Anisotropic Electrochemical Lithiation of Single Crystal Silicon Electrodes Assembled in an All-solid-state Battery Configuration

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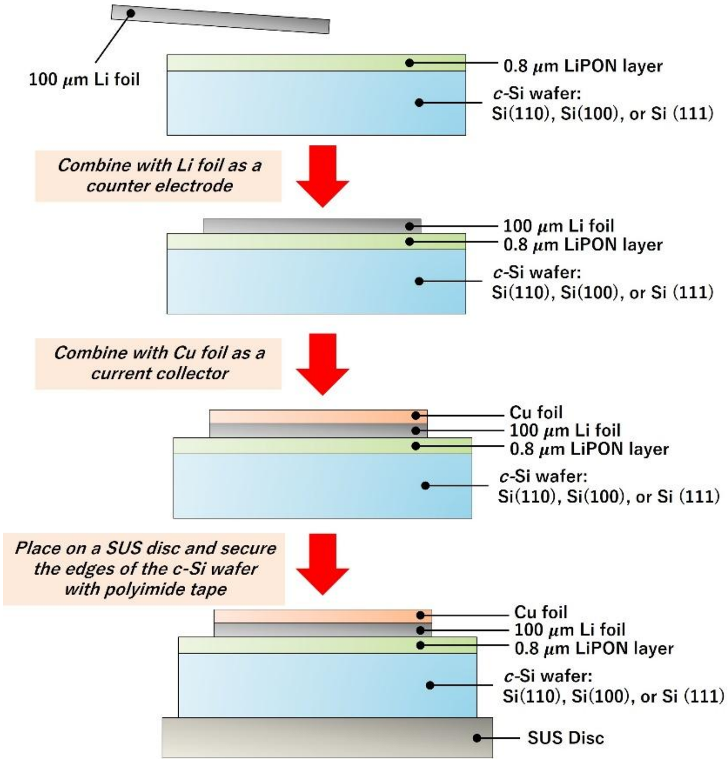
Experimental Section

Sample Preparation

Undoped *c*-Si wafers (Yamanaka Hutech Co., Ltd.) with a resistivity of 1000 Ω·cm and thicknesses of 390 μm for the (110) surface, 540 μm for the (100) surface, and 525 μm for the (111) surface were cut into *c*-Si electrodes with average dimensions of approximately 6 mm × 6 mm, comprising square, rectangular, and trapezoidal shapes. The *c*-Si electrodes were used as received without any pre-treatment. A lithium phosphorous oxynitride (LiPON) solid electrolyte layer with a thickness of ~800 nm was deposited on the *c*-Si electrodes using radio frequency (RF) magnetron sputtering. The RF sputtering was carried out at an Ar/N_2 pressure of 0.4 Pa using a commercial lithium phosphate (Li_3PO_4) as a target, yielding *c*-Si/LiPON samples with different surface orientations of (110), (100), and (111).

All subsequent procedures were carried out in a dry room controlled to a dew point below -50°C, as shown in **Scheme S1**. A piece of Li metal foil (Honjo Metal Co., Ltd.) with a thickness of 100 μm and an average size of approximately 4 mm × 4 mm (rectangular or square) was attached to the LiPON layer of *c*-Si/LiPON samples to yield ASSLIB cells with a configuration of *c*-Si/LiPON/Li. It should be noted that, due to the process described later, the Li foils may extend laterally, and the contact area between the

Li foil and the *c*-Si electrode can become larger than the actual size of the Li foil. Therefore, the Li foils were made smaller than the *c*-Si electrodes to prevent short-circuiting caused by the lateral extension. Then, a Cu foil was placed on top of the Li foil of the *c*-Si/LiPON/Li cell. Finally, the *c*-Si/LiPON/Li/Cu sample was placed on a SUS disk, and its edge was secured with polyimide tape as shown in **Scheme S1**.



Scheme S1. Procedures of *c*-Si/LiPON/Li cell assembly.

Electrochemical Lithiation

After pre-lithiation treatment under a current density of 0.5 μA cm^{-2} at 60 °C for 10 h, electrochemical lithiation was conducted at a current density of 1 μA cm^{-2} at 60 °C for each cell with a different face orientation, where the areal current density was determined based on the contact area between the LiPON layer and the Li metal foil. Typical galvanostatic voltage profiles for *c*-Si(110), (100) and (111) in the *c*-Si/LiPON/Li configuration were shown in **Figure S1**.

While the electrochemical lithiation can be performed at room temperature, it is more stable and reproducible at 60 °C. Accordingly, it was conducted at 60 °C.

