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Electrodeposition and characterization of silicon films obtained through electrochemical reduction of SiO_2 nanoparticles

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ABSTRACT

We have reported electrodeposition of silicon films on metal substrates obtained through electrochemical reduction of silicon dioxide nanoparticles (SiO_2-NP) at high temperature of 855 °C in the calcium chloride ($CaCl_2$) melt. Electrodeposition was conducted using a three-electrode based electrochemical cell. Reduction of the SiO_2 was found possible with applying a negative potential of 0.9 V or more negative on the metal substrate with respect to the graphite reference electrode. Mechanism of the reduction and electrodeposition process was discussed using cyclic voltammetry (CV), and chronoamperograms (CA) techniques in relation to the applied reduction potentials during experiments. Raman spectroscopy, and X-ray diffraction method confirmed formation of the Si-film on the silver (Ag) substrate using the electrodeposition technique. Effect of the various reduction potentials on the properties of the formed Si layer was studied using Raman spectroscopy, photoluminescence (PL), and Scanning electron microscopy (SEM). Crystallinity of the electrodeposited Si-films were found to be correlated with the reduction potential. Nanocrystalline Si (nc-Si) film was obtained through electrodeposition with lower reduction potentials, while higher reduction potential was found to be effective to get Si-films with uniform crystalline quality, and better morphology. Effect of the substrate materials on the electrochemical reduction of SiO_2 was also investigated.

1. Introduction

To meet the demand of the future energy supply in the framework of a sustainable society, it becomes necessary to produce electricity from the renewable energy sources. Thus, research and development of solar cells with earth abundant and nontoxic absorber materials become crucial. Most of the commercially available solar cells are fabricated with silicon (Si) material. Si is mainly produced through reduction of the of silicates or silica (SiO_2), which is the most abundant element in the earth-crust. Thus, production cost of the Si has significant impact on the application of the solar cells for future energy supply. In general, solar-grade silicon (SOG-Si) which is used for the fabrication of solar cell requires very high level of purity (99.9999%, 6 N). However, present commercial production of high purity Si through carbothermic reduction of the SiO_2 involves multiple steps at high temperature of ~1700 °C [1]. The process is highly endothermic which leads to huge energy consumption along with significant emission of carbon dioxide (CO_2). Thus, this process eventually leads to high production cost, and poses an environmental concern.

In recent years, various groups reported about electrodeposition of Si from molten salts, where Si is electrodeposited through electrochemical reduction of the SiO_2. This is considered as a low-cost method which requires less energy consumption comparing to the current carbothermic process. In fact, electrodeposition of the Si was first reported in late eighteenth century [2]. Later at 1980's, deposition of the Si layer on the Ag-substrate was reported as achieved by electrolysis of K_2SiF_6-floride systems at 745 °C [3], and also by electrolysis of SiO_2 from BaO-SiO_2-BaF_2 melt at temperatures above 1415 °C [2]. Electrodeposition of Si has also been performed in organic solvents [4] or room temperature ionic liquids [5–7], where silicon halide compounds (e.g., $SiCl_4$ and $SiHCl_3$) are usually used as source materials. However, issues of the purity level, and slow growth rate of the deposited Si films in the above experiments restricted its application in the commercial level [8–12]. A novel process to produce metals and alloys from their solid oxides in

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molten salts by electrolysis was reported in 1997 [13–15]. In addition, recently several groups reported electrochemical-reduction of the solid SiO_2 using calcium chloride ($CaCl_2$) molten salt as electrolytes [16,17]. Electrochemical reduction of the SiO_2 occurs at high temperature of 850 °C in $CaCl_2$ molten salt following the equation:

$$SiO_2(s) + 4e^- \rightarrow Si(s) + 2O^{2-} \quad (1)$$

In the $CaCl_2$ melt electrons can be transferred from a metal (molybdenum, tungsten, iron, nickel etc.) cathode directly to a mechanically contacted solid quartz piece, thereby, reducing it to Si. In another approach, direct electrodeposition of the Si was obtained through colliding and adsorbing of SiO_2 powder on the metal substrates followed by the reduction of SiO_2 by accepting electrons from the metal substrates [18,19]. Electrochemical reduction occurs in the $CaCl_2$ melt at 850 °C where reduction reaction starts at the metal substrate/ $CaCl_2$ electrolyte/SiO_2 three-phase interface, and oxygen gets removed from the SiO_2 [16]. Through nucleation it forms Si layers on the metal substrates. Very recently, similar group reported the formation of Si *p-n* junction solar cells from SiO_2 source through above mentioned electrodeposition techniques [20].

In general, Si materials obtained through electrochemical reduction at high temperature molten salt are crystalline in nature, irrespective of the precursor materials used. This is mainly because high temperature during electroreduction assists in crystallization of the silicon. However, application of the crystalline Si in modern electronics largely depends on the structure and dimension of its crystallinity. In particular, nanocrystalline Si (nc-Si), due to its unique quantum confinement properties can be used in various application including high efficiency Si-based solar cells, and also as anode materials in lithium-ion batteries [21]. In the meantime, few reports have been published on the formation of nanocrystalline (nc) based Si materials through electrochemical reduction of solid Si pellets [22,23], or from carbon-coated silica nano-particles [24]. Nevertheless, although successful electrodeposition of moderately pure Si (99.9%) on silver (Ag)-substrate with photoactive quality has been reported in the above-mentioned references [19], detail discussion on the crystalline nature (e.g., nano or multi-crystallinity) of the electrodeposited Si, obtained from SiO_2 powder has been largely absent. Thus, to our knowledge, no such formation of the nc-Si thin films through electrodeposition on the metal substrates through electroreduction has been reported so far.

