

Supporting Information

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Electrodeposition of Crystalline and Photoactive Silicon Directly from Silicon Dioxide Nanoparticles in Molten CaCl₂**

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Experimental details

Electrodeposition of silicon was performed in a homemade quartz tube (5 cm dia. and 40 cm long) with a stainless steel cap that has electrode feedthroughs and inlet and outlet valves for Ar gas flow (Fig. S1a). Experimental details have been described in our previous report (S. K. Cho, F.-R. F. Fan, A. J. Bard, *Electrochim. Acta* **2012**, *65*, 57-63). The quartz tube assembled with a stainless steel cap was inserted into a vertical tube furnace and heated to 850°C at increments of 10°C per min. Argon gas was kept flowing over the melt during the electrolysis. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99.5%, Sigma-Aldrich, St. Louis, MO), which was dried in vacuum at 200°C for over 6 h was used as the electrolyte. It was then placed in a cylindrical alumina crucible at the bottom of the quartz tube in the furnace (21100, Barnstead/Thermolyne, Dubuque, IA). The silicon precursor was colloidal nm-sized silicon dioxide (SiO_2 , 5 to 15 nm dia., amorphous, $\geq 99.5\%$, Sigma-Aldrich, St. Louis, MO). The working electrode was a 0.025 cm thick silver foil (2 cm², $\geq 99.998\%$, Alfa Aesar, Ward Hill, MA). The counter electrode was glassy carbon or a graphite rod (0.25 cm dia., Alfa Aesar, Ward Hill, MA). The reference electrode was graphite (0.25 cm dia., Alfa Aesar, Ward Hill, MA) as a QRE. After the experiments were finished, the whole cell was cooled slowly ($\sim 2^\circ\text{C}/\text{min}$) under Ar flow and the electrodes were cleaned and sonicated in water.

The morphology, composition and crystallinity of the Si deposit were characterized with a scanning electron microscope (SEM, Quanta 650 FEG, FEI Company, Inc., Hillsboro, OR), energy dispersive spectroscopy (EDS) (XFlash® Detector 5010, Bruker, Fitchburg, WI), X-ray photoelectron spectroscopy (Kratos XPS, Kratos Analytical Ltd, UK) equipped with a monochromatic Al X-ray source, X-ray diffractometry (XRD) with a D8 ADVANCE (Bruker,

Fitchburg, WI) equipped with a Cu K α radiation source, and time-of-flight secondary ion mass spectroscopy (TOF-SIMS, Ion-Tof GmbH, Münster, Germany) equipped with a bismuth liquid metal primary ion source and cesium sputtering ion source.

The photoactivity of silicon deposit was measured with the PEC cell (Fig. S2b). The electrolyte was acetonitrile (Sigma-Aldrich, St. Louis, MO) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka, Allentown, PA) as the supporting electrolyte and 0.05 M ethyl viologen dication (EV²⁺, Sigma-Aldrich, St. Louis, MO) as the redox reagent. The current and potential of the silicon deposit was measured in the electrolyte under Xe lamp irradiation and in the dark using a three-electrode cell consisting of a platinum counter electrode and a silver QRE. The potential of the silver QRE was calibrated using the EV²⁺/EV⁺ redox couple ($E^0 = -0.449$ V vs. NHE), and all potentials are given versus the normal hydrogen electrode (NHE). UV-visible light was irradiated through the electrolyte solution with a Xe lamp incident light intensity of about 100 mW/cm² at the electrode surface without correction for the solution absorption. The standard Si sample was a silicon wafer (0.27 cm², 3 ohm-cm resistivity, p-type, (100), University Wafer, Boston, MA).

