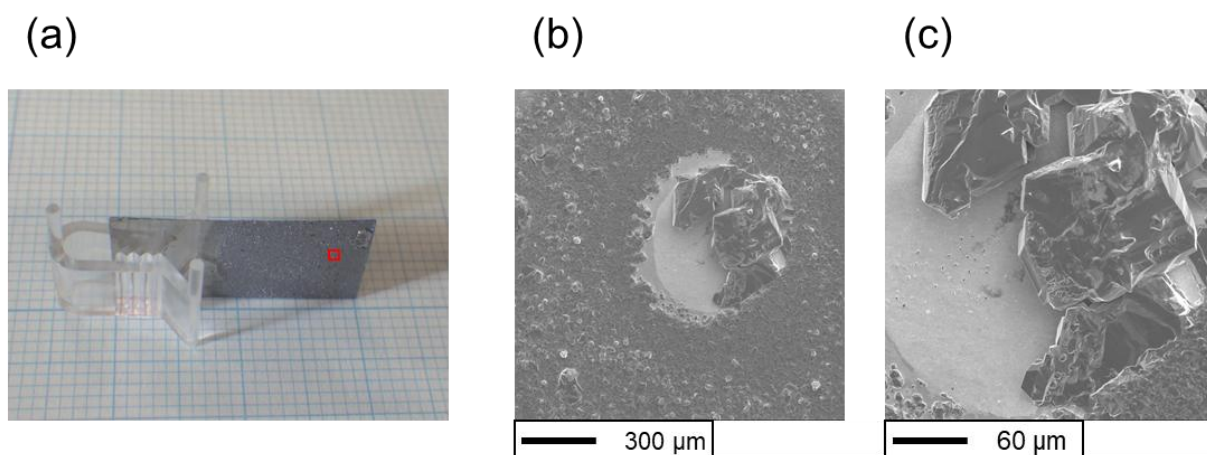


Fig. 4-10 (a) Location of SEM observation (red square) of sample shown in Fig. 4-7 where Si with particularly large grain size existed. (b) Low- and (c) high-magnification SEM images of the area shown in (a). Both (b) and (c) represent SE images.

where particularly large Si grains are observed on the sample surface, along with low- and high-magnification SEM images ((b) and (c), respectively) of that area. In the low-magnification SEM image (Fig. 4-10(b)) and EDX analysis of that area, particularly large crystals were observed near the boundary between the exposed W substrate and the Si film. The high-magnification SEM image in Fig. 4-10(c) shows that the maximum grain size is close to 80 μm. Although it is desirable to obtain Si with larger grain sizes, exposure of the W substrate is not desirable.

The reason why larger Si grains and exposed W substrates were observed side by side is thought to be the presence of areas on the substrate where Si dissolved in Zn can easily reach and areas where it cannot easily reach. Figs. 4-11(a) and (b) show schematic illustrations of the movement of Si in the liquid Zn at locations where the substrate is not exposed and Si is deposited in a film (a), and at locations where the substrate is exposed (b). As shown in Fig. 2-7 in Chapter 2, solid Si deposits preferentially at the interface between the substrate and the liquid Si–Zn alloy, which is saturated with Si in the liquid phase. When the interface between molten salt and liquid Zn (Liquid-Liquid interface; LL-IF) and the substrate are kept parallel (a), Si dissolved in liquid Zn diffuses uniformly and reaches the substrate without bias, causing the deposited Si to form a film. When LL-IF and the substrate are not parallel (b), on the other hand, the area marked with

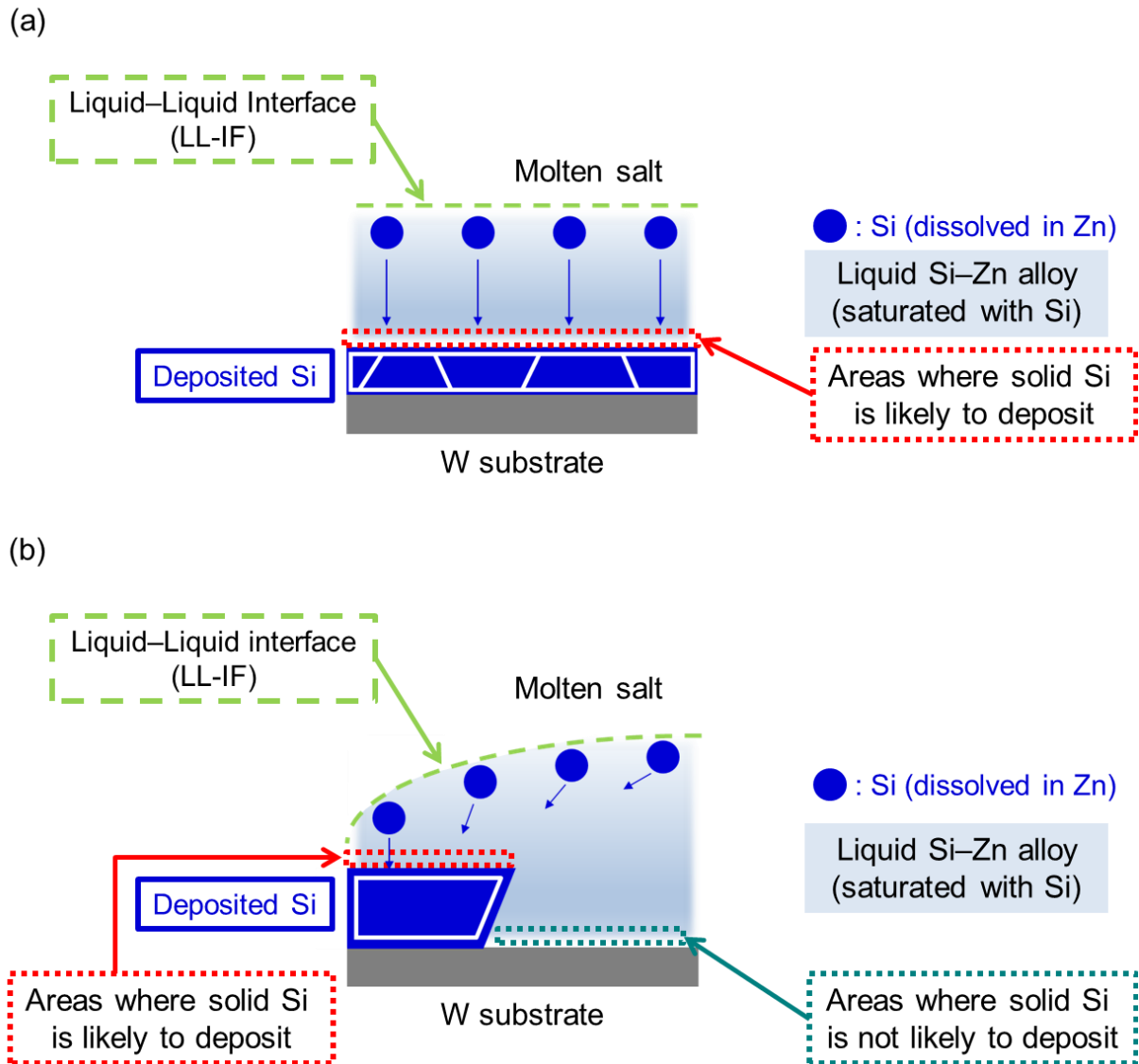


Fig. 4-11 Schematic illustrations of the movement and concentration of Si in the liquid Zn. (a) At areas where the substrate is covered with Si films, and (b) at areas where the substrate is not covered with Si films.

red broken lines is closer to LL-IF than the area marked with green broken lines. Thus, dissolved Si can easily reach the area marked with red broken lines, where solid Si is likely to deposit. As a result, Si crystal grows larger in the areas marked with red broken lines, and the substrate remains exposed in the areas marked with green broken lines.