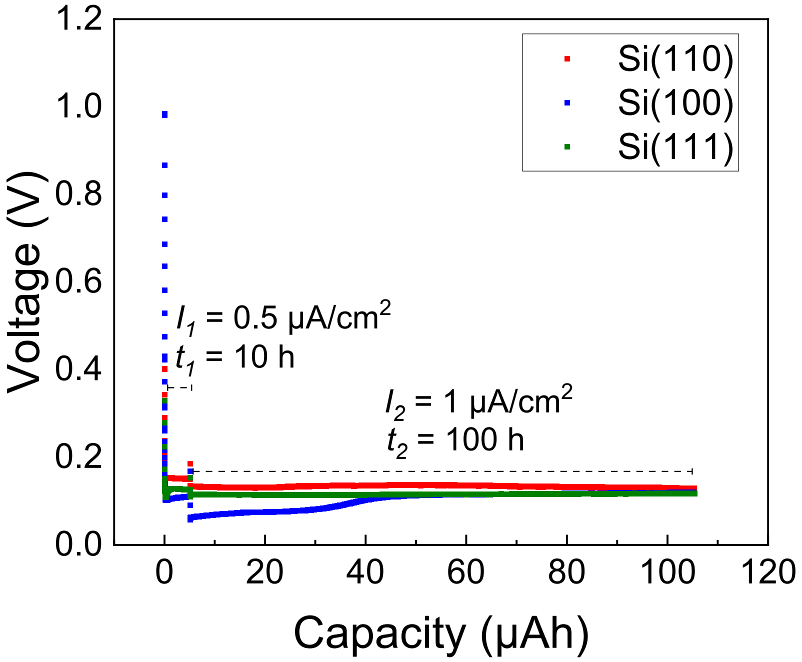


Figure S1. Typical galvanostatic voltage profiles of *c*-Si electrodes: (red) Si(110), (blue) Si(100), and (green) Si(111) assembled in the *c*-Si/LiPON/Li configuration acquired during the first electrochemical lithiation at 60 °C.

After the electrochemical lithiation, the cross-sections of the electrochemically lithiated *c*-Si/LiPON/Li cells were exposed by mechanical cleavage in the Ar-filled glove box (H_2O < 0.1 ppm, O_2 < 0.1 ppm) and transferred to the vacuum chamber for microstructural and surface chemical analyses, to avoid the exposure of generated Li_xSi layers to atmospheric air.

Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Scanning electron microscopy (SEM) analysis combined with energy dispersive X-ray spectroscopy (EDS) mapping was carried out on a JSM-7800F (JEOL Ltd., Japan) equipped with an Aztec EDS system (Oxford Instruments, United Kingdom). SEM images of the cross-sections of the electrochemically lithiated *c*-Si/LiPON/Li cells were acquired under an accelerating voltage of 5 kV. EDS mapping was subsequently performed at an accelerating voltage of 5 kV.

Transmission Electron Microscopy and Selected Area Diffraction

Focused-ion beam equipped with scanning electron microscope (FIB-SEM; SMF2000, Hitachi High-Tech Co., Japan) was used to prepare the samples for transmission electron microscopy (TEM) measurements. A carbon protecting layer with a thickness of ~1 μm was deposited on the electrochemically lithiated *c*-Si/LiPON/Li sample. Ion-milling was performed using a Ga-ion source at an accelerating voltage of 30 kV to trim the sample. The ion-milling was carried out either with or without sample cooling at -100 °C, through a process of trial and error, depending on whether successful ion-milling was achieved, as assessed by the final morphology of the sample.

