Supporting Information

Electrochemical Formation of a *p-n* Junction on Thin Film Silicon Deposited in Molten Salt

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Experimental section

Chemical materials

The chemical materials used in this work for silicon film include calcium chloride ($CaCl_2$, Sigma-Aldrich, ACS reagent, 99%, St. Louis, MO. Ba ≤ 0.005%, Fe ≤ 0.001%, K ≤ 0.01%, Mg ≤ 0.005%, NH_4^+ ≤ 0.005%, Na ≤ 0.02%, Sr ≤ 0.01%, heavy metals ≤ 5 ppm), calcium oxide (CaO, Sigma-Aldrich, 99.9%, trace metals basis), calcium silicate ($CaSiO_3$, Sigma-Aldrich, 99.9%), silicon oxide (SiO_2, Sigma-Aldrich, nanopowder, 10-20 nm, 99.5%, trace metals basis), antimony oxide (Sb_2O_3, Sigma-Aldrich, 99.999%) and calcium phosphate ($Ca_3(PO_4)_2$, Sigma-Aldrich, > 96.0%) powders.

Molten salt electrodeposition process

Figure 1a shows a schematic diagram of the molten salt electrolytic cell for the electrochemical deposition of silicon *p-n* junction film. The assembled electrochemical deposition system comprised of a one-end-closed fused quartz-flanged tube (O.D. 52 mm, length 500 mm) with an O-ring and a stainless steel lid, and a one-end closed quartz crucible (I.D. 37 mm, length 150 mm, Technical Glass Products, Inc., Painesville, OH). The flanged lid has O-ring structured holes through which the conducting wires with electrodes are inserted. $CaCl_2$, $CaSiO_3$, CaO and SiO_2 were used for the electrodeposition of thin film silicon *p-n* junction.

In a typical experiment, 100 g $CaCl_2$, 1.0 g $CaSiO_3$, 1.8 g CaO and 1.4 g SiO_2 were weighted and poured into a one-end closed quartz crucible, and then the crucible was placed into a one-end closed fused quartz tube. The lid was affixed and the entire vessel was sealed. The bottom part of the assembled tube was heated in a furnace (Model F21135, 1350 W, Thermo Scientific, Waltham, MA) in a

vacuum for 24 h at 500 °C to completely remove the possible moisture. Then, high purity argon gas (99.99%) was purged into the tube, and the furnace was heated up to 850 °C and kept at 850 °C for 24 to 48 h (to form sufficient silicates ions concentration), then the electrodeposition experiment was carried out in an argon gas atmosphere. The molten salt bath was about 50 mm in depth. The working electrode (cathode substrate) was a POCO graphite (AXF-5Q, Entegris POCO, Decatur, TX) cut into 75 mm in length, 6 mm in width, and 1 mm in thickness. The counter electrode was a graphite rod (Alfa Aesar, 99.995%, diameter 6 mm, 5 cm immersion in electrolyte, Haverhill, MA) or graphite plate. The electrode leads were tungsten wires (Alfa Aesar, 99.9%, diameter 1 mm) protected by quartz tube.

Electrodeposition experiments were carried out by using a CH Instruments model 760E potentiostat (Austin, TX). Pre-electrolysis was performed at 2.5 V for 12 h between two graphite rod (Alfa Aesar, 99.995%, diameter 6 mm, 5 cm immersion in electrolyte, Haverhill, MA) electrodes to remove the possible impurities. After that, silicon films include *p*-type and *n*-type films were electrodeposited at 15 mA cm^{-2} to 20 mA cm^{-2} in the two-electrode manner with a graphite plate (POCO Graphite, AXF-5Q, width 6 mm × thickness 1 mm, 50 mm immersion in electrolyte, Decatur, TX) as the cathode substrate and a graphite rod/plate as the anode. After the electrodeposition process, the deposited silicon film was removed slowly from molten electrolyte and cool down in an argon gas atmosphere. Then the sample was taken out and washed with water and ethanol and then dried at 100 °C. More experimental details can be found in our previous work.[1,2]