Furthermore, in addition to the purity of the electrodeposited Si films, an intensive study of the material properties of the Si film in relation to the electrodeposition process parameters is inevitable for better understanding of the quality of the obtained Si films for application to the devices. Detail understanding of the electrodeposition mechanism on various substrate materials is also necessary to apply the technique on more cost-effective substrates. Considering these issues, in this paper, we have studied electrodeposition of the Si film mainly on the Ag-substrate obtained directly from the electrochemical reduction of SiO_2-NP in $CaCl_2$ melt. Effect of reduction potentials (i.e., electrolysis potential) during electrodeposition experiment on the quality and microstructural properties (crystallinity) of the deposited Si films were studied. Primary evidence for the formation of nc-Si films on the Ag substrates, obtained at lower reduction potential through electrochemical reduction of the SiO_2 nanoparticles (SiO_2-NP) in high temperature $CaCl_2$ molten salts has been reported. Formation of the nc-Si has been confirmed by Raman and photoluminescence (PL) techniques. Nickel (Ni) was also used as a substrate to study the effect of the substrate material on the quality of the deposited film. Mechanism of the reduction and electrodeposition process has been intensively investigated using cyclic voltammetry (CV), and chronoamperometry (CA) techniques in relation to the applied reduction potential.

2. Materials and methods

Electrodeposition experiments were carried out in a Al_2O_3- crucible (Outside diameter: 6.2 cm; Length: 7.0 cm) placed inside a quartz electrochemical-cell (Outside diameter: 7 cm; Length: 40 cm). Top of the quartz cell was covered with a stainless-steel cap which was equipped with several feedthroughs (hole) for the electrodes, inlet and outlet for inert gas, and thermocouple etc. In addition, the top steel-cap was combined with five sets of steel-flanges connected through steel-rods. Each flange has several holes at different locations. The assembly of the steel-flanges, set inside the quartz cell, can resist and reflect the circulation of the heat flow that is generated at the bottom of the quartz cell as it is placed inside a high-temperature furnace. Thus, steel cap at the top of the cell could avoid being overheated, and connecting wires of electrodes at the top of the cell could be controlled easily form outside. Of course, in addition, all the steel-flanges were equipped with the feedthroughs exactly at the same position of the steel-cap so that all the electrodes and gas pipes can go through easily to the bottom of the cell. A vertical electrical furnace (FUC150FB, ADVANTEC, Japan) was used to increase the temperature of the electrochemical cell during experiment.

Electrochemical analysis was performed dynamically that involves a three-electrode configuration. Two separate graphite-rods (99.995%, 3 mm dia., 8 cm long, Sigma-Aldrich, USA) were used as a counter electrode (CE or anode), and a reference electrode (RE), respectively. Ag-sheet or Ni-sheet (99.9%, 0.5 mm × 1.5 cm × 4 cm, Nilaco, Japan) was used as a working electrode (WE or cathode) as well as a substrate for the electrodeposition experiment. All three electrodes were connected to three separate Mo rods (99.95%, 1.5 mm dia., 50 cm long, Nilaco, Japan) using tungsten wires. Mo rods were extended out of the quartz cell through feedthroughs of the steel cap and Si stoppers, and then connected to the power source. Si stopper controls the vertical movement of the electrodes inside the electrochemical cell. Inside the cell, Mo rods were covered with a Al_2O_3-insulator (99.5%, 3 mm inside dia., Nilaco, Japan) to avoid direct contact of the rods with the steel flanges, and thus to prevent short circuiting of the electrodes inside the electrochemical cell. Chronoamperograms (CA) has been done at a constant potential (E) applied between metal substrate (WE, cathode) and graphite RE. Cyclic voltammetry (CV), and all the constant potential (chronoamperometry, CA) electrolysis were carried out with an automatic polarization system (HSV-110, Hokuto Denko Co. Ltd., Japan). SiO_2 nanoparticles (5–15 nm of particle size, 99.5%, Sigma-Aldrich, Japan) were considered as the feed materials (source material) for the electrochemical reduction.

75 g of $CaCl_2$ electrolyte (anhydrous powder, 97%, Sigma-Aldrich, Japan) has been taken at the Al_2O_3-crucible which was placed inside the quartz electrochemical- cell. Although $CaCl_2$ used for this experiment is already anhydrous (i.e., no water molecules are bonded chemically) we have dried the $CaCl_2$ at 550 °C for 5 h under Ar gas environment (flow rate ~150 ml/min) to remove any possible moisture. 515 mg of SiO_2 nanoparticles were taken in the same Al_2O_3-crucible and mixed together with $CaCl_2$. Electrodeposition was performed under inert atmosphere of Ar gas (flow rate ~150 ml/min) at 855 °C in $CaCl_2$ melt. After electrodeposition experiment, formed Si layer on the metal substrate were washed ultrasonically using 0.2 mol% hydrochloric (HCl) acid for 10 min followed by washing with pure water.

Characterization of the electrodeposited Si layer was performed using Raman spectroscopy, PL, scanning electron microscope (SEM), and X-ray diffraction (XRD) technique. XRD was taken in the range of 10°–90° by philips X'pert diffractometer at θ-2θ mode with Cu-Kα (α = 1.541837 Å) radiation operated at 45 kV and 40 mA. A 532-nm excitation line from a Nd:YAG laser source has been used for the PL and Raman spectroscopy. All the characterization of the Si layer has been done at room temperature (RT).