Purification and Reduction of Silica for Solar-Cell Application

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1. Introduction

To step forward for achieving the carbon-di-oxide (CO₂) free green and sustainable society, one way is generate the electricity from renewable energy sources. Thus, we would like to focus on the research and development of low production-cost based solar cells with earth-abundant and non-toxic absorber materials. Silicon (Si) is the most abundant solar-energy material which is found in the form of silicates and silica (SiO₂). Solar grade silicon (SOG-Si) requires very high level of purity (99.9999 %, 6N) that assures low impurities with longer carrier life time, and more collection of photo-generated carriers in the fabricated device. Nevertheless, current commercial production of high purity Si goes through multiple steps including the carbothermic reduction of SiO₂ at very high temperature of ~ 1700°C [1] followed by the conversion to SiHCl₄ or SiCl₄, and finally reduction of the silicon-halides to polycrystalline Si at ~ 1100°C. This Si is then converted to Si-wafer for the application of electronic devices. The process involves huge energy consumption along with significant amount of CO₂ emission leading to high production cost. In fact, roughly 50 % of the cost of a Si-based solar cell- module comes from the high production cost of Si- wafers.

On the other hand, to obtain SOG-Si, it evidently requires pure source material, i.e. pure SiO₂. A new possible approach is proposed to purify the natural Si, which is obtained as oxide. The purification process of the metal oxides could be achieved only by wet chemical way at moderate temperature.

Considering the above challenges, at first, we are proposing a new procedure for the purification of silica from different siliceous resources (e.g., sand, diatom, rocks etc.) to get high-purity silica. Later, we aim to develop cost-effective technology for the large scale production of SOG-Si from SiO₂ with minimum energy consumption. In particular, we are focusing on the electrochemical reduction process of SiO₂ to get high purity Si, mainly because this is a low-cost environment-friendly method without any requirement of vacuum technology, and associated with simple experimental parameters. Most importantly the reduction temperature required in the proposed electrochemical process is around 850°C, which is half of the current carbothermic process. Thus, electrochemical methods were considered as an alternative process for the production of high purity Si. Electrodeposition of Si was first reported in 1854 [2]. Later on 1980, deposition of 99.999 % purity Si on the silver (Ag)-substrate was reported which was achieved by electrolysis of K₂SiF₆-fluoride systems at 745°C [3]. Another process was reported to obtain Si by electrolysis of SiO₂ from BaO-SiO₂-BaF₂ melt at temperatures above 1415°C in 1981 [2]. Purity of Si, obtained in this study was 99.97 %. However, all these methods of electrochemical production of Si [4-9] were not industrialized mainly due to lower growth rate and related issues. A novel process for the production of metals and alloys from their solid oxides in molten salts by electrolysis was reported in 1997 [10-12]. This process is called as Fray–Farthing–Chen (FFC) Cambridge process. It was first discovered by reducing solid oxide thin films on titanium foil in molten calcium chloride (CaCl₂) bath by electrolysis [10-12]. Recently, several groups reported electrochemical reduction of Si from
solid SiO$_2$ as well as electrodeposition of Si-layer using CaCl$_2$ molten salt [13-15]. In a CaCl$_2$ melt, electrons can be transferred from a metal (molybdenum, tungsten, nickel etc.) cathode directly to a mechanically contacted solid quartz piece. The reduction reaction starts at metal/electrolyte/metal oxide three-phase interface and the oxygen ion is removed from the solid structure.

In this paper, we propose electrodeposition of Si on metal substrate obtained directly from SiO$_2$ source-material using high temperature CaCl$_2$ molten salt at 850$^\circ$C. Quality and purity of the deposited film might depend on the substrate material used. Moreover, Si-film/metal-substrate interface must be smooth and inclusion of impurity free to have good solar cell which in turn depends on the adhesion properties of the substrates. Therefore, we have investigated nickel (Ni), and silver (Ag) substrate to study the effect of substrate on the grown Si-layer using electrodeposition technique.

2. Materials and methods

For purification of silica, the conventional process, an alkaline dissolution followed by acid precipitation of silica gel was adopted and has been reviewed. An additional delicate acid leaching process using hydrochloric acid (HCl) and separation reagents was applied for elimination of heavy metals and light elements such as boron (B).

For the electroreduction of SiO$_2$, we have considered the thermodynamic properties of SiO$_2$, where reduction occurs at high temperature of 850$^\circ$C in CaCl$_2$ molten salt following the basic equation:

$$\text{SiO}_2 \text{(Solid)} + 4e^- \rightarrow \text{Si (reduced)} + 2\text{O}^{2-} \quad (1)$$

Experiment for the electrodeposition of Si has been carried out in a Al$_2$O$_3$- crucible placed inside a 40-cm long, and 7-cm wide quartz electrochemical-cell. Long quartz-cell was closed at the upper end with a stainless steel cap. The steel-cap has been designed in way to have several holes those work as feedthroughs for the electrodes, inert gas inlet and outlet, and thermocouple etc. Each electrode was connected with a 1.5 mm-diameter Mo-rod passing through a rubber stopper set in to a stainless steel tube fittings in the hole of the stainless-steel cap. The rubber stopper helps to control the vertical movement of the electrode inside the closed tube cell. A vertical electrical furnace has been used to increase temperature of the electrochemical-cell placed inside it during experiment. Electrochemical analysis was performed under a dry Ar atmosphere at 850$^\circ$C using CaCl$_2$ electrolyte using primarily a two-electrode system and also with three-electrode configuration. Graphite has been used as counter electrode as well as reference electrode, while silver (Ag), and nickel (Ni) were used as working electrode and also as the substrate for the electrodeposition experiment. A complete setup for the electrodeposition experiment has been shown in the Fig. 1.

