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Experimental Procedures

Apparatus and materials: Molten salt electrodeposition was conducted in a SiO_2 crucible (Technical Glass Products, o.d. 40 \times i.d. 37 \times height 120 mm, Painesville, OH) under Ar atmosphere (80 ml min^{-1}) at 1123 K. The apparatus is shown in Figure S1. The electrolyte bath was a mixture of reagent grade CaCl_2 (Sigma-Aldrich, 99%, St. Louis, MO) and CaO (Sigma-Aldrich, 99.9%). SiO_2 NPs (Sigma-Aldrich, 99%, size: 10 to 20 nm) were added as the Si precursor. Prior to melting, the electrolyte was dried under vacuum at 773 K for 24 h to remove the residual moisture. The electrolyte composition was adjusted and optimized to improve the quality of the deposit.

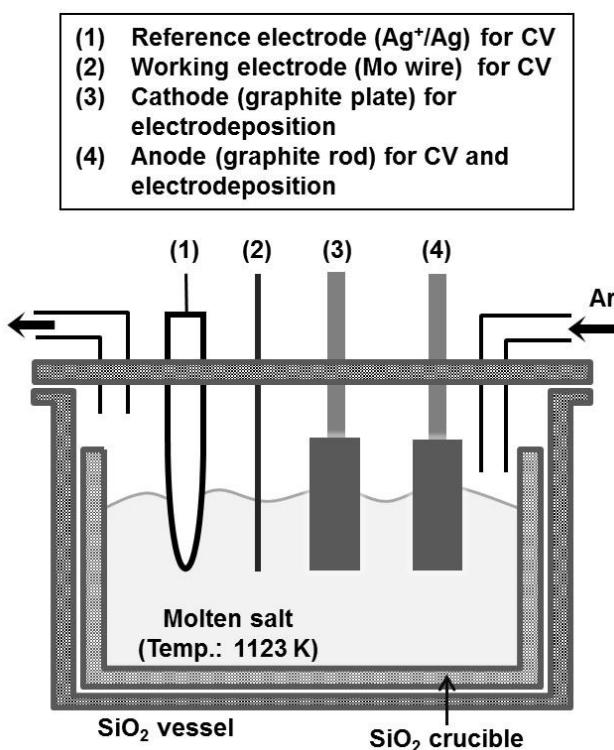


Figure S1. A schematic drawing of the setup for the electrochemical experiments in molten salt.

Electrochemical experiments: Electrochemical experiments were conducted by using a CH Instruments model 760E potentiostat (Austin, TX). Cyclic voltammetry (CV) was conducted in the three-electrode manner with a molybdenum wire (Alfa Aesar, 99.995%, diameter 0.25 mm, 5 mm immersion in electrolyte) as the working electrode and a graphite rod as the counter electrode, respectively. After conducting CV in pure CaCl_2 , CaO (1 mol%) was added into the melt and CV was conducted again. The reference was an Ag^+/Ag electrode prepared by immersing a silver wire (Alfa Aesar, 99.9%, diameter 1 mm) into CaCl_2 containing 0.5 mol% AgCl (Sigma-Aldrich, 99%) in a quartz tube (Technical Glass Products, o.d. 6 \times i.d. 4 \times height 600 mm).^[1] In molten $\text{CaCl}_2\text{-CaO-SiO}_2$, pre-electrolysis at controlled cathodic current (30 mA cm^{-2}) was performed for 3 h between two graphite rod (Alfa Aesar, 99.995%, diameter 6 mm, 2.5 cm immersion in electrolyte, Haverhill, MA) electrodes, to remove possible impurities and suspended SiO_2 NPs in the melt as much as possible. After pre-electrolysis, Si films were deposited at constant cathodic currents of 8 to 23 mA cm^{-2} in the two-electrode manner with a graphite plate (POCO Graphite, AXF-5Q, diameter 6 \times thickness 1 mm, 2.5 cm immersion in electrolyte, Decatur, TX) as cathode and a graphite rod as anode. Tungsten wires (Alfa Aesar, 99.9%, diameter 1 mm) were used as the current leads for the electrodes. We conduct electrodeposition experiment in one bath for at least 1 week. The SiO_2 crucible is with good stability. Decrease in wall thickness of the crucible is diminutive according to direct observation after experiment.