4.4 Conclusion

Highly crystalline Si films were electrodeposited via a two-step process using a thin film of liquid Zn as the electrode. In the first step, solid Zn thin films were deposited on a substrate via Zn electrodeposition in a sulfuric acid solution at 313 K. The film form was maintained even after Zn changed to a liquid state. In the second step, Si electrodeposition on the liquid Zn thin-film electrode was conducted with 100% current efficiency. After Zn removal via hydrochloric acid treatment, a crystalline Si film consisting of Si with a grain size of $\geq 20\text{ }\mu\text{m}$ was confirmed on almost entire surface. Part of the substrate was undesirably left uncovered with Si films. The cause was considered to be the presence of areas on the substrate where Si dissolved in Zn can easily reach and areas where it cannot easily reach, resulting in localized crystal growth.

References

1. K. Yasuda, T. Kato, Y. Norikawa, and T. Nohira, *J. Electrochem. Soc.*, **168**, 112502 (2021).
2. K. Yasuda, K. Saeki, T. Kato, R. Hagiwara, and T. Nohira, *J. Electrochem. Soc.*, **165**, D825 (2018).
3. G. A. Panov and M. A. Zakharov, *J. Phys.: Conf. Ser.*, **541**, 012097 (2014).

Chapter 5

Electrochemical Formation of Si Films by Co-deposition of Si and Zn in Molten $\text{KF-KCl-K}_2\text{SiF}_6\text{-ZnCl}_2$ Systems

5.1 Introduction

In the previous Chapter 4, the electrodeposition of crystalline Si film with large grain sizes was successfully achieved using thin liquid Zn on a W substrate as an electrode in molten $\text{KF-KCl-K}_2\text{SiF}_6$ at 923 K. However, Zn did not form a film on a graphite substrate because of its poor wettability with graphite. In the present chapter, to deposit crystalline Si film on the graphite substrate, the method involving the co-deposition of Si and Zn was investigated. Initially, cyclic voltammetry was performed to study the behavior of Si(IV) and Zn(II) ions in molten $\text{KF-KCl-K}_2\text{SiF}_6\text{-ZnCl}_2$. Galvanostatic electrolysis was then conducted, and Si deposition on the substrate via liquid Si-Zn alloy was confirmed by analyzing the surface and cross-sectional morphologies. The electrolytic conditions for electrodeposition of highly crystalline Si films were optimized by varying the concentration of ZnCl_2 and current density.

5.2 Experimental

A preparation method of KF-KCl molten salt and analysis methods are almost the same as Chapter 3. Important and/or different points are described below.

Fig. 5-1 presents a schematic of the experimental apparatus. After blank measurements in

KF–KCl, K_2SiF_6 (Junsei Chemical Co., Ltd., purity >99.0 %) was added to the melt to achieve concentrations of 0.1 or 2.0 mol%, and ZnCl_2 (FUJIFILM Wako Pure Chemical Corp., purity >98.0 %) was added to the melt to achieve concentrations of 0.1, 0.5, 1.0, or 2.0 mol%. ZnCl_2 salt was dried in an alumina crucible at 453 K for 72 h and 523 K for 24 h before use.

In the electrochemical measurements and galvanostatic electrolysis, the working electrodes were a glassy carbon (GC) rod (Tokai Fine Carbon Co., Ltd., >99.9998 %, diameter = 3.0 mm) and a graphite plate (Toyo Tanso Co., Ltd., IG-15, width: 10.0 mm, thickness: 1.0 mm), respectively. GC rods were used as the counter electrodes. A Pt wire (Tanaka Precious Metal Technologies Co., Ltd., purity >99.98 %, diameter = 1.0 mm) was used as the quasi-reference electrode. The potential of the quasi-reference electrode was calibrated considering the dynamic Cl_2/Cl^- potential measured on the GC rod.

Backscattered electron (BSE) compositional images and BSE topographic images were acquired using SEM (Thermo Fisher Scientific K. K., Phenom Pro Generation 5). For the cross-

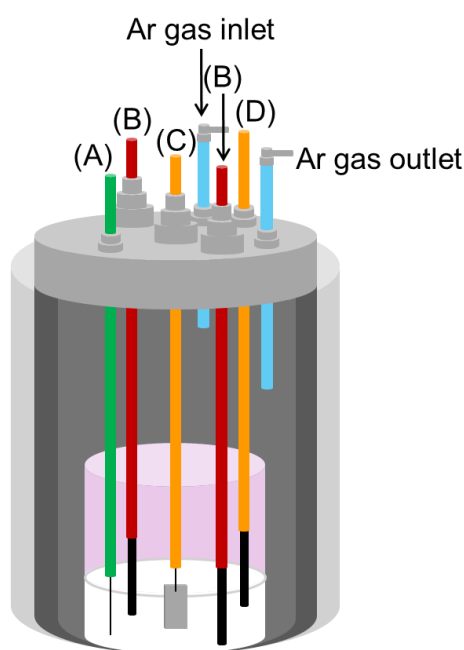


Fig. 5-1 A schematic drawing of the experimental apparatus for the electrochemical measurements: (A) Pt wire electrode (QRE), (B) glassy carbon electrodes (CE), (C) graphite plate electrode (WE), (D) glassy carbon electrode (WE). QRE: quasi reference electrode, CE: counter electrode, WE: working electrode.

sectional SEM observation, the samples were embedded in resin (Nissin ES Co., Ltd., room temperature curing epoxy resin NER-814, medium) and then polished using emery paper (#320, #600), abrasives (SANKEI Co., Ltd., polycrystalline diamond suspension (diameter = 9 and 3 μm), and high-purity alumina (diameter = 0.05 μm)) using a rotary polishing machine (Buehler Ltd., Ecomet III). After polishing, the samples were coated with Au using an ion sputtering apparatus (Hitachi High-Tech Corp., E-101) to ensure conductivity. To analyze the surface morphology of Si film, any residual Zn on the deposit was dissolved in 50 mL of HCl solution (20 wt%).

