Supporting Information

Ultrafast chemical lithiation of single crystalline silicon nanowires: in-situ characterization and first principles modeling

Jong-Hyun Seo^{a,b,1}, Chia-Yun Chou^{c,1}, Yu-Hao Tsai^c, Yigil Cho^d, Tae-Yeon Seong^b, Woo-Jung Lee^e, Mann-Ho Cho^e, Jae-Pyoung Ahn^a, Gyeong S. Hwang^{c,f,*} and In-Suk Choi^{d,*}

Part 1. Supplementary experimental information

1. Fabrication of single crystalline Si nanowires

Si NWs with [111] axial orientation were synthesized on the Si (111) substrate by the vapor–liquid–solid (VLS) method using an ultrahigh vacuum chemical vapor deposition (CVD) system as shown in Figure S1(a) and (b). Their dimension is approximately 2-3 μ m in length and 70-110 nm in diameter. A 2 nm thick Au film (as a catalyst) was deposited on a cleaned Si (111) substrate in a metal growth chamber at a growth pressure of ~5 × 10⁻⁷ Torr by thermal evaporation. The sample was transferred to the main chamber and annealed at a pressure of ~1 × 10⁻⁸ Torr for 5 min, resulting in the formation of Au-Si alloy droplets from the Au film on the Si substrate. After the formation of droplets, Si NWs were synthesized by filling the main chamber with a mixture of SiH₄ as precursors, and H₂ as the carrier gas, while maintaining a fixed total pressure of 2 Torr by a feedback system using a throttle valve and a baratron gauge. The process temperature was set to 400-450°C at Au-Si cutectic temperatures. As shown in Figure S1(c), the vertically grown Si nanowire has its [111] axial orientation with hexagonal cross-section surrounded by (110) planes. The grown NWs were cleaned with a dilute HF solution before chemical lithiation to remove residual gold atoms on the surface which is typically formed on the surface during VLS process [S1-S4].



Figure S1. (a) As-grown Si nanowires by chemical vapor deposition with gold catalyst. Their dimension is approximately 2-3 μ m in length and 70-110 nm in diameter. (b) the enlarged side view of crystalline (pristine) Si nanowire before lithiation and (c) TEM image of a Si nanowire (cross-section). Grown direction is <111> with clearly shown six-fold {110} side planes.

2. In-Situ direct contact lithiation

The direct solid state lithiation test without an external electrical potential was performed using a nanomanipulator (MM3A, Kleindiek) installed in focused ion beam system (FIB, Quanta 3D, FEI). We first chose a Si nanowire on the substrate in the Figure S1 (a); fixed the projected end of the Si nanowire to the nanomanipulator tungsten tip by Pt deposition in the FIB chamber using electron beam; and then fractured the other side from the substrate by wiggling the manipulator. Subsequently, we translated the harvested Si NW to the bulk Li and made direct contact of the fractured side end of the Si NW to the surface of the bulk Li as shown in the Figure S2. The bulk Li was cut into pieces by a micro-blade inside the FIB chamber to prepare fresh surface without oxidation.



Figure S2. Schmematics of In-situ direct contact chemical lithiation. The Si NW attached to the manipulator make direct contact to the surface of the bulk Li

3. Cross-sectional view of litheated Si nanowire

Figure S3 shows the cross-section of the nanowire cut by Focused Ion Beam after lithiation. We can clearly see that the initial hexagonal cross-section of the Si nanowire with the 110 axial axis in Figure S1 (c) becomes circular after lithiation.

By further FIB cutting, we prepared the cross-sectional TEM sample as shown in Figure S4, The SAD pattern of the cross section indicates the amorphous structure of the fully lithiated Si nanowire. The EELS spectroscopy analysis at the center of the cross-section exhibited lithium peaks which implied the lithiation down to the center of the nanowire. Hence we concluded that our Si nanowire were lithiated down to the center with amorphization.



Figure S3. (a) and (b) the cross-section of the nanowire cut by Focused Ion Beam after lithiation.



