Electrodeposition of Crystalline-silicon on Metal-substrate from SiO$_2$ in Molten-salt

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Most of the commercial solar cells are based on silicon (Si) which is most abundant solar energy material in form of silicates and silica (SiO$_2$). Thus, production cost of Si has significant impact on the application of solar electricity for the general people. For the fabrication of solar cell Si with 99.9999% (6N) is necessary which is called solar-grade silicon (SOG-Si) However, there remain several challenges in the current production of Si using carbothermic reduction which is associated with huge energy consumption and carbon-di-oxide emission.

We aim to study formation of Si layer through reduction of SiO$_2$ using alternative method comparing to carbothermic process. We propose electrodeposition of SOG-Si films on low-cost substrate from of SiO$_2$-powder through electrochemical-reduction.

According to thermodynamic properties of SiO$_2$, reduction occurs at high temperature of 850$^\circ$ C in CaCl$_2$ molten salts following the basic equation:

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

Experiments for the electrodeposition Si-film has been carried out in a Al$_2$O$_3$- crucible placed inside a quartz electrochemical cell equiped with three-electrode system. Graphite has been used as counter electrode (CE) as well as reference electrode (RE), while silver sheet (Ag) was used as the working electrode (WE) as well as substrate for the electrodeposition. Electrochemical analysis has been done under Ar-gas at 850$^\circ$ Celsius using CaCl$_2$ molten salt. Chronoamperograms has been done at constant potential (E) applied between Ag-substrate (WE) and graphite reference electrode. Cyclic voltammetry (CV), 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 has been taken as SiO$_2$ nano-particle (Sigma-Aldrich, 99.9 %). Fig. 1 shows the experimental set up for the electrodeposition system.

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Raman spectroscopy of the electrodeposited Si-layer on Ag-substrate deposited with potential, $E = -1.22$ Volt, applied between the Ag-substrate and Graphite-RE shows a sharp and symmetric peak at $\sim 524$ cm$^{-1}$. It suggests formation of crystalline silicon on the Ag-substrate. Mapping of Raman peak at 100 $\mu$m $\times$ 100 $\mu$m area shows uniform formation of crystalline Si-phase with no amoraphous phase. X-ray diffraction (XRD) pattern also supports the formation of crystalline silicon. Scanning electron microscopy (SEM) images suggest that deposit Si is composed of small grains with formation of pores inside. Also deposited films is not continuous rather clusters of silicon crystals. Mechanism of the formation of Si layer on metal substrate through electrochemical reudction of SiO$_2$ has been discussed.


Fig. 1 (a) Electrolytic cell setup for the electrodeposition experiment; (b) Optical image of the Ag-substrate before experiment (top), and after electrodeposition of silicon (bottom)