5.3 Results and Discussion

5.3.1 Electrochemical Behavior of Si(IV) and Zn(II) Ions

Cyclic voltammetry was conducted to study the reduction behavior of Si(IV) and Zn(II) ions. Fig. 5-2 shows a cyclic voltammogram of a GC electrode in molten KF–KCl at 923 K containing 0.1 mol% K_2SiF_6 and 0.1 mol% ZnCl_2 . IR correction was conducted with a feedback rate of 80 %. When the potential was scanned from the rest potential toward the negative direction, the cathodic current peaks a and b were observed around -2.6 V and -3.1 V , respectively. As

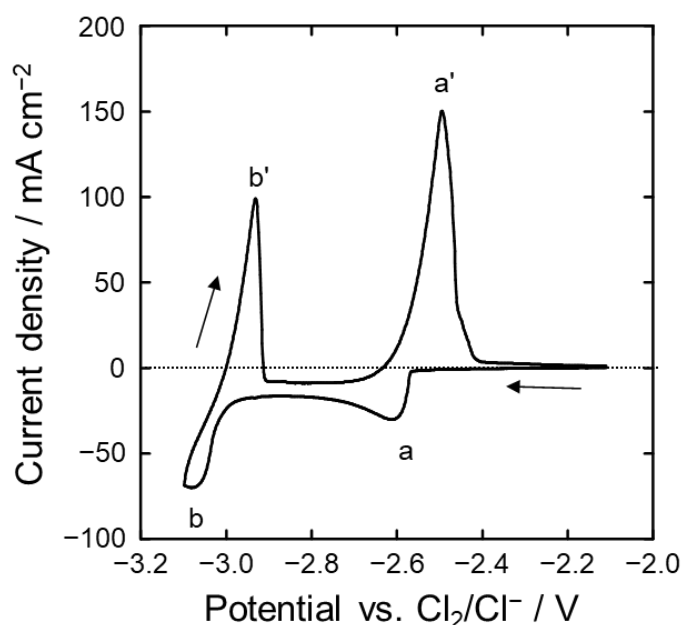
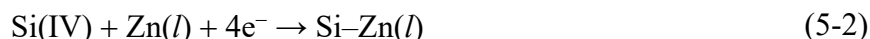


Fig. 5-2 A cyclic voltammogram at a glassy carbon electrode in molten KF–KCl– K_2SiF_6 (0.1 mol%)– ZnCl_2 (0.1 mol%) at 923 K. Scan rate: 0.10 V s^{-1} .

mentioned in Chapter 2 using a liquid Zn electrode, the rest potential of liquid Zn electrodes was more positive than the Si–Zn liquid alloy formation potential. Therefore, the cathodic current peak around -2.6 V is attributed to the reduction of Zn(II) ions, as expressed in reaction (5-1).



The cathodic current peak around -3.1 V is attributed to the Si–Zn liquid alloy formation, as expressed in reaction (5-2).



As mentioned in Chapter 1, only 1 at% of Si dissolves in liquid Zn at 923 K [1]. Although Si can supersaturate in liquid Zn during the short period of CV measurement, the solid Si formation expressed in reaction (5-3) is considered to progress simultaneously with the reaction described in reaction (5-2).



When the potential scanning direction was reversed, anodic current peaks a' and b' corresponding to a and b were observed. These currents result from the reverse reactions, as described in reactions (5-1)–(5-3). The above results indicated the reduction of Si(IV) ions during electrolysis at a current exceeding the diffusion-limiting current of the Zn(II) ions, signifying the feasibility of co-deposition of Si and Zn.

5.3.2 Si Deposition via Liquid Si–Zn Alloy during Co-deposition

To confirm Si deposition via liquid Si–Zn alloy during co-deposition, galvanostatic electrolysis was conducted on a graphite substrate in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)– ZnCl_2 (1.0 mol%) at a current density of 150 mA cm^{-2} and a charge density of 90 C cm^{-2} . During the electrolysis, the potential was more negative than -3.0 V, indicating the occurrence of co-deposition. As shown in an optical image in Fig. 5-3(a), the obtained sample exhibits a metallic luster across

the entire surface, indicating that the Si–Zn alloy formed a film covering the electrode surface. A surface SEM image is shown in Fig. 5-3(b). EDX mapping image (Fig. 5-3(c)) and spectrum (Fig. 5-3(d)) showed that the entire surface was covered with Zn and only Zn and Si were detected. Unlike the electrodeposits obtained in a bath containing only the Zn(II) ions (Fig. 4-3 in the previous chapter), the liquid Si–Zn alloy remained nearly entirely on the surface of electrodeposits, attributable to the presence of Si. The good bonding between Si and graphite enabled the liquid Si–Zn alloys to remain on the substrate.

Figs. 5-4(a) and (b) show a cross-sectional SEM and EDX mapping images of the sample,

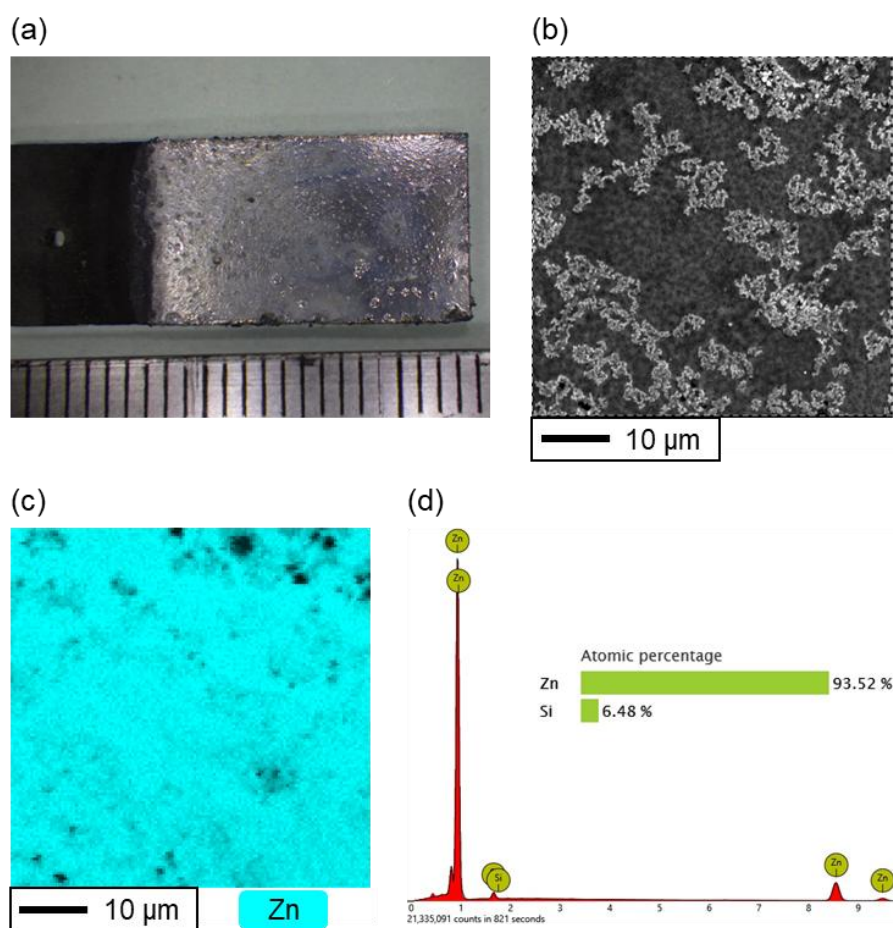


Fig. 5-3 (a) A photograph and (b) a surface SEM image of sample obtained by galvanostatic electrolysis of graphite plate electrode at 150 mA cm^{-2} for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)– ZnCl_2 (1.0 mol%) at 923 K. The SEM image represents a backscattered electron (BSE) compositional image. (c) The corresponding EDX mapping image of elemental zinc shown in (b). (d) EDX spectrum of the sample in (b) and atomic percentages of elements.