Molten salt electrodeposition of p-type silicon film

Generally, the electrochemical deposition process for thin film silicon *p-n* junction includes two-step electrodeposition process, *i.e.*, electrodeposition of *p*-type silicon film and electrodeposition of *n*-type silicon film (**Figure S1**). For the electrodeposition of *p*-type silicon film, the electrolyte contains $CaCl_2$ dissolved with $CaSiO_3$, CaO and SiO_2 particles, and a quartz crucible (Technical Glass Products, O.D. 40 × I.D. 37 × height 180 mm, Painesville, OH. Al: 14 ppm, B < 0.2 ppm, Ca: 0.4 ppm, Cu < 0.05 ppm, Cr < 0.05 ppm, Fe: 0.2 ppm, K: 0.6 ppm, Li: 0.6 ppm, Mg: 0.1 ppm, Mn < 0.05 ppm, Na: 0.7 ppm, Ni <0.1 ppm, P < 0.2 ppm, Sb < 0.003 ppm, Ti: 1.1 ppm, Zr: 0.8 ppm) was used as electrolytic cell. The quartz crucible contains 14 ppm Al which can be served as dopant for *p*-type silicon film, therefore, it is not necessary to add other dopant for the *p*-type silicon film. The electrolyte was firstly kept at 850 °C

for 48 h to confirm the dissolution process for silicates. Then the electrolyte was pre-electrolyzed with a reducing current between a graphite substrate cathode electrode and a graphite anode electrode for 12 h. After pre-electrolysis, the electrodeposition process for *p*-type silicon film was carried out by using pulse electrodeposition process. During electroreduction, SiO_2 reacts with CaO to form calcium silicates,[3] calcium silicates were dissolved into molten electrolyte to form silicates ions (such as $SiO_3^{2-}$and SiO_4^{4-}, *etc.*), silicate ions were reduced to silicon crystallites and then gradually to form a dense *p*-type silicon film on the POCO graphite substrate. The possible reactions may be expressed as reactions (1)-(7), as shown in **Figure S2**.

$$CaSiO_3 \rightarrow Ca^{2+} + SiO_3^{2-} \quad (1)$$

$$CaO \rightarrow Ca^{2+} + O^{2-} \quad (2)$$

$$SiO_2 + O^{2-} \rightarrow SiO_3^{2-} \quad (3)$$

$$SiO_2 + 2O^{2-} \rightarrow SiO_4^{4-} \quad (4)$$

$$SiO_3^{2-} + O^{2-} \rightarrow SiO_4^{4-} \quad (5)$$

$$SiO_3^{2-} + 4e^- \rightarrow Si + 3O^{2-} \quad (6)$$

$$SiO_4^{4-} + 4e^- \rightarrow Si + 4O^{2-} \quad (7)$$

Molten salt electrodeposition of n-type silicon film

To produce thin film silicon *p*-*n* junction, the produced *p*-type silicon film was polished to form a mirror finish. After that, the polished *p*-type silicon film was used as substrate to further electrodeposit *n*-type silicon film in another electrodeposition bath. Sb_2O_3 was added into the molten electrolyte containing $CaSiO_3$, CaO and SiO_2 to provide Sb as dopant for the *n*-type silicon film. The possible reactions for the antimony dopant may be expressed as: $Sb_2O_3 + x CaO \rightarrow Ca_xSb_2O_{(3+x)}$; $Ca_xSb_2O_{(3+x)} \rightarrow x Ca^{2+} + Sb_2O_{(3+x)}^{2x-}$; $Sb_2O_{(3+x)}^{2x-} + 6e^- \rightarrow 2Sb + (3+x)O^{2-}$.[4] In addition, it is proved that phosphorous can also be used as dopant for *n*-type silicon in molten salt. $Ca_3(PO_4)_2$ can be added into the electrolyte to provide P as dopant, the possible reactions for the phosphorous dopant may be expressed as: $Ca_3(PO_4)_2 \rightarrow 3Ca^{2+} + 2PO_4^{3-}$; $PO_4^{3-} + 5e^- \rightarrow P + 4O^{2-}$.[5] It should be noted that the detailed doping mechanisms are not well understood, which are currently being investigated and will report separately in future work. After the *n*-type silicon film was electrodeposited on the *p*-type silicon film, the fabricated silicon *p*-*n* junction film was then taken out from the molten salt, washed thoroughly with water and ethanol and

then polished to form a mirror finish. Then the polished thin film silicon *p-n* junction was prepared for silicon solar cells. For comparison, the commercial *p*-type silicon wafer (~1e16 cm^{-3}) has also been used as a substrate to produce *p-n* junction in molten salt.