Characterization: The post-electrolysis samples were rinsed in hydrochloric acid (0.1 M) for 1 h and later in distilled water for 1 h to remove the residual salt. The deposited Si films were characterized by scanning electron microscopy (SEM, Quanta 650 FEG, FEI Inc., Hillsboro, OR), energy dispersive spectroscopy (EDS, XFlash Detector 5010, Bruker, Fitchburg, WI) and X-ray diffraction (XRD, R-Axis Spider, Rigaku Corp., Japan). The impurity concentrations were analyzed by glowing discharge mass spectrometry (GDMS, VG 9000, Thermo Fisher Scientific Inc., Waltham, MA).

Photoelectrochemical measurements: The deposited Si films were tested as photoelectrodes for the photoelectrochemical measurements. Photoelectrochemical properties under UV-visible light illumination by a xenon lamp at 100 mW cm^{-2} were investigated and compared with a commercial p-type Si wafer (University Wafers, 1 mm thick, 5 to 10 ohm cm, (100), boron-doped, Boston, MA). The procedures were described in a previous paper in detail.^[2] Ar-purged MeCN (CH_3CN , Acros, 99.9%, Extra Dry, Fair Lawn, NJ) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka, ≥99.9%, Allentown, PA) was the electrolyte and 0.05 M ethyl viologen diperchlorate ($\text{EV}(\text{ClO}_4)_2$, Sigma-Aldrich, 98%) was added as the redox agent.

Post-deposition fabrication of p-n junction and evaluation of PV effects: The deposited Si films exhibiting good photoelectrochemical properties were fabricated into p-n junctions to evaluate the PV effects. Figure S2 shows the procedure. First, the deposited Si film was polished to create a flat and clean surface (I). Then, a layer of n-type spin-on-dopant (SOD) was deposited on the Si surface by spin-coating (II). Later, rapid thermal annealing at 1223 K was conducted for 30 s to induce the dopant diffusion from SOD into Si to form a p-n junction (III). Finally, SOD was removed by Ar plasma ashing and metal contacts (Cr/Au) were made by e-beam evaporation (IV). The top contacts were patterned via a photolithography lift-off process. PV effects of the fabricated p-n junctions were evaluated using a B1500A Semiconductor Device Analyzer (Agilent Technologies) and Summit 11000 AP probe station (Cascade Microtech). Solar simulator (Newport) with AM 1.5G filter, calibrated to 100 mW cm^{-2} , was used as the light source.

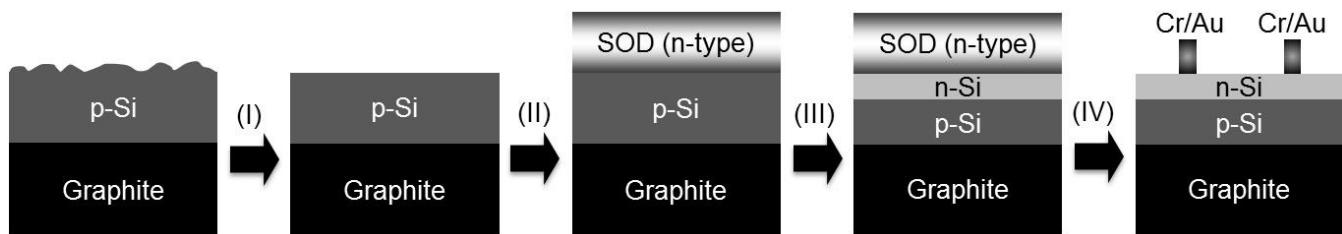


Figure S2. Fabrication procedure of p-n junctions from the deposited Si films. (I) polishing to create a flat and clean surface; (II) deposition of n-type spin-on-dopant (SOD); (III) formation of p-n junction by rapid thermal annealing; (IV) removal of SOD by Ar plasma ashing and making of metal (Cr/Au) contacts by e-beam evaporation.