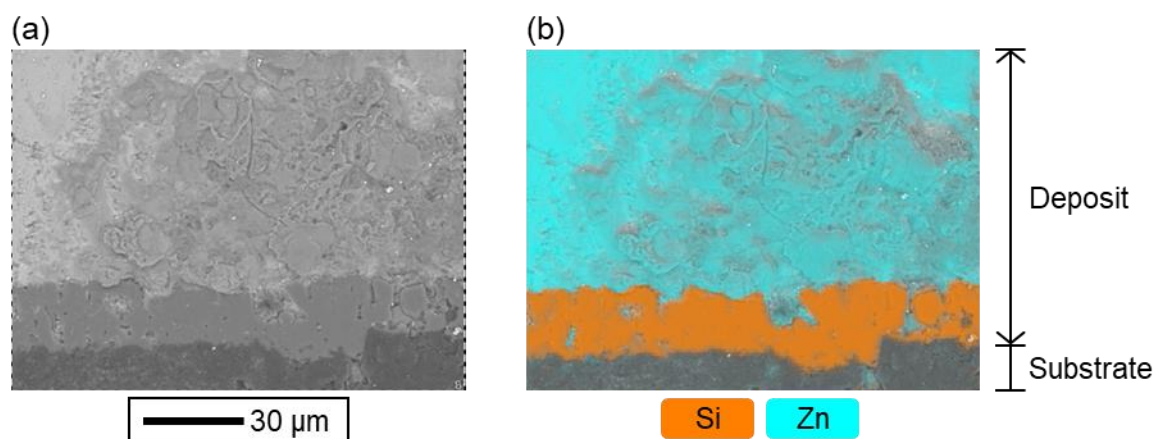


Fig. 5-4 (a) A cross-sectional SEM and (b) EDX mapping images of samples obtained by galvanostatic electrolysis of graphite plate electrode for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)- ZnCl_2 (1.0 mol%) at 923 K. Current density was 150 mA cm^{-2} . The SEM image represents a BSE compositional image.

respectively. Two-layered electrodeposits were observed on the substrate in the SEM image. EDX mapping image confirmed that the layer closest to the substrate was Si and the layer on the molten salt side was Zn. The Si layer was assumed to be deposited from the liquid Si-Zn alloy during electrolysis, confirming that Si was deposited via the liquid Si-Zn alloy during co-deposition.

To confirm that the deposits were crystalline Si, XRD analysis was conducted. Fig. 5-5 shows an XRD pattern of the sample shown in Fig. 5-3 after removing Zn via HCl treatment. The diffraction peaks except for those of the graphite substrate were attributed to Si.

5.3.3 Electrolysis Conditions for Highly Crystalline Si Films

To investigate the conditions for obtaining highly crystalline Si films via co-deposition, electrolysis was performed with different ZnCl_2 concentrations and current densities. First, electrodeposition was conducted on graphite substrates in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)- ZnCl_2 (0.5 mol%) at a current density of $100\text{--}200 \text{ mA cm}^{-2}$ and a charge density of 90 C cm^{-2} . Under these conditions, Zn deposit was granular and did not cover the entire surface. Fig. 5-6 shows cross-sectional SEM and EDX mapping images of the sample after electrodeposition, particularly where Zn is present on the surface. Under the conditions of (a) 100 and (b) 150 mA cm^{-2} , distinct

Si and Zn layers were formed with the Si layer closest to the substrate. Despite the incomplete surface coverage by Zn, solid Si was deposited on the graphite substrate from the Si–Zn liquid alloy. Conversely, at a current density of (c) 200 mA cm^{-2} , the deposit on the substrate was not divided into two layers of Si and Zn. The finding could be attributed to the large reduction in the amount of Si(IV) ion compared to that of the Zn(II) ion reduction, resulting in rapid deposition of solid Si from the liquid alloy. Furthermore, Si deposition occurred on top of the protruding deposits of Si, resulting in a dendrite-like shape.

Second, electrodeposition was carried out on graphite substrates in molten $\text{KF–KCl–K}_2\text{SiF}_6$ (2.0 mol%)– ZnCl_2 (1.0 mol%) at a current density of $100\text{--}200 \text{ mA cm}^{-2}$ and a charge density of 90

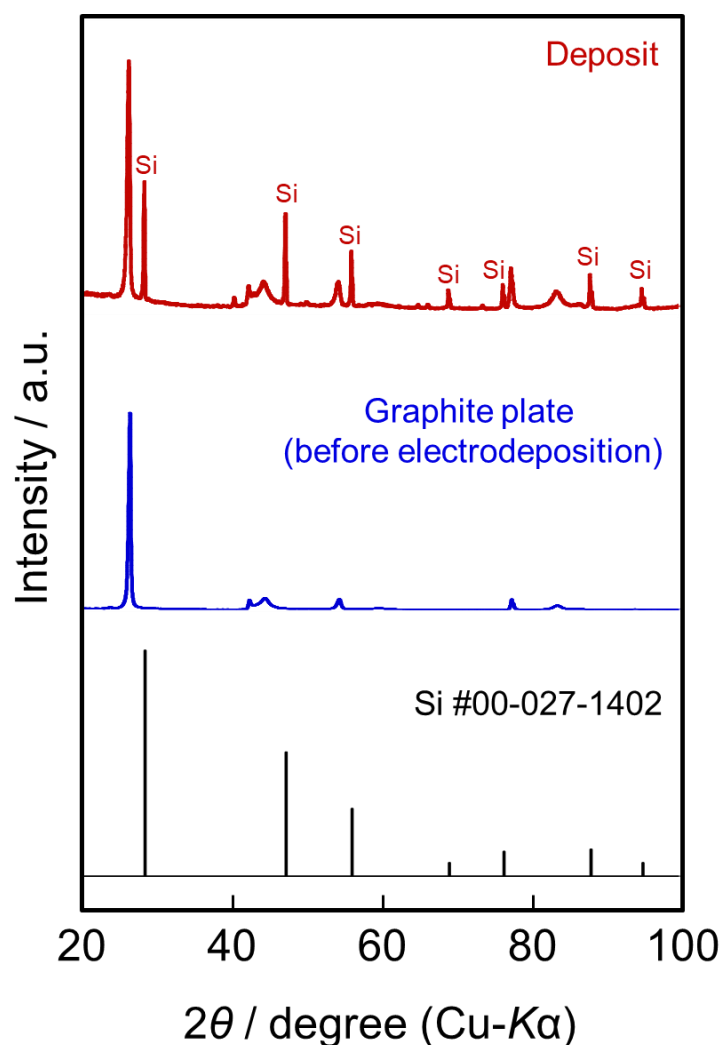


Fig. 5-5 An XRD pattern of the sample shown in Fig. 5-3 after removing Zn via HCl treatment. An XRD pattern of the graphite plate is also shown for comparison.