TEM analyses were conducted on a JEM-ARM200F (JEOL Ltd., Japan) after transferring the lithiated *c*-Si/LiPON/Li sample prepared on the FIB-SEM instrument via an air-protected sample holder. TEM imaging was conducted at an accelerating voltage of 200 kV in the scanning TEM (STEM) mode. Prior to the TEM and selected area electron diffraction (SAED) analyses, EDS mapping was initially performed under an accelerating voltage of 200 kV to identify each component in the lithiated *c*-Si/LiPON/Li sample. SAED analysis was carried out using an aperture of ~200-600 nm to obtain the diffraction patterns, which were further used to determine the phases of the unreacted *c*-Si electrodes and the Li_xSi layers. Annular dark-field (ADF) and bright-field (BF) STEM images were collectively acquired at the *c*-Si/Li_xSi interfaces to provide compositional variations and morphological features at the interfaces.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was performed on a VersaProbe II (ULVAC-PHI, Japan). A monochromatic Al-Kα (1486.6 eV) source operated at 25 W power and 15 kV accelerating voltage was used as an incident X-ray with a spot diameter of ~100 μm. The hemispherical photoelectron analyzer is positioned at a 45° take-off angle. The base pressure of analysis chamber was maintained better than 1×10^{-7} Pa during the measurements. Before recording the photoelectron spectra, X-ray induced secondary electron images were acquired to capture the generated Li_xSi layer. For each sample, XPS measurements were performed at a minimum of 10 analysis points with interpoint intervals of ~20-50 μm. All measurements were performed at the cross-sections of the electrochemically lithiated *c*-Si/LiPON/Li cells without Ar^+ sputtering. The photoelectron spectra in the Si 2p and C 1s regions were acquired, and the binding energies of the obtained spectra were calibrated with reference to the C 1s peak at 285 eV, assigned to the hydrocarbon species.

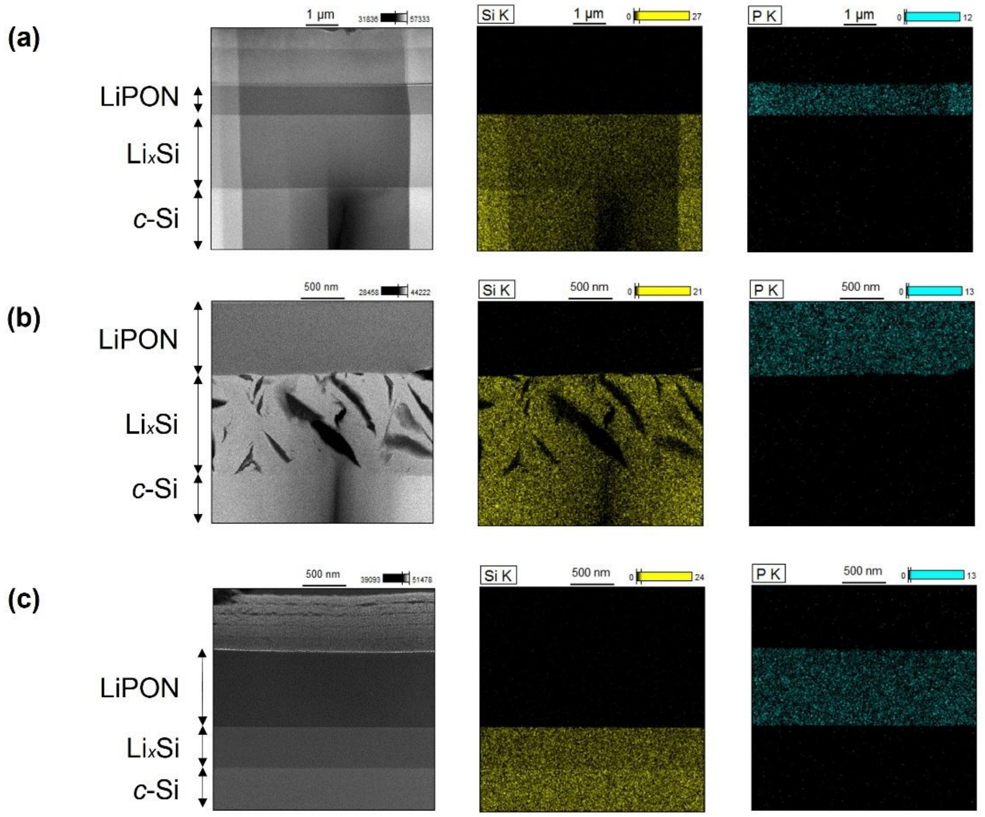


Figure S2. SEM images and EDS mappings of cross-section polished electrode surfaces after the electrochemical lithiation for TEM analysis: **(a)** Si(110) surface, **(b)** Si(100) surface, and **(c)** Si(111) surface. In the EDS maps, the Si and P maps are displayed.

