Electrochemical Reduction of SiO₂ Granules to One-Dimensional Si Rods Using Ag-Si Eutectic Alloy

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ABSTRACT

Producing solar grade silicon using an inexpensive method is a key factor in lowering silicon solar cell costs; the direct electrochemical reduction of SiO₂ in molten salt is one of the more promising candidates for manufacturing this silicon. In this study, SiO₂ granules were electrochemically reduced in molten CaCl₂ (850°C) using Ag-Si eutectic droplets that catalyze electrochemical reduction and purify the Si product. When Ag is used as the working electrode, the Ag-Si eutectic mixture is formed naturally during SiO₂ reduction. However, since the Ag-Si eutectic droplets are liquid at 850°C, they are easily lost during the reduction process. To minimize the loss of liquid Ag-Si eutectic droplets, a cylindrical graphite container working electrode was introduced and Ag was added separately to the working electrode along with the SiO₂ granules. The graphite container working electrode successfully prevented the loss of the Ag-Si eutectic droplets during reduction. As a result, the Ag-Si eutectic droplets acted as stable catalysts for the electrochemical reduction of SiO₂, thereby producing one-dimensional Si rods through a mechanism similar to that of vapor-liquid-solid growth.

Keywords : SiO₂, Electrochemical Reduction, Ag-Si Eutectic, Molten Salt, CaCl₂

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Introduction

In recent years, renewable energy sources, such as sunlight, wind, and flowing water, have attracted considerable attention as alternatives to non-renewable fossil fuels that cause environmental pollution. Among these, solar energy is the most ubiquitous energy source. Photovoltaic (PV) cells that convert solar energy into electricity are made using various materials, such as Si, GaAs, CdTe, and perovskites [1-6]. Crystalline Si-based PV cells are the most widely used and account for more than 90% of the commercial PV cell market due to their high stability, conversion efficiency, and economic feasibility [1]. Though extensive research has been conducted on further increasing the cost efficiency, the cost of solar power generation is still 2–3 times more expensive than that of conventional thermal power generation

using fossil fuels, hindering the widespread use of solar energy [7]. The high cost of solar power generation is mainly attributed to the high manufacturing cost of Si-based PV cells, with 30–40% of the cost coming from the production and processing of solar grade Si [8]. Therefore, to lower the cost of solar power generation, it is necessary to develop an inexpensive production process for solar grade Si.

The electrochemical reduction of bulk SiO₂ to Si is considered one possible production alternative. Nohira et al. first reported that bulk SiO₂ was electrochemically reduced to Si in molten CaCl₂ at 850°C [9]. The electrochemical reduction of SiO₂ starts from the three-phase interface, where the insulating material (SiO₂), conductor (electrode), and electrolyte (molten CaCl₂) meet, and propagates as the three-phase interface spreads due to the formation of Si, which is conductive at 850°C.

However, the complete reduction of bulk SiO₂ has always been difficult because the propagation of a

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three-phase interface into the bulk SiO_2 is not facile. It is difficult for the electrolyte to infiltrate into the bulk material, even though the oxygen extraction from SiO_2 during the electrochemical reduction results in porous Si [10,11]. The trapping of oxygen ions (O^{2-}), which are the product of the electrochemical reduction of SiO_2 , in the porous Si structures also hinders the complete reduction of the bulk SiO_2 [12,13].

Therefore, to promote the electrochemical reduction of SiO_2 , the formation of the three-phase interface must be encouraged. Recently, studies have been conducted on the electrodeposition of a polycrystalline silicon thin film in molten CaCl_2 at 850°C using SiO_2 nanoparticles [14,15]. SiO_2 nanoparticles are not soluble; however, they are small enough to be dispersed in molten CaCl_2 . The dispersed SiO_2 nanoparticles are transported by convection and collide with the cathode, resulting in Reaction (1). The small size of the SiO_2 nanoparticles facilitates the formation of a three-phase interface and the diffusion of oxygen ions, allowing for a complete reduction of the SiO_2 nanoparticles. The use of Ag as a cathode material has also been reported to enhance the electrochemical reduction of the SiO_2 nanoparticles [16,17]. During the reduction at 850°C , the deposited Si and Ag form liquid droplets of the Ag-Si eutectic mixture that catalyzes the electrochemical reduction of SiO_2 and purifies Si. The Si formation mechanism with Ag-Si eutectic droplets was similar to the vapor-liquid-solid (VLS) growth mechanism involving supersaturation and nucleation at the liquid/solid interface [18,19]. However, the loss of the Ag-Si eutectic droplets and Si at the Ag electrode is significant because the unstable interface between the Ag electrode and Si is formed by the liquid Ag-Si eutectic mixture. At the interface, Si and the Ag-Si eutectic droplets constantly fall off the Ag electrode surface during the electrochemical reduction [16]. This results in the formation of irregular Si dendrites.