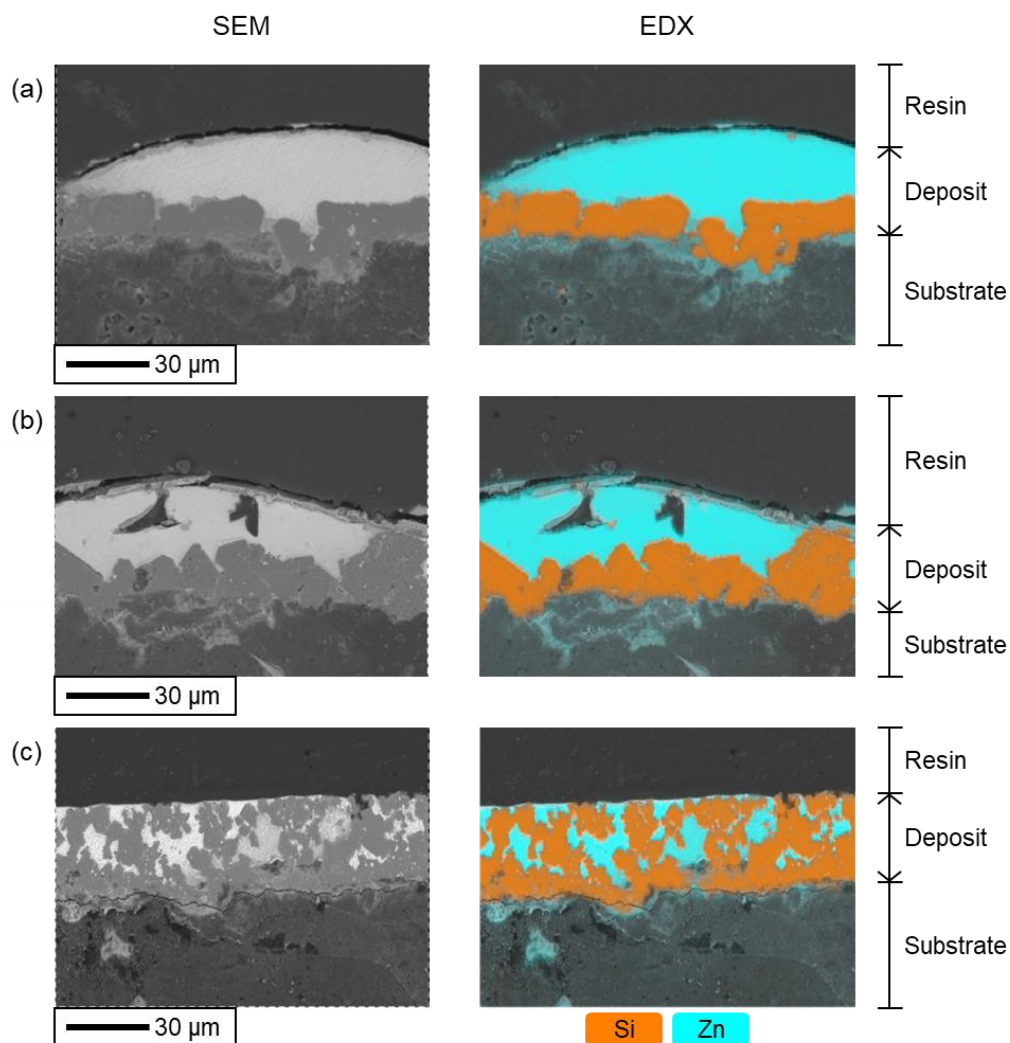


Fig. 5-6 Cross-sectional SEM and EDX mapping images of the samples obtained by galvanostatic electrolysis of graphite plate electrode for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)- ZnCl_2 (0.5 mol%) at 923 K. Current densities were (a) 100 mA cm^{-2} , (b) 150 mA cm^{-2} , and (c) 200 mA cm^{-2} . The SEM images represent BSE compositional images.

C cm^{-2} . At this ZnCl_2 concentration, Zn uniformly covered the entire surface of the deposit. Cross-sectional SEM and EDX mapping images of the samples after electrodeposition are shown in Fig. 5-7. At current densities of (a) 100 and (b) 150 mA cm^{-2} , the Si and Zn layers on the graphite substrate were observed in sequence from the substrate. At a current density of (c) 200 mA cm^{-2} , a Si layer was deposited on the substrate; however, several Si lumps were found in the Zn layer, likely representing cross-sectional observations of dendrite-like Si deposits. These results suggest that the appropriate current density at a ZnCl_2 concentration of 1.0 mol% was (a) 100 or (b) 150

mA cm^{-2} .

Third, electrodeposition was carried out on graphite substrates in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)- ZnCl_2 (2.0 mol%) at current densities in the range $200\text{--}300 \text{ mA cm}^{-2}$ and a charge density of 90 C cm^{-2} . At this ZnCl_2 concentration, the entire surface of the deposit was covered with Zn. Cross-sectional SEM and EDX mapping images of the samples after electrodeposition are shown in Fig. 5-8. At all values of current densities, the amount of Si relative to the overall thickness of the deposit was less than that for a ZnCl_2 concentration of 1.0 mol%. This result was