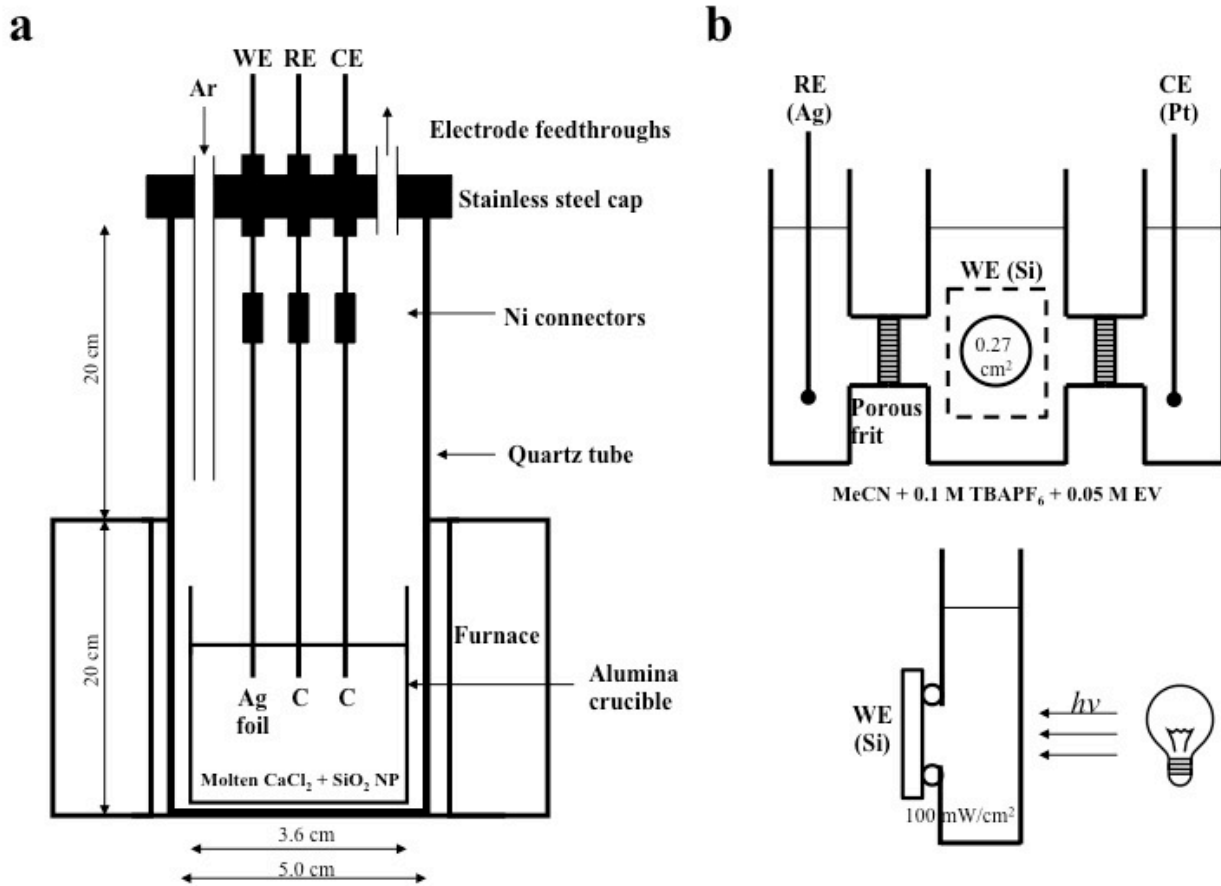


Figure S1. The schematic diagrams of (a) a high temperature electrochemical cell for silicon electrodeposition and (b) a PEC cell for the measurement of the photoactivity of silicon deposit.

Silver electrode in molten CaCl₂ (at 850°C)

Silver, whose use we feel is essential for the quality of the deposit, in fact can be physically unstable in the molten salt due to its relatively low melting temperature (962°C) and high thermal expansion coefficient (18.9 $\mu\text{m}/\text{m}^\circ\text{C}$), and can also be chemically unstable, especially in CaCl₂ media as it can form many low eutectic points with calcium (470 to 655°C). We observed the dissolution of silver at potentials where the reduction of Ca²⁺ occurs, and this region must be avoided in the Si deposition process.