In this study, a cylindrical graphite container working electrode was introduced to minimize the loss of the Ag-Si eutectic mixture and Si. The use of this working electrode effectively prevented the loss of the liquid Ag-Si eutectic mixture, and as a result, one-dimensional Si rods could be formed. Furthermore, we conducted a fundamental investigation into the effect of the electrochemical parameters on the electrochemical reduction of SiO_2 and proposed an Si growth mechanism based on it.

2. Experimental

Fig. 1 shows the schematic of the electrochemical cell used in this study. The cell consisted of inner and outer quartz tubes with a sealed bottom. The top of the cell was sealed with a stainless-steel cap, and during the experiment Ar gas (99.9%) was continuously injected into the cell to block the influx of oxygen and moisture. The electrochemical measurements were performed using a potentiostat (PGSTAT302N, Metrohm) with a 3-electrode configuration. The working electrode (WE) was a cylindrical graphite container capable of accommodating SiO_2 granules (0.5–10 μm in size, Sigma-Aldrich) and Ag (0.05 mm-thick foil, 99.9%, Alfa Aesar). The counter electrode (CE) was a graphite rod (6.15 mm in diameter, 99.99%, Alfa Aesar). The graphite rod was also used as the pseudo-reference electrode (RE). W wires (1.0 mm in diameter, 99.95%, Alfa Aesar) were used for the electrode contacts. The electrolyte, CaCl_2 molten salt, was placed in an alumina crucible. To prepare the electrolyte, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Daejung Chem-

Fig. 1. Schematic diagram of the electrochemical cell used in this study.

ical and Metals) was dried at 200°C in vacuum overnight. Thereafter, 50 g of the dried CaCl_2 was placed in an alumina crucible, which was then loaded into the electrochemical cell. The temperature of the electrochemical cell was raised to 400°C at a rate of 6°C min^{-1} and maintained for 3 h to remove residual water from the dried CaCl_2 . Subsequently, the cell temperature was further increased to 850°C at a rate of 6°C min^{-1} . The graphite container holding the SiO_2 granules and Ag foil was then inserted into the electrochemical cell. The weight of the SiO_2 granules was 0.1 g, and the quantity of Ag foil was added at an SiO_2 to Ag weight ratio of 1:1, except for cases where Ag was excluded. The Ag foil was wrapped around the inner wall of the graphite container, touching the working electrode, as shown in Fig. 1. The electrochemical reduction of SiO_2 was performed by applying various different potentials to the working electrode. After reduction, the Si samples were sequentially immersed in deionized water for 24 h, followed by submersion in an aqueous solution of 0.1 M HCl for 14 h to remove the CaCl_2 and other byproducts such as CaSiO_3 and CaO . The sample was then dried in a vacuum oven at 50°C for 12 h. For the cyclic voltammetry (CV) measurements, a graphite rod and molten CaCl_2 containing 1 wt% SiO_2 nanoparticles (10–20 nm in size, Sigma-Aldrich) were used as the working electrode and electrolyte, respectively. The potential was scanned from 0 to -2.0 V (vs. C) at a scan rate of 0.1 V s^{-1} .

The shape and composition of the Si sample after the electrochemical reduction of SiO_2 was observed using a field emission secondary electron microscope (FE-SEM; GeminiSEM 300, Zeiss) equipped with an energy dispersive spectrometer (EDS; XFlash 6130, Bruker). The crystalline structure of the Si sample was also examined using an X-ray diffractometer (XRD; D2 Phaser, Bruker).

3. Results and Discussion

Fig. 2 shows the CV curve of a graphite electrode in the molten CaCl_2 containing SiO_2 nanoparticles. The cathodic peak observed at -1.25 V was associated with the reduction of SiO_2 nanoparticles in contact with the graphite working electrode. The increase in the reduction current at potentials more negative than -1.5 V indicated the formation of a Ca-Si alloy and/or the reduction of Ca ions. The anodic

Fig. 2. CV curve of the graphite electrode in the molten CaCl_2 containing 1 wt% SiO_2 . The scan rate was 0.1 V s^{-1} .

peak observed at -1.6 V was related to the oxidation of metallic Ca. It was also observed that the Si, electrodeposited on the graphite electrode during the forward scan, was electrochemically oxidized at -1.0 V, indicating that the SiO_2 nanoparticles in the molten CaCl_2 were directly reduced to Si. This result was consistent with previous reports [14, 15].