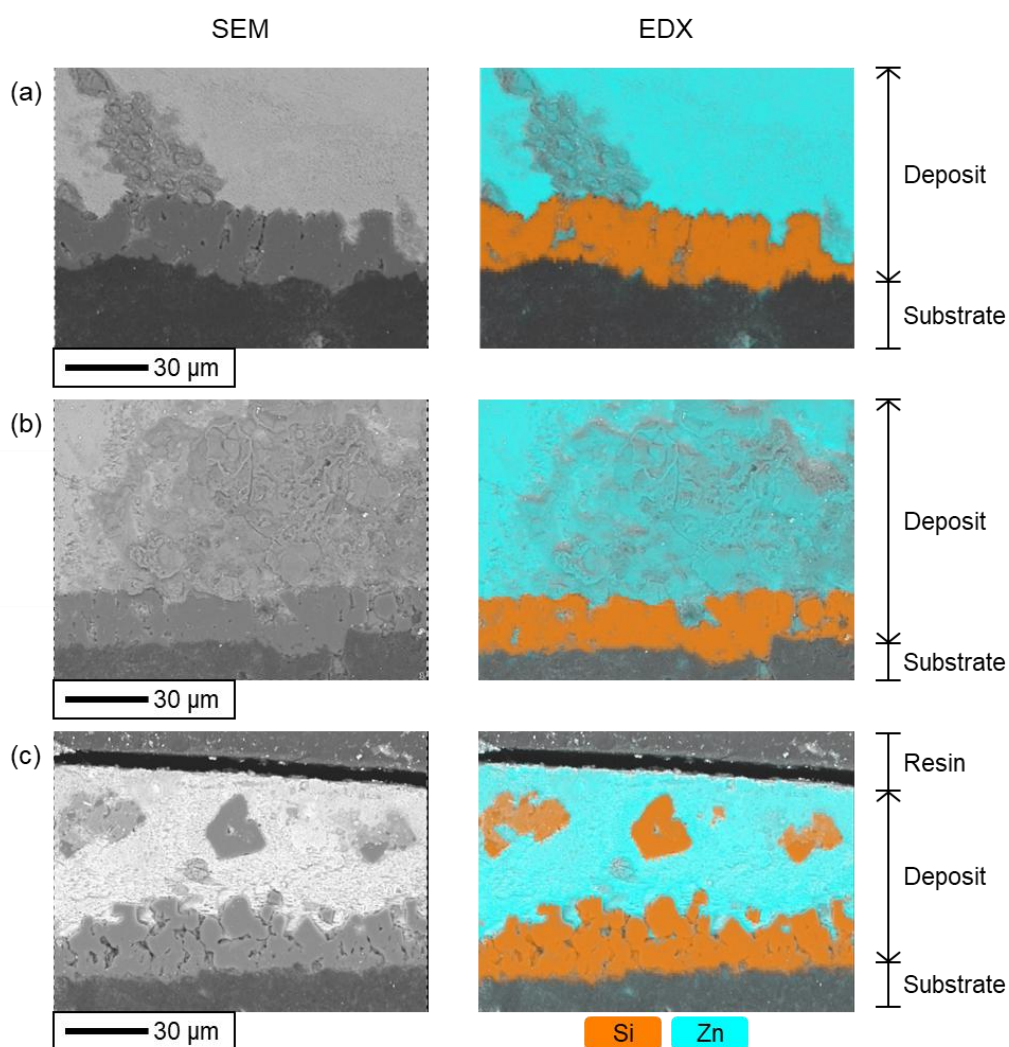


Fig. 5-7 Cross-sectional SEM and EDX mapping images of the samples obtained by galvanostatic electrolysis of graphite plate electrode for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)- ZnCl_2 (1.0 mol%) at 923 K. Current densities were (a) 100 mA cm^{-2} , (b) 150 mA cm^{-2} , and (c) 200 mA cm^{-2} . The SEM images represent BSE compositional images.

attributed to the larger amount of reduced Zn, and smaller amount of reduced Si compared to those obtained in the melt with 1.0 mol% of ZnCl_2 .

By comparing the cross-sectional morphology of the electrodeposits obtained in the above three melts, it is possible to clarify the relationship between the ZnCl_2 concentration and the morphology of electrodeposits. In the melt containing 0.5 mol% ZnCl_2 , Zn did not cover the entire surface of the electrode owing to the low concentration of Zn(II) ions present in the melt. Consequently, only a small amount of Zn was reduced compared to that required to cover the entire

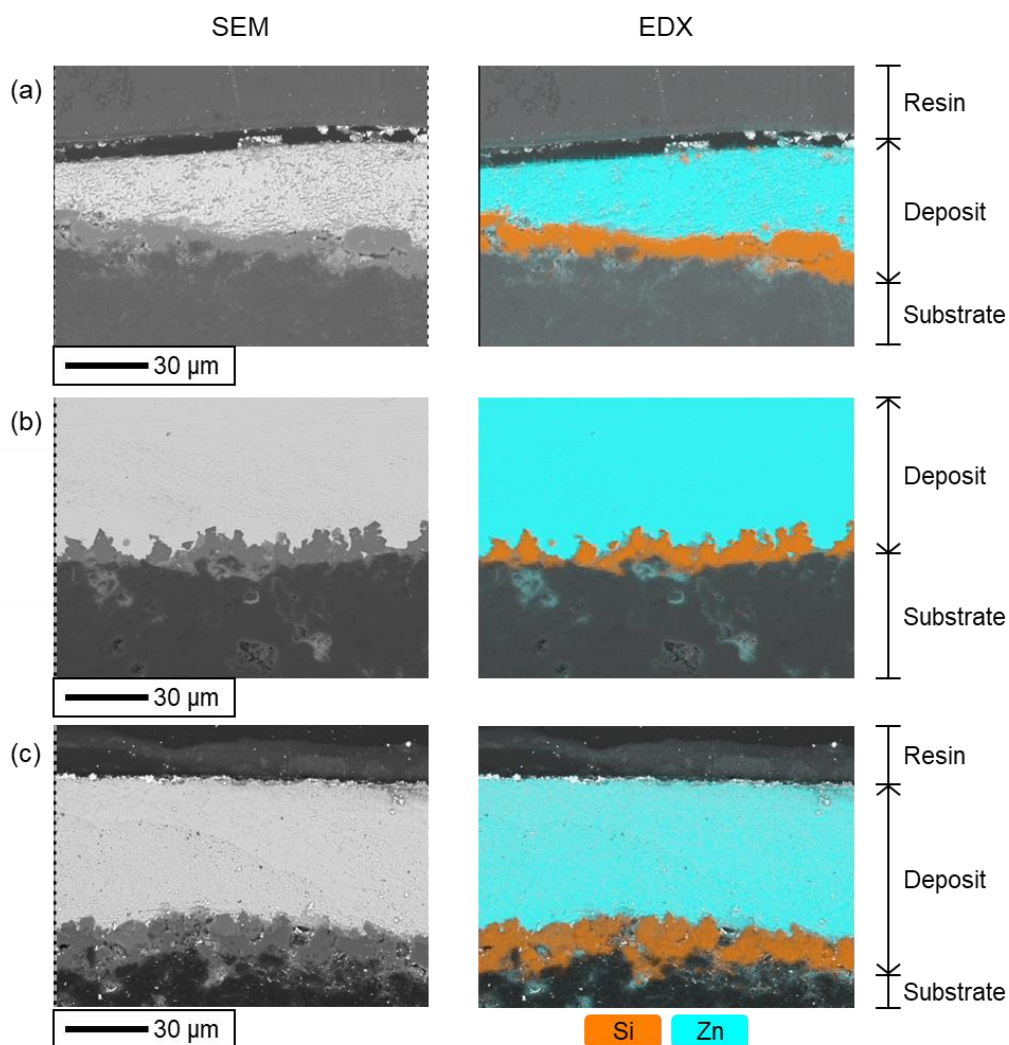


Fig. 5-8 Cross-sectional SEM and EDX mapping images of the samples obtained by galvanostatic electrolysis of graphite plate electrode for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%)- ZnCl_2 (2.0 mol%) at 923 K. Current densities were (a) 200 mA cm^{-2} , (b) 250 mA cm^{-2} , and (c) 300 mA cm^{-2} . The SEM images represent BSE compositional images.

electrode surface. In the melt containing 2.0 mol% ZnCl_2 , Zn covered the entire electrode surface. However, the amount of reduced Si was small, raising concerns regarding the decrease in the current efficiency of the target product of the Si film. The melt containing 1.0 mol% ZnCl_2 offered better conditions than the melt containing 0.5 mol% ZnCl_2 because Zn covered the entire substrate surface of the deposit. Furthermore, considering the current efficiency for the target Si film, this melt is superior to the melt containing 2.0 mol% ZnCl_2 . Based on the cross-sectional morphology results described above, electrolysis at a current density of 100 or 150 mA cm^{-2} in a melt with a ZnCl_2 concentration of 1.0 mol% is considered to be an optimal condition.

To investigate the optimal electrolysis conditions also from the surface morphology of the deposited Si, as shown in Fig. 5-9, the BSE topographic images were observed using SEM for the electrode surfaces after electrolysis and HCl treatment. In Figs. 5-9(a-3), (c-1), and (c-3), the crystal size of the electrodeposited Si is small, so the electrolysis conditions are unfavorable. In the samples obtained under electrolytic conditions excluding these three, crystals with a size of 20 μm or more were observed. These values were clearly larger than the 50 nm crystal size that was obtained in the previous study on Si electrodeposition at a solid Ag electrode in $\text{KF-KCl-K}_2\text{SiF}_6$ at 923 K [2]. The surface morphology with larger crystal sizes indicated Si deposition via the liquid Si-Zn alloy, as expected from chapter 2. The electrodeposits obtained under the aforementioned optimal conditions, shown in Figs. 5-9(b-1) and (b-2), which yielded a good cross-sectional morphology, also exhibit a good surface morphology because of their large grain sizes. The above observations of surface morphology also confirmed that the optimal electrolytic condition is a current density of 100–150 mA cm^{-2} in a melt with a ZnCl_2 concentration of 1.0 mol%.