Metallization and characterization of photovoltaic devices

The top contact pattern was formed by lithography (photoresist, AZ 5209) and a lift-off process. Electron-beam evaporator (CHA, Industries) with a base pressure of 1.0E-6 torr were used for metal deposition. The film thickness was monitored using a quartz-crystal monitor and the deposition rates were maintained at 0.1 nm/s.

The fabricated devices were characterized 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 light source.

Materials Characterization

The produced silicon film was characterized by scanning electron microscopy (SEM, Quanta 650 FEG, FEI Inc., Hillsboro, OR) and energy dispersive spectroscopy (EDS, XFlash Detector 5010, Bruker, Fitchburg, WI). The impurity concentration of the film was analyzed by glowing discharge mass spectrometry (GDMS, VG 9000, Thermo Fisher Scientific Inc., Waltham, MA). X-ray diffraction spectroscopy (XRD, Philips X-ray diffractometer equipped with Cu Kα radiation) was also used to analyze the produced silicon film.

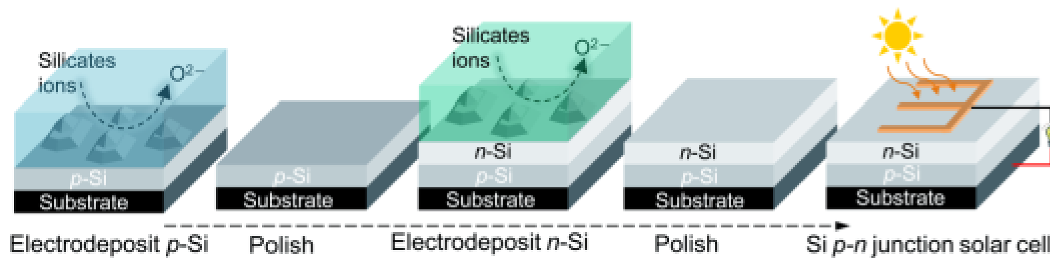

Figure S1. Schematic illustration of the two-step electrodeposition process for the production of thin film silicon *p-n* junction.

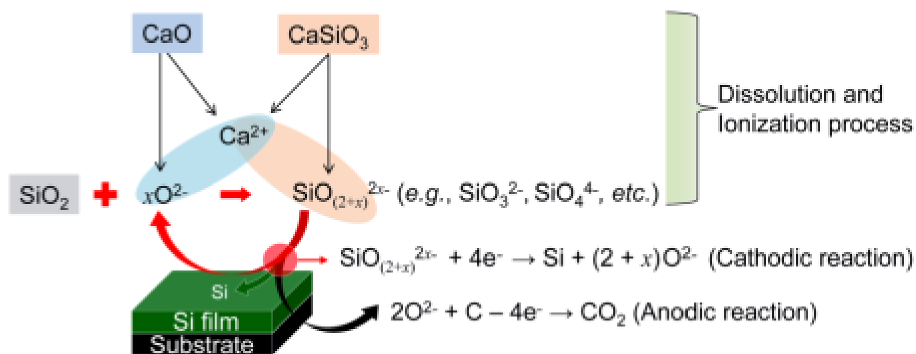

Figure S2. The reaction mechanism of the electrodeposition process for thin film silicon *p-n* junction in molten salt.