![Fig. 1: Basic setup of the three-electrode system electrochemical cell.](image-url)
Electrodeposition on the Ni-substrate has been conducted at constant potential of 2.8 eV applied between counter electrode (graphite) and the working electrode (Ni-substrate). Chronoamperograms has been done at constant potentials (E) applied between Ag-substrate (cathode/WE) and graphite reference electrode. Cyclic voltammetry and all the constant potential electrolysis were carried out with an HSV-110 potentiometer (Hokuto Denko, Japan). Feed materials (source material) for the electrochemical reduction have been taken as SiO$_2$ nano-particle (Sigma-Aldrich, 99.9 %). Shown in Fig. 1 is the three-electrode system electrochemical cell along with all basic setup to run the electrodeposition experiment.

3. Results and Discussion

3.1 Purification of silica

Shown in Fig. 2 is the flow chart of achieving Si-based solar-cell device directly from silica (i.e., SiO$_2$ in the form of sand or diatom) as a raw material. As a first step, we have attempted to purify silica. Fig. 3 shows the major step of the purification process. Pre-treatment step has been applied to upgrade purity of diatom and sand. A new chemical process to remove light elements such as B has been established. The D-Mannitol shows high efficiency to improve the acid leaching. The purification process demonstrated an extremely high efficiency for eliminating B to 6N (99.9999%) level of purity. Strategy of three-time purifying of the ores has been reviewed. Only two time processing was proved to be enough to get 5N (99.9999 %) purity. Double-stage of the established purification pilot line is guaranteed and promising method to obtain high-pure amorphous SiO$_2$ (5N) adequate to the production of SOG-Si.

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**Fig. 2:** Flow chart of the fabrication of Si-based solar cell directly from SiO$_2$ source material
3.2 Electrodeposition of Silicon-layer

Electrodeposition of Si-layer from SiO₂ nano-particle has been performed on Ni and Ag-substrates using two or three-electrode system.

Fig. 3: Flow chart of the silica purification process

Fig. 4: Photographic image of the substrate just after the electrodeposition of Si-layer on metal substrate (left) and after water and acid-washing (right)

Fig. 4 shows the photographic image of the electrodeposited Si-layer taken out from the electrochemical cell and follow up image after washing the substrate with pure water and acid. Si-layer with grayish color has been apparent deposited on the metal substrate. Fig. 5 shows optical image of the Ni-substrate before electrodeposition and also image of the Si-layer formed on the Ni substrate after 1 hr of electrodeposition. A thin layer of Si material with gray color has been observed on the Ni-substrate. It is apparent that grown Si-layer on Ni-substrate is composed of many grains. Fig. 6 shows Raman spectroscopy of the electrodeposited Si on the Ni-substrate. A broad peak at approximately, 450 cm⁻¹ has been apparent from the figure. For crystalline silicon, a sharp peak, attributed to the transverse optical (TO) vibrational mode has been reported to appear at 520 cm⁻¹ [16]. As the long range order is lost, the TO peak becomes broad and shifts to lower wave numbers [17,18]. Thus, In case of amorphous-Si, the peak corresponding to TO phonon appears at 480 cm⁻¹.
Nevertheless, it is clear from Fig. 6 that for the deposited Si-films, no sharp peak at 520 cm$^{-1}$ was observed, whereas a broad peak with the peak position around 450 cm$^{-1}$ was found. It suggests that the deposited Si-film is basically amorphous in nature.

Later we have electrodeposited Si layer on Ag-substrate using three-electrode system applying constant potential between Ag-working electrode and graphite-reference electrode. SEM images of the electrodeposited Si-layer reveals that deposited Si is composed of small grains with formation of pores inside. Moreover, formed Si-layer is not a continuous film rather clusters of silicon crystals. A sharp and symmetric peak at ~ 524 cm$^{-1}$ suggests formation of crystalline silicon on the Ag-substrate. Raman mapping of electrodeposited Si-layer over 100 μm × 100 μm confirms that deposited Si-layer is uniform in crystalline composition without any amorphous phase. X-ray diffraction (XRD) also supports the formation of crystalline silicon using electrodeposition on the Ag-substrate. Thus crystallinity of the electrodeposited Si depends on the substrate used.

![Fig. 5: Optical image of the Ni substrate before (left) and after electrodeposition of Si-layer (right)](image)

**Fig. 6: Raman spectroscopy of the electrodeposited Si-layer grown on Ni-substrate**

Finally, we have discussed the mechanism of the electrodeposition of Si-layer on the metal substrate (Fig. 7). In general, electrodeposition of Si proceeds by the following process [19]. There are colliding and adsorbing of SiO$_2$ powder on the metal substrates then reduction of Si by accepting electron from metal-substrate. According to thermodynamic properties of SiO$_2$, reduction occurs at high temperature of 850°C in CaCl$_2$ molten salts as of the Ellingham diagram following the Eq.1. Reduction reaction starts at metal substrate/ CaCl$_2$ electrolyte/SiO$_2$ three-phase interface where oxygen gets removed from SiO$_2$. Through nucleation it forms continuous crystalline Si-films on the
metal substrate.

![Diagram](image)

**Fig. 7:** Mechanism of the formation of Si layer through electrochemical reduction of SiO₂

### 4. Conclusions
We have demonstrated 5N (99.999 %) purity of SiO₂ using chemical purification process obtained from diatom or sand as silica source. Later we have tried electrodeposition of Si-layer directly from SiO₂ source material using electrochemical reduction technique. Electrodeposited Si-layer was found amorphous in nature when Ni was used as the working electrode or substrate. Crystalline Si with very sharp peak at ~ 524 cm⁻¹ at Raman spectroscopy was obtained on the Ag-substrate. Thus crystallinity of the electrodeposited Si depends on the substrate used.

### References


