Review Article

High purity silicon materials prepared through wet-chemical and electrochemical approaches

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Abstract

A new approach to produce high purity solar grade silicon (SOG-Si) using wet-chemical and electrochemical processes was proposed. First, diatomaceous earth was used as a source of silica and wet-chemical purification by acid leaching and solvent extraction processes were applied for eliminating heavy metal and light element such as boron, respectively. In particular, the solvent extraction using channel flow reactor demonstrated extremely high efficiency for eliminating boron to 7N (99.99999%) level purity. Secondly, the high-purity silica was reduced to silicon by the direct electrolysis method using molten CaCl_2 as an electrolyte and Si plate as cathode. We proposed the continuous electrolysis system by feeding silica granules to the Si cathode set at the bottom of the cell. It was confirmed that the reduction proceeded steadily to form crystalline Si with a sufficient reduction rate. We also attempted electrodeposition of Si films and have developed a process using $\text{KF} \cdot \text{KCl} + \text{K}_2\text{SiF}_6$ molten salt, from which uniform layer of Si with a thickness larger than 100 μm could be formed.

1. Introduction

Si is a key material for various applications such as semiconductor and photonic devices, solar cells, MEMS and related functional micro/nano devices and systems, etc. In particular, solar cell industry needs enormous amount of high-purity Si at lower cost and continuously increasing needs for renewable energy have been further pushing upward this demand, for Si is main material for solar cells, especially for large-scale power generation[1-3]. For the application of Si material to solar cells, purity with 6N (99.9999%) or higher level is required, which is so-called solar grade Si (SOG-Si). Significant issues for producing SOG-Si are (i) supply of high-purity source of Si, which naturally obtained as oxide (silica), (ii) reduction process of silica to Si, (iii) purification, and (iv) formation of cell structure.

Figure 1 illustrates conventional processes to produce SOG-Si. Major processes to produce SOG-Si are based on Siemens process, which use carbothermic reduction process, and distillation of chlorosilane species to achieve sufficient purity. The process has been originally developed for production of semiconductor-grade Si (SG-Si) which requires 11N level purity, and the “off-grade” products have been used as SOG-Si. While numbers of processes have been proposed to produce SOG-Si with less expensive approaches, they are basically based on high-temperature, vapor phase processes [4], and energy cost and throughput have been the issues to be improved, together with the additional costs to machine bulk Si ingots, such as slicing and polishing, to form cell structure. In addition, these processes need high-purity silica ore, so called “white-silica,” for starting material. However, the ore distributes unevenly in the earth crust and is said that the world-wide reserves might not be sufficient to fulfill the increasing demands.

In order to explore an alternative way to solve these issues, we have investigated a new approach to produce SOG-Si material using wet-chemical purification and direct

electrochemical reduction processes by designing and optimizing their interfacial reactions, as is shown in Fig. 2. For this process, we focus upon diatomaceous earth as source of high purity Si, and we also attempt to develop electrodeposition process to form Si layers which are applicable for the cells. In this paper we describe our attempts on developing these processes, mainly focusing upon our recent results.

2. Purification process of silica using wet-chemical process - solvent extraction using channel-flow type reactor -

As mentioned above, we apply diatomaceous earth as a source of Si. Diatomaceous earth is composed of shells of diatom which is amorphous silica. Since it is Earth-abundant material and can be obtained from open pit mining [5, 6], it could be a good candidate for the source of SOG-Si. Moreover, as shown in Fig. 3, it basically has porous structure so that it can be easily dissolved into aqueous alkaline solution, which enables low-temperature, liquid phase process for purification. We have proposed a procedure to purify silica obtained from diatomaceous earth using wet chemical treatment [6]. For this, first the silica was dissolved into aqueous alkaline solution at pH 12.0, and by controlling pH to 10.5, heavy-metal impurities can be removed as precipitates; for example, the amount of Al and Fe could be decreased to be 2.6 ppm and 4.3 ppm, respectively, from the starting silica material containing these species with the amount of 10^4 ppm level [6]. However, light-element impurities such as B remained in the solution at this pH. Thus solvent extraction is applied to remove these light elements.

Solvent extraction has been widely employed for the separation of metals such as Cu, Ni, Co, and rare earth elements, as well as in the field of nuclear fuel technology like actinide recovery and purification, radionuclide production [7-9]. It is basically composed to mixing for extraction, settling and stripping procedure in each stage. Smaller separation efficiency is industrially

compensated by designing multiple series operations with numbers of stages. Important aspects for practical application are how to design an appropriate extraction molecule structure with higher separation efficiency and how to decrease the amount of solvent loss in each stage.