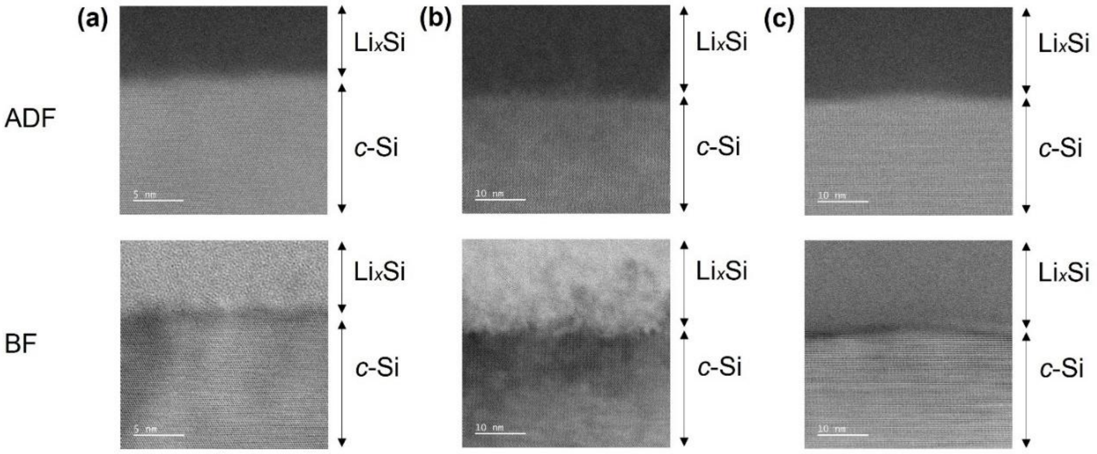


Figure S3. ADF and BF STEM images of the Li_xSi/*c*-Si interfaces in electrochemically lithiated **(a)** Si(110), **(b)** Si(100), and **(c)** Si(111) surfaces.

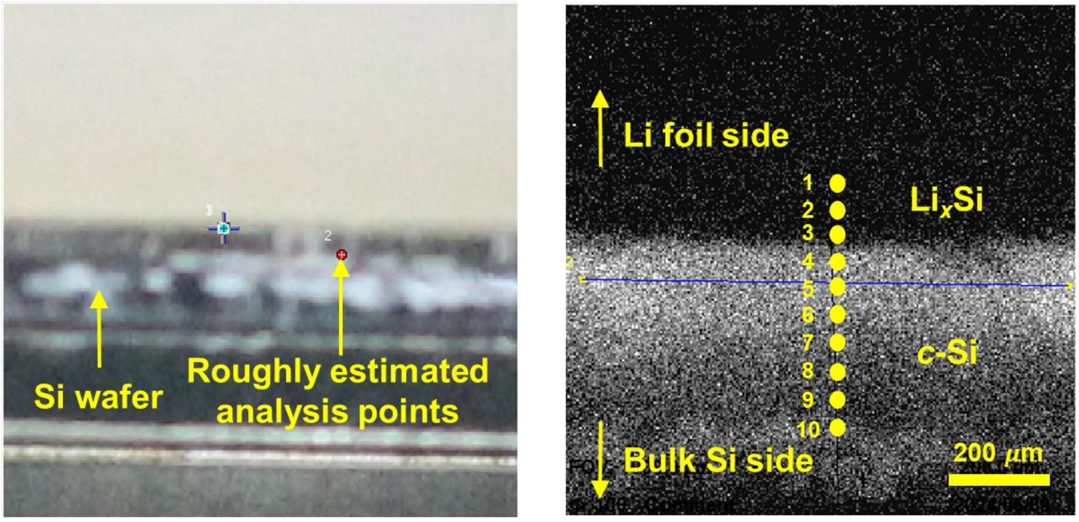


Figure S4. Typical optical (left) and X-ray induced secondary electron images (right) of the cross-section of the electrochemically lithiated *c*-Si electrode together with roughly estimated analysis points.