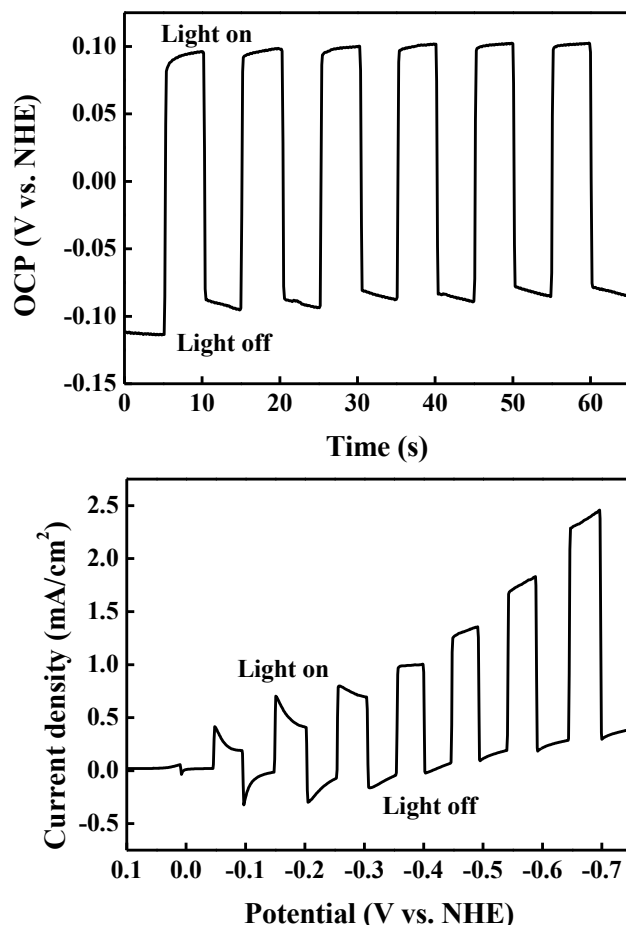


Figure S2. The photoresponse of a silicon wafer (0.27 cm^2 , 3 ohm-cm resistivity, p-type, (100)) in a photoelectrochemical cell. The electric contact was made on the backside of a silicon wafer with silver paste, which gives a contact configuration the same as silicon deposit on silver. The electrolyte was acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate and 0.05 M ethyl viologen dipherchlorate. UV-vis light intensity of 100 mW/cm^2 from a xenon lamp was illuminated on the silicon deposit, which was immersed in the electrolyte solution. The measured photocurrent is slightly lower than the reported values ($5\sim 8 \text{ mA/cm}^2$) of photo-reduction of viologen compounds (p-Si: A. B. Bocarsly, D. C. Bookbinder, R. N. Dominey, N. S. Lewis, and M. S. Wrighton, *J. Am. Chem. Soc.* 1980, 102, 3683. p-GaAs: F.-R. F. Fan, B. Reichman, and A. J. Bard, *J. Am. Chem.* 1980, 102, 1488.) because of a Schottky barrier at the silicon-silver contact.

Production of N-type silicon in molten CaCl₂ (at 850 °C)

In one experiment an n-type silicon deposit was produced (see Supplementary Figure S2). We thought this arose because in this case accidental exposure of the stainless steel components in the cell to elevated temperatures led to Fe outgassing after the completion of the deposition (as indicated by a deposit on the walls of the cell), and perhaps Fe served as a dopant diffusing into the Si. This suggests that the electrical properties of the deposited silicon can be changed by doping during or after silicon deposition, which would be an important property in device fabrication.

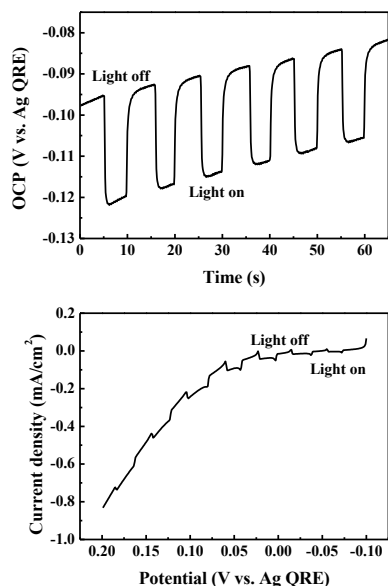


Figure S3. The photoresponse of a silicon deposit, which was measured in a photoelectrochemical cell. The electrolyte was acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate and 0.05 M *N,N,N',N'*-tetramethyl-*p*-phenylenediamine. 100 mW/cm² UV-vis light from a xenon lamp was illuminated on the silicon deposit, which contacted to the electrolyte.