In order to reduce the light element concentration in refined diatomaceous earth, we employed 2-Ethyl-1,3-hexanediol (EHD) with toluene as extractant solvent [6]. The proposed reaction is as follows;

The preliminary experiment with separation funnel clearly demonstrated that the strategy was promising. In order to further improve the removal efficiency of the solvent extraction process, we attempted to apply channel-flow reactors, which are expected to have very high efficiency [10,11].

Figures 4 and 5 show overall process for the purification of silica and schematic image of the reactor we applied for the initial investigation [12, 13], which is Y-shaped flow reactor made of micromachined Si wafer and glass-sealing with 10mm-long and 100 μm -wide single channel. Toluene solution containing 0.5 mol L^{-1} of EHD and aqueous solution with dissolved silica were introduced to the inlets (1) and (2), respectively, and by adjusting their flow rates, stable liquid-liquid interface was formed as is shown in Fig. 6. In this figure, flow rate was 100 $\mu\text{L min}^{-1}$ and the reaction duration was estimated to be 30 msec, and under this condition, it turned out that high efficiency for B extraction could be obtained as is listed in Table 1 [13]; the initial contents of some 5 ppm of B has been decreased to be 0.5 ppm, and the elimination ratio is 90 %. This performance is almost equal to that obtained by using separatory funnel for 120 min (2 stages for 60 min treatment), showing the high potential of this process for effective

purification of silica.

In order to further improve the extraction performance, application of multi-stage extraction should be effective. Thus we designed the channel-flow reactor with two stages. At the same time, it is significant to increase the yield of purified silica so that scaling-up of the reactor is necessary. However, it is difficult to scaling up the reactor shown in Fig. 5, since stability of the liquid-liquid interface could not be maintained for larger scale channel. In order to solve this problem, we attempted to form the liquid-liquid interface in horizontal plane, and following these concepts, we developed a channel-flow reactor with two stages, as is shown in Fig. 7. Horizontally designed liquid-liquid interface enables widening, i.e., scaling up of the channel, so it is expected that this type of reactor could achieve larger volume production. We fabricated this reactor using the same procedure described above and examined its performance. The silica solution is fed to inlet (1), and the 0.5 mol L⁻¹ EHD/toluene solution is introduced to the inlets (2) and (4) to perform two-stage extraction. In order to keep steady flow, toluene is introduced to inlet (3). We changed flow rate of the solutions and examined the elimination behavior of B for optimized operational condition. Table 2 shows representative results, and as is seen in this table, it turned out that the content of B can be decreased down to 0.07 ppm, indicating that the 7N-level purity could be achieved by using this process.

As described, purification of silica, especially for the light elements, can be achieved by using channel-flow reactor, and for the next step, we are continuing to further optimize the reactor design with wider and longer channels, as well as attempt to find better extractant species with higher performance [14]. We also attempted to improve the acid-leaching process, which is a "pre-treatment" before the solvent extraction using the channel-flow reactor to eliminate the light elements, focusing upon the formation behavior of the silica precipitation. It was found that by controlling the parameters

such as concentration of silica in the solution, mean diameter of precipitated silica was changed, which affected not only the elimination behavior of heavy metal impurities but also those of light elements such as B, as shown in Table 3. Thus detailed analysis and optimization of the acid leaching process should be necessary to achieve further higher purity.

3.Direct reduction of silica to silicon using molten-salt electrolysis

The conventional method to produce silicon from silica is carbothermal reduction which was developed for the production of metallurgical-grade silicon (MG-Si, 2N). The carbothermal reduction is not suitable for the production of SOG-Si from high purity silica because many impurities including B and P are mixed. Thus, a new contamination free method of silica reduction has been long required. From this background, we proposed a process using molten salt electrolysis with a contacting electrode method for direct reduction of SiO₂ to crystalline Si in CaCl₂-based electrolyte, and demonstrated its effectiveness to a quartz plate [15,16] as well as powder molded silica pellets [17]. In this process, SiO₂ is directly reduced at the three-phase interface of SiO₂-CaCl₂ electrolyte- electrode as follows;

Therefore, if the electrode material is Si, contamination free reduction of silica to Si can be achieved in principle [18, 19]. However, there was a problem of low productivity for such early-stage study because batch type electrolysis was used. Considering this problem, we attempted to develop a process which can produce high-purity Si from silica continuously [20].