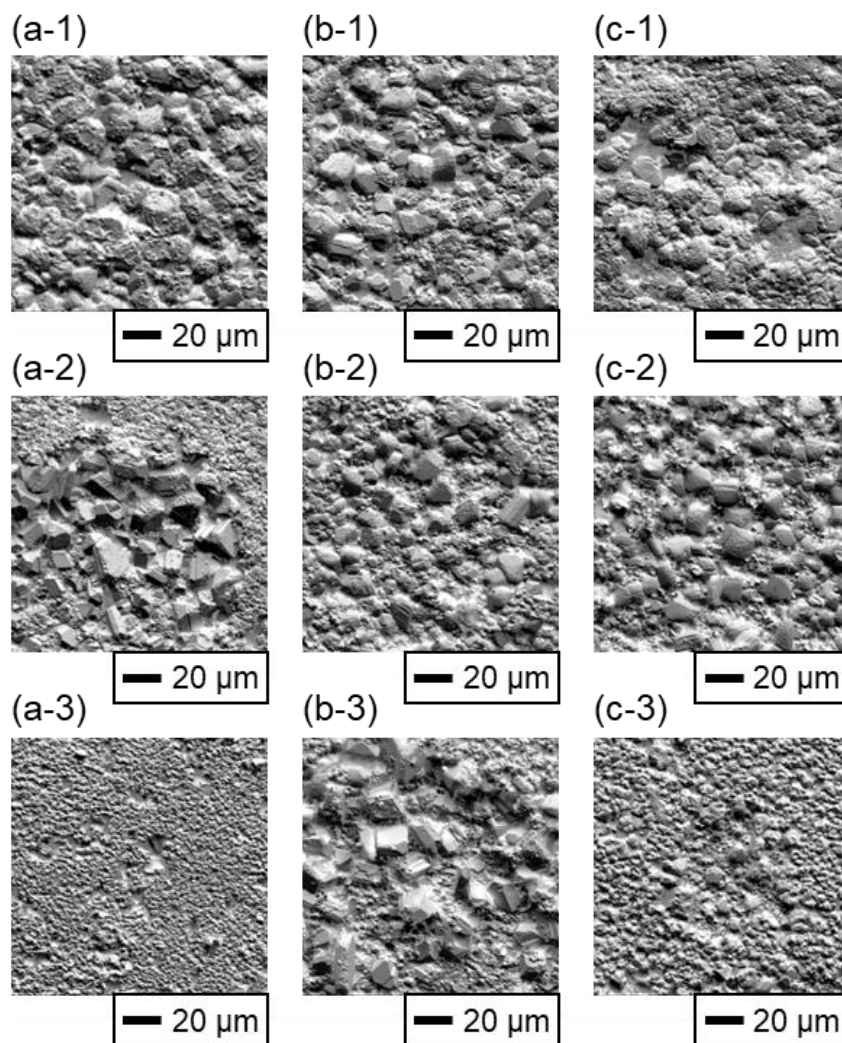


Fig. 5-9 Surface SEM images of samples obtained by galvanostatic electrolysis of a graphite plate electrode for 90 C cm^{-2} in molten $\text{KF-KCl-K}_2\text{SiF}_6\text{-ZnCl}_2$ at 923 K. K_2SiF_6 concentration was 2.0 mol%. ZnCl_2 concentrations were (a) 0.5, (b) 1.0, and (c) 2.0 mol%. (a) Current densities were (a-1) 100 mA cm^{-2} , (a-2) 150 mA cm^{-2} , and (a-3) 200 mA cm^{-2} . (b) Current densities were (b-1) 100 mA cm^{-2} , (b-2) 150 mA cm^{-2} , and (b-3) 200 mA cm^{-2} . (c) Current densities were (c-1) 200 mA cm^{-2} , (c-2) 250 mA cm^{-2} , and (c-3) 300 mA cm^{-2} . The SEM images represent BSE topographic images.

5.4 Conclusion

Co-deposition of Si and Zn resulted in the formation of highly crystalline Si films on graphite substrates in molten KF-KCl at 923 K. Cyclic voltammetry revealed the simultaneous reduction of Si(IV) and Zn(II) ions to form a liquid Si-Zn alloy. In the electrodeposits obtained by co-deposition, a Si layer was observed on the graphite substrate with a Zn layer on top. By varying

the concentration of ZnCl_2 and current density, an optimal condition for obtaining Si films was identified as a current density of 100–150 mA cm^{-2} in a melt with a ZnCl_2 concentration of 1.0 mol%. The Si films obtained through co-deposition exhibited larger crystal sizes than those obtained via electrodeposition without ZnCl_2 , confirming deposition via liquid Si–Zn alloying.

References

1. T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak, *Binary Alloy Phase Diagrams* (2nd ed.), ASM International, Materials Park, Ohio (1990), CD-ROM version 1.0.
2. K. Yasuda, K. Saeki, T. Kato, R. Hagiwara, and T. Nohira, *J. Electrochem. Soc.*, **165**, D825 (2018).

Chapter 6

General Conclusion

Electrodeposition of crystalline Si using liquid metal electrodes in a fluoride–chloride molten salt was investigated to establish a new manufacturing method of Si substrates for solar cells. Using liquid metal electrodes is expected to result in the formation of Si films with larger crystal grains than those reported previously using solid electrodes. The molten salt used was $\text{KF–KCl–K}_2\text{SiF}_6$, in which crystalline Si can be obtained on solid electrodes. As an initial step of the study, electrochemical studies were conducted using a liquid Zn electrode held in a BN crucible. Next, for comparison, electrochemical studies were conducted using a liquid Ga electrode in the same structure. Based on these findings, in order to obtain Si in a film form, Si electrodeposition was conducted using a thin film of liquid Zn as the electrode. Finally, as another method to obtain Si in a film form, co-deposition of Si and Zn was conducted. The results are summarized below.

In Chapter 2, electrochemical studies using a liquid Zn electrode were conducted in a $\text{KF–KCl–K}_2\text{SiF}_6$ molten salt at 923 K. The reaction of Si(IV) ions on a liquid Zn electrode was investigated using cyclic voltammetry. The potential at which liquid Si–Zn alloy was formed was more positive than that at which Si deposits on the solid substrate. In potentiostatic electrolysis, large Si crystals with a maximum size of approximately 2 mm were obtained in a liquid Zn electrode. In galvanic electrolysis with various amounts of charge, the proportion of Si with large crystal sizes became larger as the charge on the electrode increased. Compared to when solid electrodes were used, very large Si crystals were formed. A mechanism for Si deposition via liquid Si–Zn alloy was proposed, including continuous liquid Si–Zn alloy formation on the liquid Zn

electrode surface and solid Si deposition inside the liquid Zn electrode.