Fig. 3 shows FE-SEM images of the Si samples after the electrochemical reduction of SiO_2 with Ag at different applied potentials when a cylindrical graphite container was used as the working electrode. Since the electrochemical reduction of SiO_2 mainly occurred in the potential range between -1.0 and -1.3 V (Fig. 2), the applied potential was set within this range. In Fig. 3a–c, when the applied potentials were more positive than -1.2 V, Si rods were found after the reduction. It was also observed that as the reduction potential decreased, the thickness of the Si rods decreased and the number density increased. However, the formation of Si rods was hardly observed at -1.2 V (Fig. 3d). Fig. 3e shows the FE-SEM image of the Si sample after the electrochemical reduction of SiO_2 without Ag. In this case, particulate Si was obtained in a form similar to the pristine SiO_2 granules shown in Fig. 3f. These results indicated that Ag induced Si to grow into a rod-like shape during the electrochemical reduction of SiO_2 . In addition, most of the formed Si exhibited a one-dimensional structure, which was different from the previous reports on the formation of dendritic Si via an Ag-Si eutectic mixture [16,20]. In the course of the electrochemical reduction of SiO_2 , the Ag reacted

Fig. 3. FE-SEM images of Si samples after electrochemical reduction of SiO_2 granules with Ag for 3 h at (a) -1.0, (b) -1.1, (c) -1.15, and (d) -1.2 V; (e) the Si sample after electrochemical reduction of SiO_2 without Ag at -1.15 V and (f) the pristine SiO_2 granules. The weight ratio of Ag to SiO_2 was 1:1 for Fig. 3a–d.

with the reduced Si to form an Ag-Si eutectic mixture. The eutectic mixture was in a liquid state in the molten CaCl_2 bath (850°C) because the melting point of the Ag-Si eutectic mixture was 835°C [21]. It is supposed that the liquid eutectic mixture existed as droplets and that these droplets acted as the catalytic liquid alloy for the SiO_2 reduction. During the continuous electrochemical reduction, Si nucleated and grew via these droplets to form rod-shaped Si, which followed a mechanism similar to the VLS growth [18,19]. If the loss and formation of Ag-Si eutectic droplets was repeated during this process, randomly oriented Ag dendrites may have been formed. Therefore, it was concluded that the use of a graphite container as the working electrode effectively prevented the loss of the Ag-Si eutectic mixture during the elec-

trochemical reduction of SiO_2 . A decrease in the thickness of the Si rod and an increase in the number density due to a decrease in the reduction potential might be related to the Si nucleation. The high overpotential for the SiO_2 reduction would have induced the formation of high-density Si nuclei, resulting in thinner Si rods in greater quantities. However, as shown in Fig. 3d, when the applied potential was more negative than -1.2 V, the formation of Si rods was rarely observed because side reactions, such as Ca ion reduction and Ca-Si alloy formation, were dominant.

Fig. 4a shows EDS elemental mapping results of the Si sample after the electrochemical reduction of SiO_2 with Ag at -1.15 V. After the reduction, Si rods were clearly observed. The rods in the FE-SEM

Fig. 4. FE-SEM and EDS elemental mapping images of Si samples after the electrochemical reduction of SiO_2 (a) with and (b) without Ag. The electrochemical reduction was performed at -1.15 V for 3 h and the weight ratio of Ag to SiO_2 was 1:1 for Fig. 4a. The light cyan color in the elemental map of Fig. 4a represents Ag.

image exactly matched the rod shape shown in the Si elemental mapping (red). However, no rod shapes were observed in the O elemental mapping (blue), indicating that the rod was mainly composed of Si. There were also unreduced SiO_2 granules, which were identified from the places where the elemental maps of Si and O matched. Ag-Si eutectic droplets were also observed, as shown in the overlap between the elemental mapping of Ag (cyan) and Si. The Si sample after the electrochemical reduction of SiO_2 without Ag is shown in Fig. 4b. The reduced Si particles were mixed with unreduced SiO_2 granules, and the two could not be distinguished in the Si and O elemental maps.