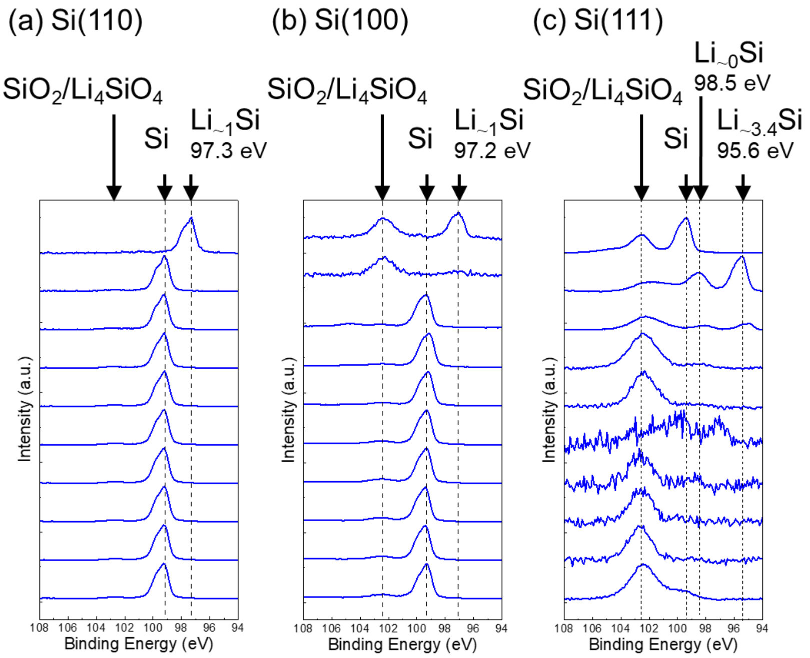


Figure S5. A series of Si 2p photoelectron spectra of cross-sections of electrochemically lithiated *c*-Si electrodes measured at 10 analysis points (typical optical and X-ray induced SEM images are shown in **Figure S4**): **(a)** Si(110) **(b)** Si(100) and **(c)** Si(111).

Delithiation Behaviors

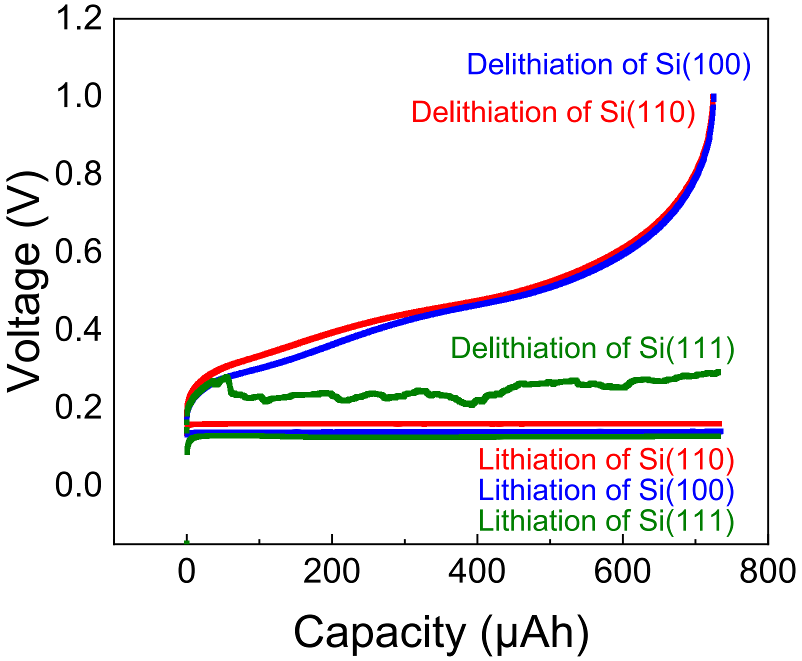


Figure S6. Typical galvanostatic voltage profiles of *c*-Si electrodes: (red) Si(110), (blue) Si(100), and (green) Si(111) assembled in the *c*-Si/LiPON/Li configuration acquired during the electrochemical lithiation and delithiation at a current density of 10 μA cm^{-2} at 60 °C.

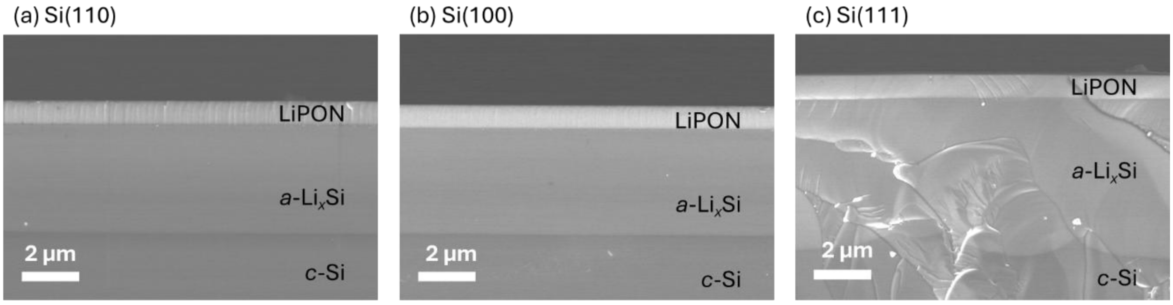


Figure S7. Cross-sectional SEM images of *c*-Si electrodes after the electrochemical lithiation and delithiation at a current density of 10 μA cm^{-2} at 60 °C, observed by SEM (S-4800, Hitachi): **(a)** Si(110) **(b)** Si(100) and **(c)** Si(111).