Results and Discussion

CVs conducted on a Mo wire in a large potential scanning range in molten CaCl_2 and $\text{CaCl}_2\text{-CaO}$ (1 mol%) are shown in Figure S3. The potential of Ca^{2+}/Ca was calibrated to be around 2.1 V (vs. Ag^+/Ag). CV curve in pure CaCl_2 in the potential range from 2 V to 0.5 V (vs. Ca^{2+}/Ca) is generally flat. After addition of 1 mol% of CaO, cathodic waves at around 1.3 V (vs. Ca^{2+}/Ca) appear clearly, indicating the existence of new species in the molten salt. Formation of Si on a graphite plate cathode (Figure 1b) after potentiostatic electrolysis at 0.7 V (vs. Ca^{2+}/Ca) for 10 min in molten $\text{CaCl}_2\text{-CaO}$ (1 mol%) indicates that new species are most likely to be soluble $\text{Si}^{IV}\text{-O}$ complex anions.

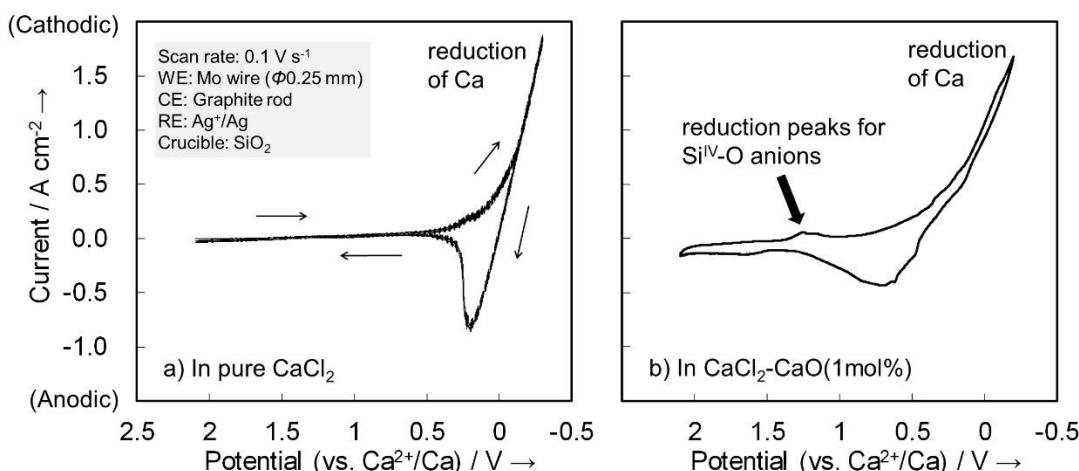


Figure S3. Cyclic voltammograms of a Mo wire in a) molten CaCl_2 and b) molten $\text{CaCl}_2\text{-CaO}$ (1 mol%) in a SiO_2 crucible at 1123 K.

Figure S4 shows photographs of a typical sample after electrodeposition and during water rinsing. Deposition of Si film on the graphite plate is clearly observed. However, the film is covered with a quantity of Si powder. We consider that film is formed from soluble ions by electrodeposition, while powder is formed mainly from undissolved SiO_2 NPs suspending in the melt via direct electrochemical reduction.^[3] Both film thickness and powder quantity increase with the elapse of electrolysis time. Most of the powdery deposits can be washed away during water rinsing.