The growth of the Si rods was monitored over the reduction period. Fig. 5a shows FE-SEM images of the Si rods after different periods of electrochemical reduction. After 30 min of reduction, only a small quantity of Si rods was observed, and the rest of the Si was mostly in the form of SiO_2 granules. During this period, Ag-Si eutectic formation prevailed over Si rod formation. The number density of Si rods was then increased dramatically with reduction time: the number densities of Si rods were $2.1 \times 10^2 \text{ cm}^{-2}$, $3.3 \times 10^3 \text{ cm}^{-2}$, and $1.0 \times 10^7 \text{ cm}^{-2}$ after 1 h, 2 h, and 3 h of

reduction, respectively. As the reduction time increased, smaller, thinner Si rods were formed, which were newly nucleated and grew on new Ag-Si eutectic droplets that formed during the reduction process. Fig. 5b shows the current-time curves obtained during the electrochemical reduction of SiO_2 at -1.15 V. The reduction current increased by more than two times when Ag was added. In general, SiO_2 reduction begins at the three-phase interface where the SiO_2 granules, molten CaCl_2 , and conductors are in contact, and the reduction propagates along with the newly formed three-phase interface due to the formation of conductive Si [22]. Therefore, the reduction current is highly dependent on the formation of a three-phase interface. In the absence of Ag, the formation of a three-phase interface within an SiO_2 granule was limited as electrochemical reduction progressed. However, in the presence of Ag, droplets of the conductive Ag-Si eutectic mixture naturally formed during the reduction, which enlarged the three-phase interface. The expansion of the three-phase interface by the Ag-Si eutectic mixture increased the reduction current. The observation of the Si rod growth also corresponded with the current-time curve obtained during the electrochemical

reduction of SiO_2 with Ag. The reduction current steadily decreased with the reduction time up to

approximately 2,500 s. It is supposed that during this time period, the formation of the Ag-Si eutectic mixture dominated. Subsequently, as the number of Si rods increased rapidly, the three-phase interface became large and the reduction current increased again after 2,500 s.

Fig. 6 shows XRD patterns of Si samples after the electrochemical reduction of SiO_2 with Ag. The crystalline peaks of Si located at 28.4° , 47.2° , 56.1° , 69.0° , and 76.3° , which correspond to Si(111), Si(220), Si(311), Si(400), and Si(331), respectively, were observed after the electrochemical reduction. The peak intensity of these peaks increased with the reduction time, while the peaks associated with SiO_2

Fig. 5. (a) FE-SEM images of Si samples depending on the electrochemical reduction time of SiO_2 with Ag at -1.15 V and (b) current-time curves recorded during electrochemical reduction of SiO_2 at -1.15 V for 3 h. The weight ratio of Ag to SiO_2 was 1:1 for the electrochemical reduction of SiO_2 with Ag.

Fig. 6. XRD patterns of Si samples after the electrochemical reduction of SiO_2 with Ag at -1.15 V. The weight ratio of Ag to SiO_2 was 1:1.

Fig. 7. The schematic diagram of the estimated Si rod growth mechanism.

decreased, indicating that SiO_2 was reduced to Si. In addition, we assumed that the formation of Si nuclei with random orientations on the Ag-Si eutectic droplets during the reduction resulted in polycrystalline Si rods.

Fig. 7 illustrates the estimated mechanism of Si rod growth during the electrochemical reduction of SiO_2 with Ag. Once the reduction started, SiO_2 was reduced to Si at the three-phase interface where Ag, SiO_2 , and molten CaCl_2 met. The Si then reacted with Ag to form an Ag-Si eutectic droplet. Upon continuous reduction, the Si became supersaturated in the Ag-Si eutectic droplets, then nucleated and grew into a rod-like shape, following a growth path similar to the VLS mechanism. During reduction, Ag-Si eutectic droplet formation, Si nucleation, and Si rod growth occurred simultaneously to form Si rods of various thicknesses and lengths.

4. Conclusions

The electrochemical reduction of SiO_2 with Ag was performed in molten CaCl_2 using a cylindrical graphite container as the working electrode. The graphite container working electrode effectively prevented the loss of the Ag-Si eutectic mixture during the electrochemical reduction, thereby expanding the three-phase interface, which increased the reduction current. Moreover, since the Ag-Si eutectic droplets were relatively well-preserved, they successfully acted as catalysts for the formation of one-dimensional Si rods.

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