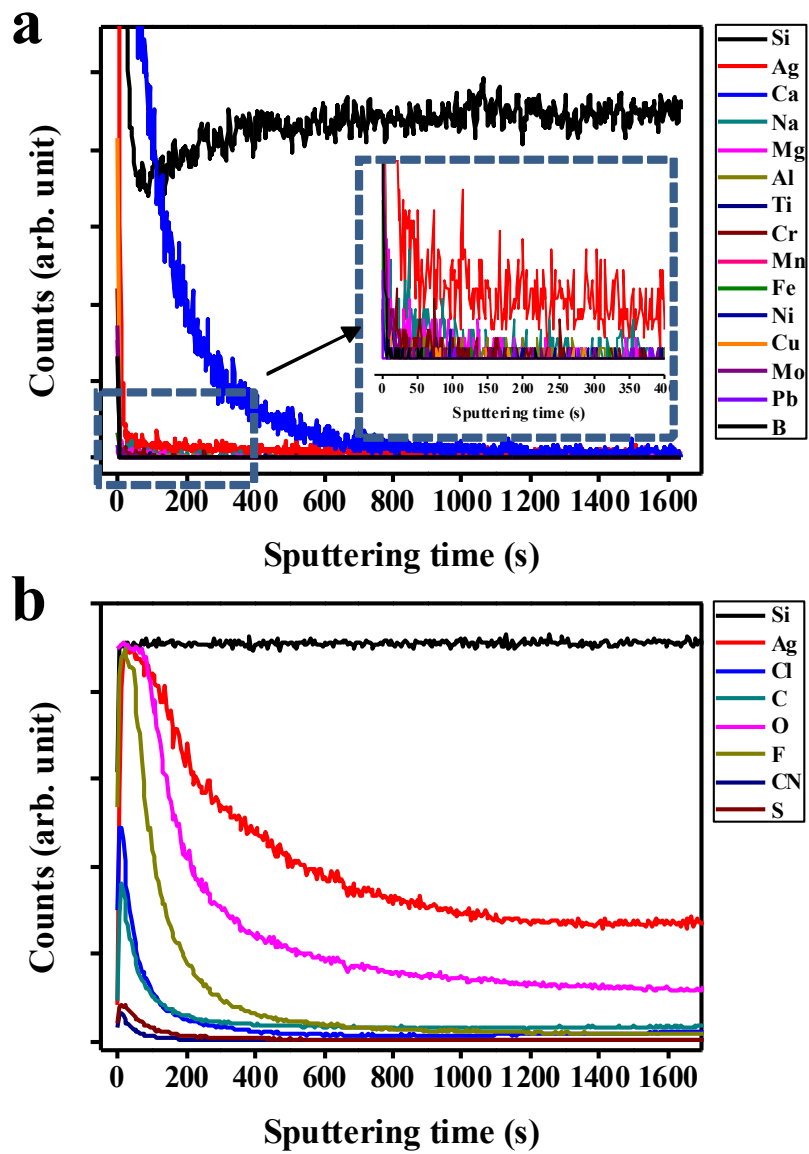


Figure S4. Secondary ion mass spectroscopic depth profiles of silicon deposit in (a) positive ion and (b) negative ion mode.

Table S1. The concentration of trace impurities in silicon deposit analyzed by inductively coupled plasma mass spectroscopy (ICP-MS, provided by Dow Corning).

Element	Concentration (ppm wt.)
B	2
Na	7
Mg	40
Al	14
Ca	793
Ti	67
Cr	44
Mn	47
Fe	383
Ni	22
Zr	12
Mo	173
Sn	5
Pb	2
Be, K, V, Co, Cu, Zn, Nb, Ta, W, U	< 1
Total	1611

ICP-MS analysis: Silicon particles were collected by ultrasonication of silicon deposited silver electrode in acetonitrile solution followed by drying at moderate temperature in an Ar atmosphere. Afterward, the silicon particles were digested using H₂SO₄, HF, HNO₃, and H₂O₂ and the digested solution was heated and reconstituted in 2% HNO₃ and then analyzed directly via ICP-MS. The detection limit of the analysis was 1 ppm wt., and accuracy and precision were estimated to be on the order of ±10% relative.

Table S2. Information of impurity level (ppm wt.) of SiO₂ nanoparticles (provided by Sigma-Aldrich®)

Purity	99.5%
Trace metals	643 ppm wt.
Al	107.5
Ba	0.5
Ca	3.7
Fe	37.1
Mg	0.6
Na	28.8
Sb	8.6
Ti	448.8
Zn	6.3