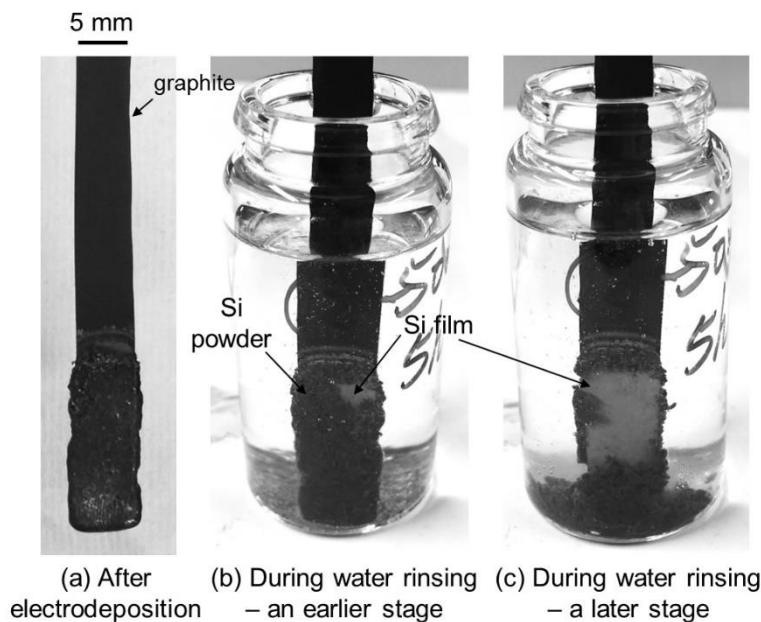


Figure S4. Photographs of a typical sample a) after electrodeposition at a constant cathodic current of 15 mA cm^{-2} for 5 h in molten $\text{CaCl}_2\text{--CaO--SiO}_2$ (CaO:4.8mol%, SiO_2 :3.9mol%) at 1123 K, b) and c) during water rinsing.

Figure S5 shows the XRD pattern of a deposited Si film. Formation of crystalline Si is confirmed.

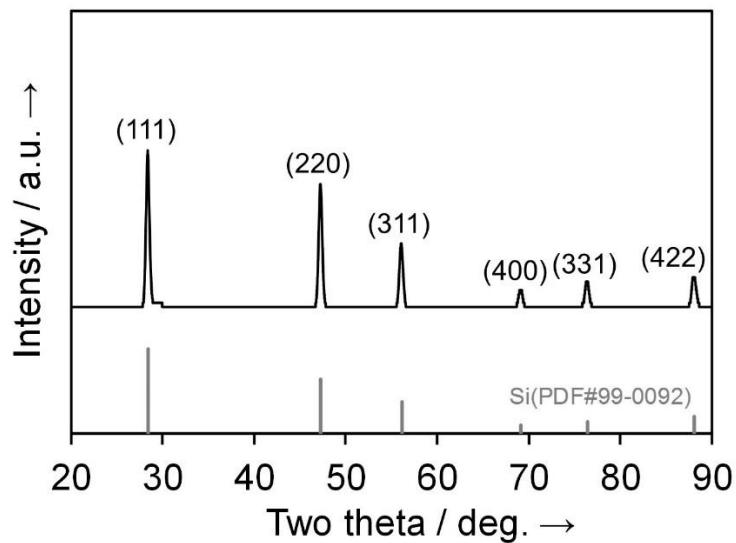


Figure S5. XRD pattern of a Si film deposited on a graphite substrate in molten $\text{CaCl}_2\text{--CaO--SiO}_2$ (CaO:4.8mol%, SiO_2 :3.9mol%) at 1123 K by electrolysis at a constant cathodic current of 15 mA cm^{-2} for 1 h.

Figure S6 shows a photograph of two graphite cathodes (after water rinsing) electrodeposited for 1 h at constant cathodic currents of a) 8 mA cm^{-2} and b) 23 mA cm^{-2} . Small current has the advantage in surface cleanliness, however the film grows slowly. Large current results in a fast reaction, however unexpected powdery deposits are also easy to form and accumulate on the surface. Based on a large amount of experiments, the current of 15 mA cm^{-2} was found to be an optimum value to obtain uniform and thick films. However, integrated understandings on the electrochemical behavior of $\text{Si}^{\text{IV}}\text{--O}$ anions and electrocrystallization mechanism of Si films are not available.