In Chapter 3, electrochemical studies were conducted using liquid Ga electrodes in a $\text{KF-KCl-K}_2\text{SiF}_6$ molten salt at 923 K. In cyclic voltammetry on a liquid Ga electrode, a liquid Si-Ga alloy was formed at a more positive potential than that of Si deposition on a solid substrate, as in the case of a liquid Zn electrode. As a result of potentiostatic electrolysis, Si with a maximum grain size of approximately 6 μm was deposited in the liquid Ga electrode. The mechanism of solid Si deposition was considered to be the same as that observed with liquid Zn electrodes. Electrodeposited Si obtained using Ga contained more grains with larger grain sizes than that obtained using Zn, as revealed by comparing the grain size distributions of both. The difference in crystal growth rates using Zn and Ga was studied, and the mass transport process was considered a primary cause. The diffusion coefficient of Si atoms in liquid Ga is estimated to be approximately three times that in liquid Zn.

In Chapter 4, thin liquid Zn was used as an electrode in a $\text{KF-KCl-K}_2\text{SiF}_6$ molten salt at 923 K. Zn films were deposited by electrolysis on a graphite substrate in molten KF-KCl-ZnCl_2 at 923 K or on a W substrate in a zinc sulfate aqueous solution at 313 K. However, due to differences in wettability with liquid Zn, liquid Zn could only be retained in a film form when W was used as the substrate. Si was electrodeposited in film form using the obtained thin-liquid Zn electrode in a $\text{KF-KCl-K}_2\text{SiF}_6$ melt at 923 K. SEM observation and XRD patterns after Zn removal confirmed a crystalline Si film with Si grains exceeding 20 μm across the entire surface. Moreover, current efficiency was as high as approximately 100%.

In Chapter 5, in order to deposit large grain size Si on a graphite substrate exhibiting poor wettability with liquid Zn, a method involving co-deposition of Si and Zn in a $\text{KF-KCl-K}_2\text{SiF}_6\text{-ZnCl}_2$ melt at 923 K was investigated. Cyclic voltammetry on a glassy carbon rod confirmed the reduction of Si(IV) and Zn(II) ions. The metallic luster of the electrodeposit and the cross section showing two layers of Si and Zn confirmed the formation of a liquid Si-Zn alloy in film form during electrolysis and the deposition of solid Si via the liquid alloy. The electrodeposit obtained

by co-deposition in a melt with 0.5 mol% ZnCl_2 contained little amount of deposited Zn, which did not cover the graphite substrate, resulting in large Si grains in limited areas. In contrast, the electrodeposit obtained in a melt with 2.0 mol% ZnCl_2 contained small amount of deposited Si although deposited Zn covered the substrate. The $\text{KF-KCl-K}_2\text{SiF}_6\text{-ZnCl}_2$ melt with a ZnCl_2 concentration of 1.0 mol% was confirmed to be suitable for the formation of Si films via co-deposition of Si and Zn. The obtained Si film exhibited larger grain size than that electrodeposited in a solution containing no ZnCl_2 , and solid Si deposition via a liquid alloy was confirmed even in the case of co-deposition. In addition, the current density for suppressing dendritic growth of Si, which occurs when the current density is high, was also found to be 100 or 150 mA cm^{-2} .

Based on the above results, Si electrodeposition using liquid metal electrodes in high-temperature molten salts can be summarized as follows. Due to the deposition via the formation of liquid alloys, Si with larger grain size is obtained compared to Si electrodeposition on a solid substrate. In addition, by using thin liquid Zn on a solid substrate as an electrode, it is possible to electrodeposit crystalline Si films with larger grain size on solid substrates. Using a method involving the co-deposition of Si and Zn, crystalline Si films with larger grain sizes can also be obtained on a solid substrate which exhibits poor wettability with liquid metals.

The findings of this study demonstrated the potential of the electrodeposition method as a new manufacturing method for crystalline Si substrates for solar cells. One of the challenges of the electrodeposition method for practical applications was the small size of the Si crystallites in the obtained film. However, this challenge is expected to be resolved by establishing a method using a liquid metal electrode in high-temperature molten salts. Notably, the findings obtained in this study are only a part of the overall process, and further research and development are necessary for practical application. One of the challenges is the design for a continuous process. Development of a method for continuously using liquid Zn and a method for removing Zn remaining on the Si film surface for reuse is needed.

The author expects that this process will be established industrially in the future, leading to

further cost reductions and widespread use of crystalline Si solar cells.

List of Publications

The main parts of this thesis are constructed from the following papers.

Chapter 2

1. Wataru Moteki, Yutaro Norikawa and Toshiyuki Nohira
“Electrodeposition of Crystalline Si Using a Liquid Zn Electrode in Molten KF–KCl–K₂SiF₆”
Journal of the Electrochemical Society, **170**, 062506 (2023).

Chapter 3

2. Wataru Moteki, Yutaro Norikawa and Toshiyuki Nohira
“Electrodeposition of Crystalline Si Using a Liquid Ga Electrode in Molten KF–KCl–K₂SiF₆”
Journal of the Electrochemical Society, **171**, 082501 (2024).

Chapter 4

3. Wataru Moteki, Yutaro Norikawa and Toshiyuki Nohira
“Electrochemical Formation of Highly Crystalline Si Film Using Thin Liquid Zn on Substrate in Molten KF–KCl–K₂SiF₆”
Journal of the Electrochemical Society, to be submitted.

Chapter 5

4. Wataru Moteki, Yutaro Norikawa and Toshiyuki Nohira
“Electrochemical Formation of Si Films by Co-deposition of Si and Zn in Molten KF–KCl–K₂SiF₆–ZnCl₂ Systems”
Electrochemistry, **93**, 027003 (2025).

Acknowledgement

First of all, the author gives his sincere gratitude to Professor Toshiyuki Nohira for his guidance, proper suggestions and fruitful discussions throughout this study, including the concrete advice in the laboratory.

Special thanks are given to Professor Kazuhiko Matsumoto for his rewarding discussions and valuable suggestions. The author also wishes to thank Professor Takashi Sagawa for fruitful discussion.

The author expresses his appreciation to Assistant Professor Yutaro Norikawa for support for experiments, deep discussions and valuable advice not only for the research but for the writing skills. Special acknowledgement is due to Junior Associate Professor Takayuki Yamamoto for his useful advice and continuous encouragement throughout this study. Also, the author would like to thank Dr. Kenji Kawaguchi at Nippon Steel Corporation for his helpful discussions, valuable advice on experiments, and continuous encouragement for this study. Special thanks are extended to Mr. Junichi Imaru for his technical support especially for constructing experimental systems.

The author would like to thank all the members of Nohira laboratory for their daily discussions, warm encouragements, and having a chance for friendly competition. Special thanks are due to Mr. Takashi Yoshida, Mr. Yuki Sugie, and Mr. Koki Manabe for their help in experiments and lively discussions. Also, the special thanks are for Ms. Hiromi Takatori, Ms. Naoko Sakamoto, and Ms. Atsuko Watabe for their help in administrative works and daily encouragement.

The author would like to thank all researchers and students for the technical discussions in the conferences, official and unofficial meetings, and the events in the Institute of Advanced Energy and in the Graduate School of Energy Science in Kyoto University. The author expresses his acknowledgment for the discussion with members of the joint research partner, Kobe Steel, Ltd. The author would like to appreciate the financial support from the JSPS and JST.

The author expresses the appreciation to all people involving his research and the chance

to learn a scientific research.

Finally, the author gratefully acknowledges the author's parents for their continual encouragement and kindheartedness.

September 2025

Wataru Moteki