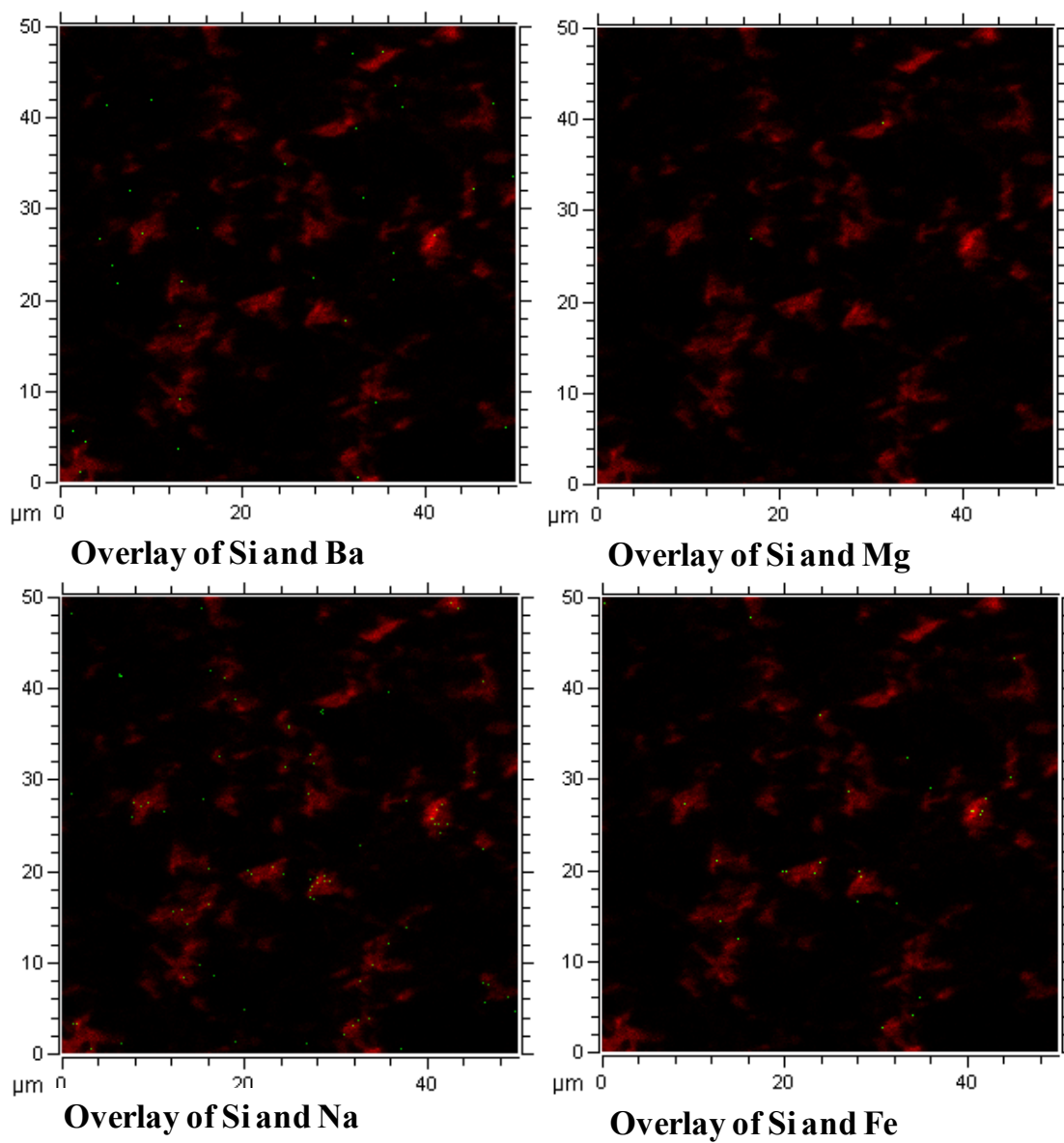


Figure S5. Secondary ion mass spectroscopic elemental mappings of silicon deposit.

Gold electrode in molten CaCl₂ (at 850 °C)

Gold is also a well-known catalyst for VLS silicon growth in the CVD process. In electrodeposition, however, a silicon deposit was not found with a gold electrode, perhaps because it also catalyzes the reduction of Ca²⁺ whereby the predominant deposition of calcium occurs simultaneously with the silicon dioxide reduction (Fig. S6). Moreover, since calcium has a low temperature eutectic point with gold (658°C), the formation of calcium on gold electrode leads to the dissolution of electrode. This was confirmed experimentally.