Figure 8 illustrates a schematic image of the reactor for our process. Silica powder is

fed from the top of the cell and is reduced at the surface of cathode, which is set at the bottom of the cell to obtain high-purity Si. While the produced Si should be continuously removed from the reactor for the practical process, first we focused upon the reaction behavior of silica powder fed to the cathode [20, 21].

Figure 9 shows a cross-sectional image of the cell after the electrolysis in molten CaCl_2 at 1123 K. We confirmed that the electrolysis proceeded steadily up to several tens of hours to form Si. After washing in 1 M hydrochloric acid and distilled water to remove the CaCl_2 electrolyte, Si powder was obtained, as is shown in Fig. 10(a). Furthermore, the obtained Si powder was successfully transformed to a crystalline Si ingot by floating zone melting, as is shown in Fig. 10(b).

In order to evaluate potential throughput of the process, we investigated the kinetic characteristics of the reduction process [22, 23]. For this purpose, we used a small electrode consisted of a graphite crucible and an alumina tube [22] because it is convenient to conduct many experiments varying parameters, e.g. diameter of SiO_2 granules, electrolysis potential and time. From the cross-sectional observation of the electrodes, it was shown that the reaction proceeded continuously from the surface of the SiO_2 granules to the inside of the granules. It was also found that the smaller diameter of SiO_2 granules is favorable to proceed the reaction effectively [22]. The time dependence of the reduction rate was investigated by measuring the weight change of the samples. Since the formula weight decreases from SiO_2 to Si, the amount of electrochemically reduced SiO_2 can be calculated from the weight change. Moreover, the average reduction rate can be estimated by dividing by the electrolysis time, which in turn, can be converted into the **effective** current density.

Figure 11 shows the average reduction rate and the corresponding **effective** current density for the electrolysis at 0.5 V vs. Ca^{2+}/Ca in molten CaCl_2 at 1123 K. The current density is as large as 0.7 A cm^{-2} for the initial 20 min, and gradually decreases

afterwards. This value is almost equal to the current density of the commercial Hall-Héroult process for aluminum production [24]. This result indicates that the direct electrochemical reduction of SiO_2 in molten CaCl_2 has the potential of being a high-throughput silicon production process.

4. Electrodeposition of Si films in molten salts and ionic liquids

As described, purification of silica and its reduction process to Si has been developed, from which bulk crystal of Si could be obtained. On the other hand, fabrication of Si solar cell from bulk crystal requires additional processes for machining, such as cutting and slicing, which require additional cost, and the kerf loss has been a significant issue to be solved in order to decrease overall cost of the production. Besides these issues, minimization of the Si usage has been highly needed with increasing demand for Si solar cells. Given this need, application of Si thin film has been proposed and various processes have been developed. However, almost all of them were based upon dry process such as chemical vapor deposition, and they have some difficulties for large scale, mass production. As an alternative approach, formation of Si thin films using electrochemical deposition process has been attempted, and several processes have been proposed. Since aqueous solution could not be applied to this process, organic solvents [25], molten salts [26], as well as ionic liquids [27] have been applied. Although it was difficult to obtain compact layers for most of these studies, we have achieved to form thick and uniform layers by molten salt electrolysis using KF-KCl plus K_2SiF_6 as an electrolyte [28].

Figure 12(a) shows a representative cross-sectional SEM image of the deposited Si. It is clearly shown that a uniform layer with a thickness larger than $100\text{ }\mu\text{m}$ could be formed. An SEM image at higher magnification (Fig. 12(b)) confirms that the deposited Si film contains very few pores. Although the accurate purity is still under

consideration, typical impurities detected by glow discharge mass spectrometry (GD-MS) were 3.2 ppm (B), 4.9 ppm (F), 2.7 ppm (P), 8.9 ppm (Cl), <2 ppm (K), 5.0 ppm (Fe), and 76 ppm (Ag). These values are encouraging results because this study is still in an early stage. We proposed a new electrodeposition process of crystalline Si film using the KF-KCl molten salt and SiCl₄ as a silicon ion source, as is shown in Fig. 13 [28]. High-purity SiCl₄ gas, which is commercially available with low cost, is introduced into the molten KF-KCl to form Si(IV) ions. Si films are electrodeposited onto a substrate used as the cathode, and Cl₂ gas is evolved at the carbon anode. The salt adhered on the Si deposit can be easily removed by washing with water because both KF and KCl are highly soluble to water.