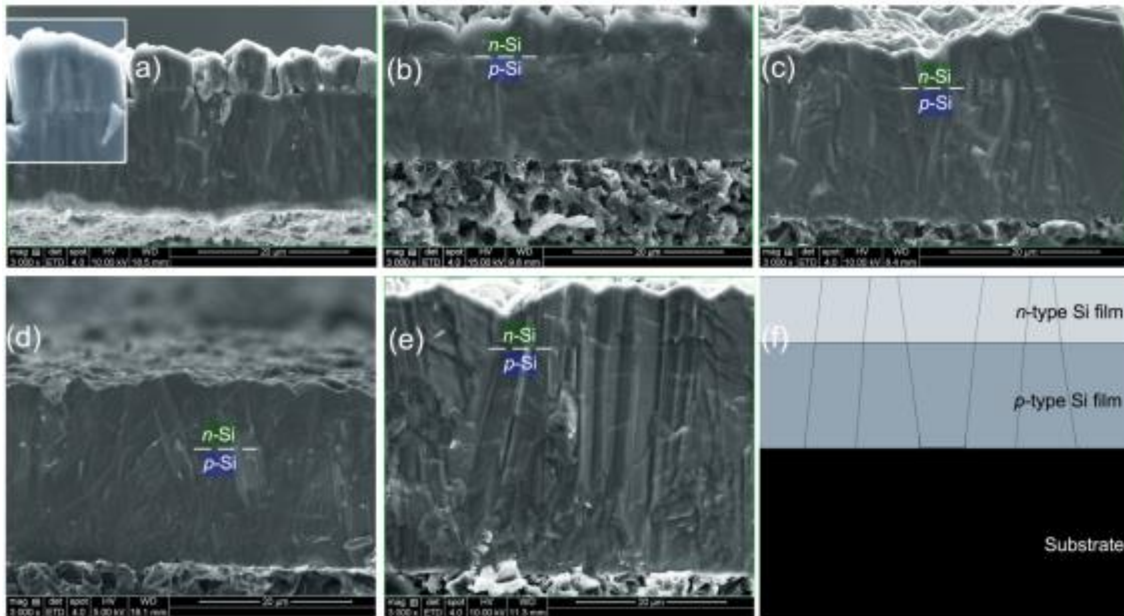

Figure S3. (a)–(e) Typical SEM images of the produced silicon *p*-*n* junction films with different thicknesses. (f) Schematic illustration of the growth process for thin film silicon *p*-*n* junction, the silicon crystal orientation of *p*-Si and *n*-Si can keep consistent.

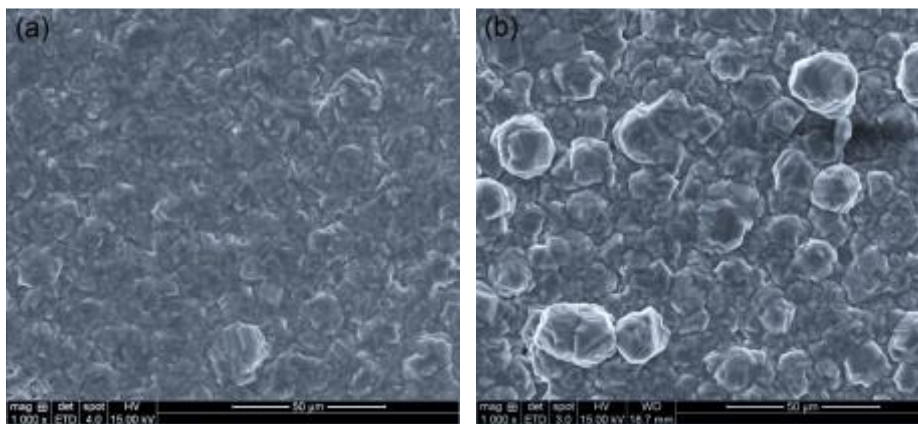

Figure S4. Typical SEM images of the electrodeposited silicon films. (a) Relatively smooth surface with small silicon crystallites and (b) rough surface with larger silicon crystallites.

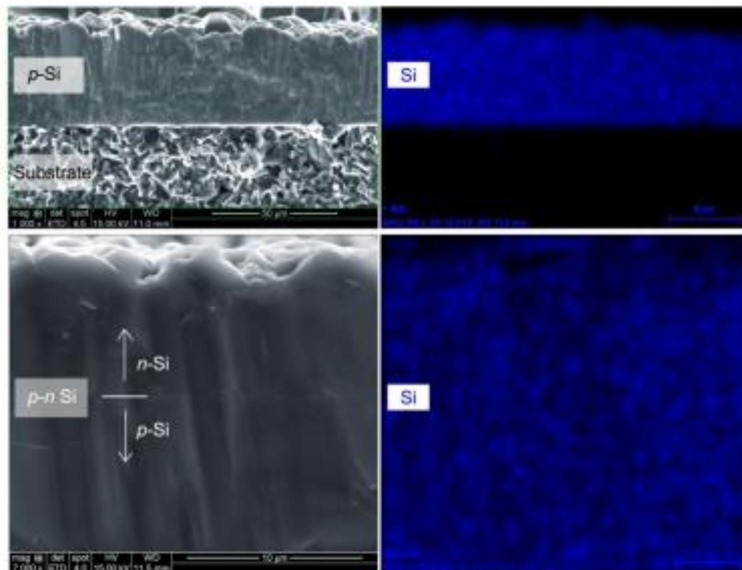

Figure S5. EDS maps of the cross-sections of the produced *p*-type silicon film and the thin film silicon *p-n* junction.