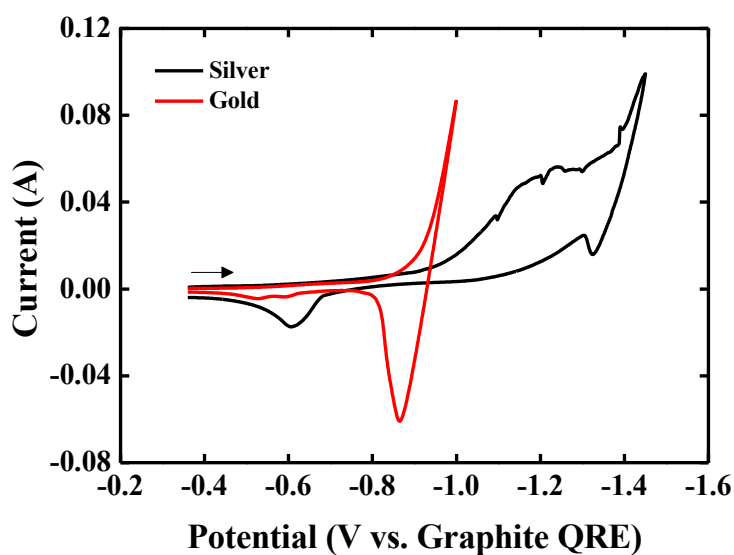


Figure S6. Cyclic voltammograms of silver and gold electrodes ($\approx 2 \text{ cm}^2$) at a scan rate of 20 mV/s in 850°C CaCl₂ melt containing 0.2 M SiO₂ NPs suspension.

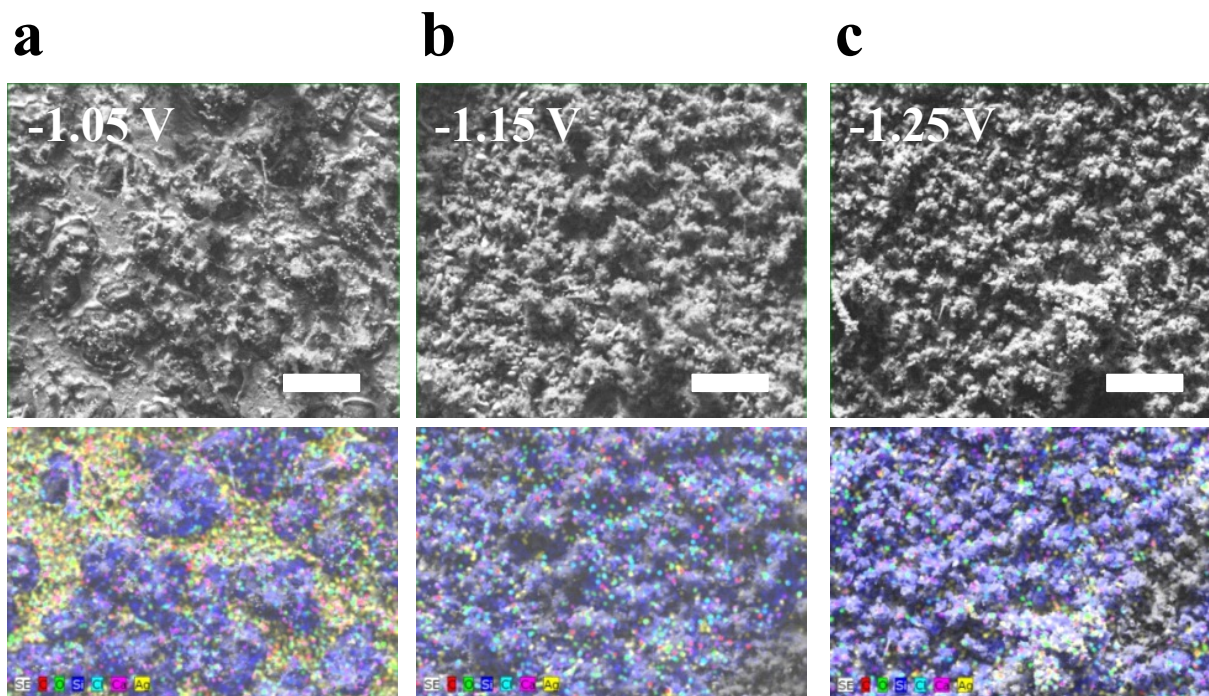


Figure S7. SEM images of Si deposited at different applied potentials (vs. graphite QRE) on silver substrate in 850°C CaCl₂ melt containing 0.2 M SiO₂ nanoparticles. The white bars scale 50 μm.