In order to study fundamental mechanism of the electrodeposition of Si in molten salt, we also attempted to apply ionic liquid such as trimethyl-n-hexyl ammonium bis-(trifluoromethylsulfonyl) imide (TMHATFSI), which is regarded as room temperature molten salt, as a model electrolyte, and investigated the deposition behavior [29, 30]. Moreover, we also attempted to fabricate micro or nanopatterned electrodeposits to explore the possibility to form nanostructured Si solar cells [31].

5. Conclusions

We have attempted to develop a new process to produce SOG-Si using wet chemical and electrochemical processes, utilizing diatomaceous earth as an abundant source of silica. It was confirmed that channel-flow type reactor with horizontally ordered liquid-liquid interface had extremely high efficiency for solvent extraction to eliminate light element such as B to achieve 7N level purity, in combination with acid leaching process to eliminate heavy metal impurities. We have also developed the direct electrochemical reduction process of silica using CaCl₂ based molten salt as an electrolyte, which enables continuous reaction with a sufficient rate by feeding silica granules with

optimized size to the Si cathode set at the bottom of the cell. Furthermore, we have also developed electrodeposition process of Si by using $\text{KF-KCl} + \text{K}_2\text{SiF}_6$ molten salt, which could form a compact and uniform layer thicker than 100 μm . These processes have advantages to conventional ones to produce SOG-Si from the view points of low energy consumption and high throughput as well as ability to directly deposit Si layers to form cell structure, and series of these processes could provide an alternative approach to produce SOG-Si material as well as to form Si based solar cells for the next generation. In order to apply these processes for practical production, capability for further larger scale of production with higher throughput should be required, and we will keep improving these processes.

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Table 1 B extraction from silica solution using separatory funnel and channel-flow reactor.

Stage number	Separatory funnel		Channel-flow reactor	
	B content (ppm)	Elimination ratio (%)	B content (ppm)	Elimination ratio (%)
0	5.29	-	5.29	-
1	0.95	82.0	0.51	90.3
2	0.53	90.0		

Table 2 B extraction from silica solution using the reactor shown in Fig. 7. The flow rate of the solutions for inlets (1) to (4) are 0.75 mL min^{-1} , 1.2 mL min^{-1} , 0.20 mL min^{-1} , and 0.20 mL min^{-1} , respectively, and estimated reaction duration is 80 msec.

	B content (ppm)	Elimination ratio (%)
Initial	0.92	-
After 1st stage	0.23	75.0
After 2nd stage	0.07	92.4

Table 3 Mean diameter and incorporated boron content in precipitated silica.

Concentration of silica / g L^{-1}	Mean diameter / nm	B content (ppm)		Elimination ratio (%)
		Before acid leaching	After acid leaching	
80	119	2.01	1.1	45
160	40.9	1.69	0.5	70

Figure captions

Figure 1 A schematic diagram of conventional processes to produce solar grade Si (SOG-Si) based on Siemens process.

Figure 2 A schematic diagram of the process proposed by the present work to produce SOG-Si.

Figure 3 A representative SEM image of diatomaceous earth.

Figure 4 Flow diagram to produce high purity silica from diatomaceous earth using wet chemical processes

Figure 5 A schematic representation of channel-flow reactor.

Figure 6 A representative micrograph for the formation condition of liquid-liquid interface in channel-flow reactor

Figure 7 A schematic representation of two-stage channel-flow reactor with horizontally ordered liquid-liquid interface.

Figure 8. A schematic representation of the proposed process for the electrochemical reduction of SiO_2 powder or granules. SiO_2 powder or granules charged from the top of the cell are reduced at the bottom.

Figure 9. A cross-sectional image of the cell after the electrolysis in molten CaCl_2 at 1123 K.

Figure 10. (a) A photograph of Si powder produced by electrochemical reduction of SiO_2 granules in molten CaCl_2 . (b) A photograph of a crystalline Si ingot made from the Si powder by floating zone melting.

Figure 11. Time dependences of the average reduction rate and the effective current density for the electrochemical reduction of SiO_2 granules at 0.5 V vs. Ca^{2+}/Ca in molten CaCl_2 at 1123 K.

Figure 12. (a) A cross-sectional SEM image of the Si layer electrodeposited on an Ag wire in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2 mol%) at 923 K. (b) A cross-sectional SEM image at higher magnification.

Figure 13. A schematic representation of the proposed electrodeposition process of crystalline Si film using molten KF-KCl as an electrolyte and SiCl_4 as a silicon source.

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