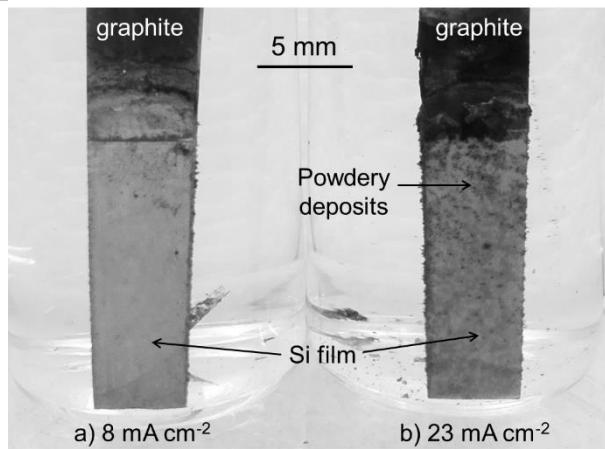


Figure S6. A photograph of two graphite cathodes (after water rinsing) electrodeposited for 1 h at constant cathodic currents of a) 8 mA cm^{-2} and b) 23 mA cm^{-2} in molten $\text{CaCl}_2\text{-CaO-SiO}_2$ (CaO:4.8mol%, SiO_2 :3.9mol%) at 1123 K.

Since both Si film and powder are formed during electrolysis, the film formation efficiency (η) is defined as

$$\eta = \frac{10h \times A \times \rho_{\text{Si}} \times 4F}{i \times A \times t \times M_{\text{Si}}} \times 100\% \quad (1)$$

where h is the film thickness (μm); A is the surface area of the electrode (cm^2); ρ_{Si} and M_{Si} are density (2.33 g cm^{-3})^[4] and molar weight (28.09 g mol^{-1}) of Si, respectively; i is the current density (15 mA cm^{-2}), t is the electrolysis time (s), and F is the Faraday constant ($96487 \text{ s A mol}^{-1}$). A decreasing trend for the efficiency is observed (Figure S7). Since Si powders are also formed as the dominant side reaction, accumulation of powdery deposits during electrolysis influences the film formation. A thick layer of powder covering the surface would preclude the mass transfer of $\text{Si}^{IV}\text{-O}$ or O^2 ions for a continuous film growth. Thus the efficiency decreases gradually.