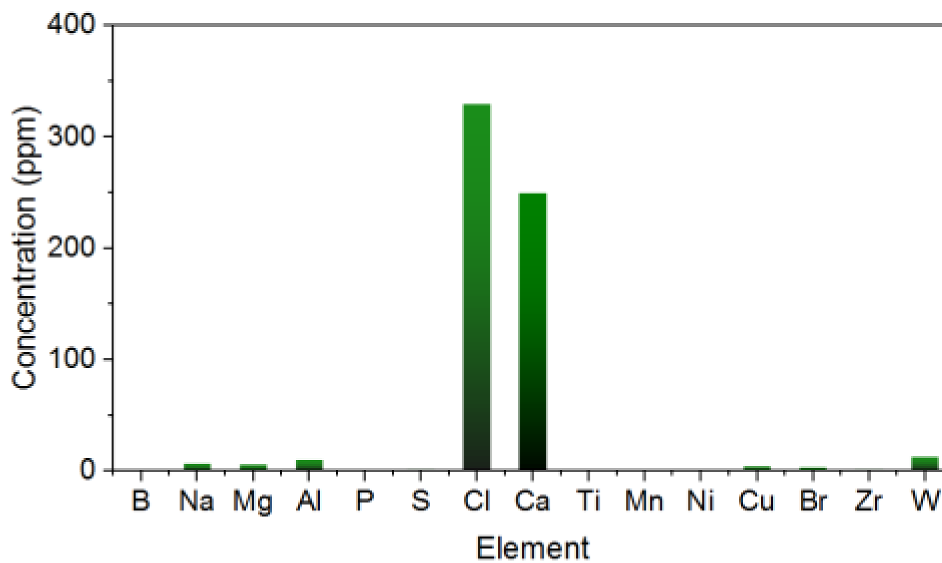

Figure S6. Typical GDMS analysis result of the produced silicon film. Element W is from electrode metal wires.

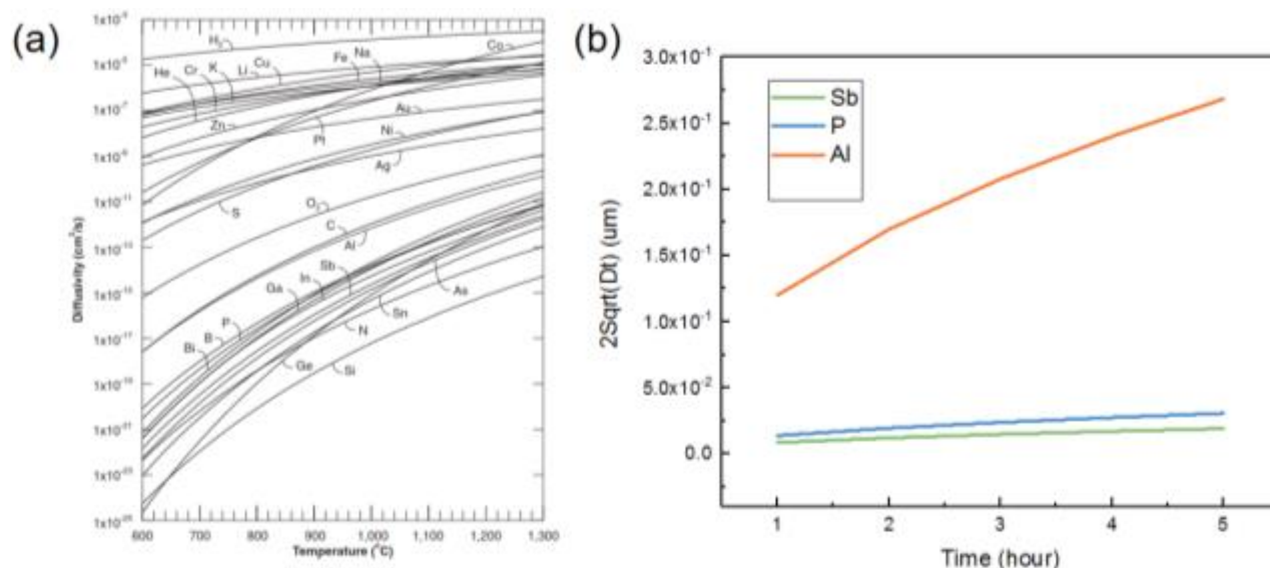

Figure S7. (a) Diffusivities of impurities elements in silicon versus temperature.[6] (b) The calculated effective diffusion length $2(Dt)^{1/2}$ of Sb, P and Al in silicon at 850 °C.

References

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