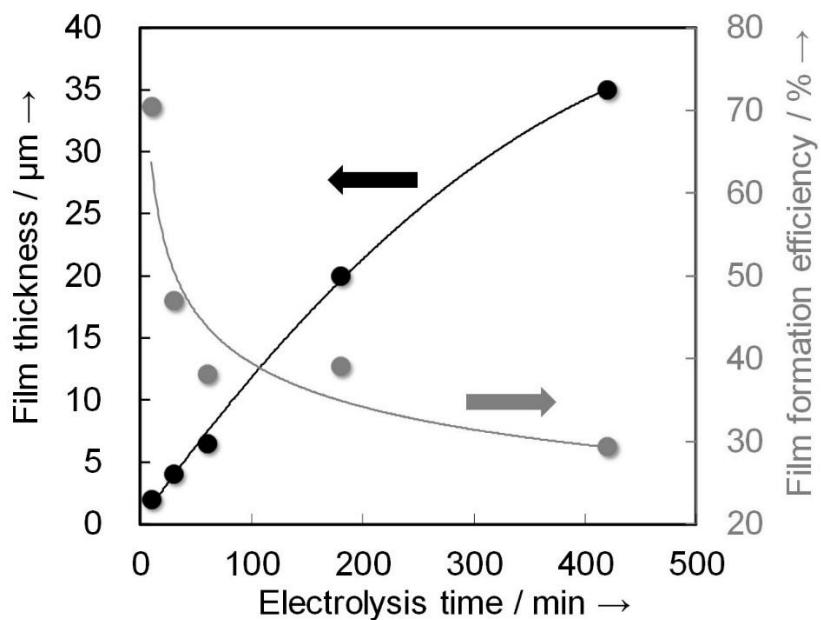


Figure S7. Variation of film thickness and film formation efficiency during electrolysis at a constant cathodic current of 15 mA cm^{-2} in molten $\text{CaCl}_2\text{-CaO-SiO}_2$ (CaO:4.8mol%, SiO_2 :3.9mol%) at 1123 K.

Figure S8 shows the variation of cell voltage during electrolysis at a constant cathodic current of 15 mA cm^{-2} . Cell voltage increases gradually with the elapse of electrolysis time until reaching a certain value (about 2.5 V). Theoretical decomposition voltages for CaCl_2 and CaO at 1123 K were calculated according to thermodynamic data.^[5] Activities of components except Ca were taken as unity in the calculation. Cell voltage during electrolysis is always lower than the decomposition voltages for CaCl_2 . However, when activity of Ca is very small, CaO decomposes at voltages lower than 2.5 V. Therefore, we consider that contamination of Ca in Si film by decomposition of CaO to form a small number of dilute Ca-Si alloys is possible.

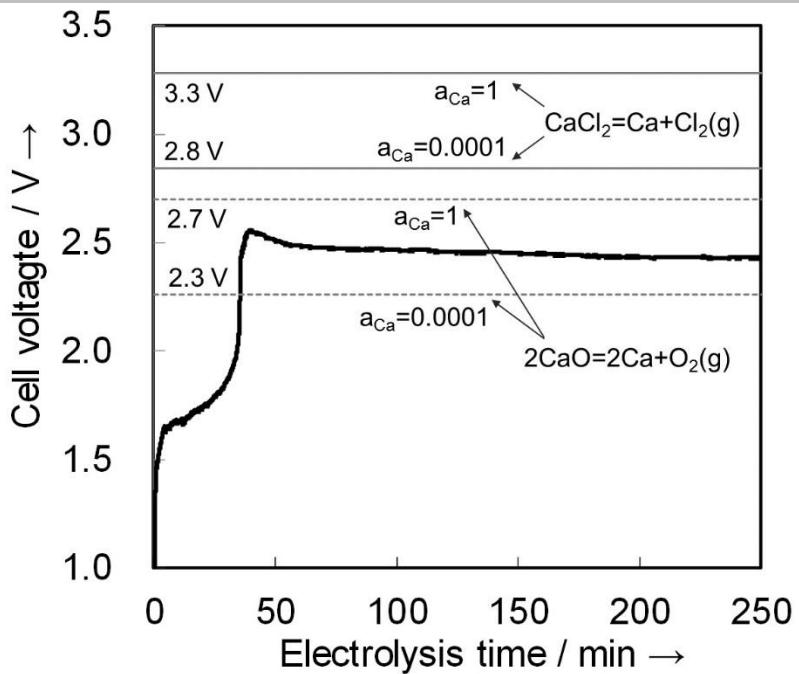


Figure S8. Variation of cell voltage during electrolysis at a constant cathodic current of 15 mA cm^{-2} in molten $\text{CaCl}_2\text{--CaO--SiO}_2$ ($\text{CaO}:4.8\text{mol\%}$, $\text{SiO}_2:3.9\text{mol\%}$) at 1123 K.

References

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Author Contributions

X. Y., L. J. and X. Z. contributed equally. X. Y. and A. J. B. conceived the concept. X. Y. conducted the electrochemical experiments, characterization and photoelectrochemical measurements. L. J. fabricated the p-n junction and evaluated the PV effects. X. Z. contributed to optimization. T. L. and J. Z. contributed to experiment design. E. T. Y. contributed to the discussion on the results. A. J. B. supervised the whole project. X. Y. wrote the draft.