Figure S4. (a) HADFF image, (b) SAED pattern and (c) EELS spectroscopy analysis of the cross section of the lithiated Si nanowire. The SAED pattern showed amorphous structure of the lithiated Si nanowire. EELS result confirm the lithiation through the center of the nanowire.[S5]

4. Volume Expansion during lithiation

The volume expansion was calculated based on the radial expansion. Since the wire was radially expanded, the increase of the cross-sectional area was equivalent to that of the volume. The cross-sectional area was estimated by measuring the diameter of the nanowire before and after lithiation from the in-situ SEM images as shown in the Figure S5. It should be noted that the measured width of the Si nanowire may represent the different side in the hexagonal cross section depending on the perspective. Here, we assumed that the width we observed from the side view is the largest side in the hexagonal cross section. Hence the area of the hexagonal cross section can be underestimated, which may result in the overestimation of the area expansion. Based on a representative hexagonal cross section given in the Figure S1 (c), we calculated the area of the hexagonal cross section with the measured width from the side view. In contrast, the circular cross section of the lithiated Si nanowire was easily calculated from the width which corresponds to the diameter of the circular cross section. As denoted in the Figure S5, the volume expansion of the fully lithiated part of the nanowire was estimated of 330%. [S6] We also indicated the volume expansion by 60% to 127 % behind the reaction front, where the alloy composition is expected to be around x = 0.7 - 1.5 (in *a*-Li_xSi) according to the previous literature. [S7]



Figure S5. The volume expansion during lithiation process was estimated based on the increase of the diameter. The low volume expansion near the reaction front implies the low concentration of Li of Li-silicide compared to the fully lithiated part.

5. References

- S1. S. H. Oh, K. V. Benthem, S. I. Molina, A. Y. Borisevich, W. Luo, P. Werner, N. D. Zakharov, D. Kumar, S. T. Pantelides, S. J. Pennycook, *Nano Lett.* 2008, *8*, 1016.
- S2. J. B. Hannon, S. Kodambaka, F. M. Ross, R. M. Tromp, Nature 2006, 440, 69.
- S3. P. Werner, N. D. Zakharov, G. Gerth, L. Schubert, U. Gösele, *Int. J. Mater. Res.* 2006, 97, 1008.
- S4. L. Cao, B. Garipcan, J. S. Atchison, C. Ni, B. Nabet, J. E. Spanier, Nano Lett. 2006, 6, 1852.
- S5. X. H. Liu, H. Zheng, L. Zhong, S. Huang, K. Karki, L. Q. Zhang, Y. Liu, A. Kushima, W. T. Liang, J. W. Wang, J. H. Cho, E. Epstein, S. A. Dayeh, S. T. Picraux, T. Zhu, J. Li, J. P. Jullivan, J. Cumings, C. Wang, S. X. Mao, Z. Z. Ye, S. Zhang, J. Y. Huang, *Nano Lett.* 2011, *11*, 3312.
- S6. S. W. Lee, M. T. McDowell, J. W. Choi, Y. Cui, Nano lett. 2011, 11, 3034.

S7. X. H. Liu, J. Y. Huang, Energy Environ. Sci. 2011, 4, 3844.

Part 2. Supplementary computational information

1. Computational methods

Quantum mechanical calculations reported herein were performed on the basis of density functional theory (DFT) within the generalized gradient approximation (GGA-PW91) [S1], as implemented in the Vienna Ab-initio Simulation Package (VASP) [S2-S4]. The projected augmented wave (PAW) method with a plane-wave basis set was used to describe the interaction between core and valence electrons. An energy cutoff of 350 eV was used for geometric optimization of model structures for (i) *a*-Si NW in direct contact with Li [Figure S6 (a)], (ii) *a*-Si/Li interface [Figure S6 (b)], (iii) *a*-LiSi and *a*-Li₂Si, and (iv) *a*-Li₄Si/Si(110) interface [Figure 4]; all atoms were fully relaxed using the conjugate gradient method till residual forces are smaller than 5×10^{-2} eV/Å. For Brillouin zone sampling, sufficient *k*-point mesh was used in the scheme of Monkorst-Pack [S5]. To simulate the diffusion and chemical lithiation processes, ab initio molecular dynamics (AIMD) simulations were performed at the temperatures of interest; a time step of 1 *f*'s was used while the temperature was controlled via Nose-Hover thermostat.

The dimensions and compositions of the model structures employed are as follows: (i) As illustrated in Figure S6 (a), the initial model for *a*-Si NW in direct contact with Li was prepared by introducing a 10-Å-thick vacuum gap into the *a*-Li (256 atoms)/*a*-Si (128 atoms) interface structure in the *z*-direction; to simulate a laterally extended surface in the *x*- and *y*-directions, we employed the repeated-slab approach by applying periodic boundary conditions to the 43.32 × 11.18 × 21.65 Å³ supercell in all dimensions. (ii) The *a*-Si/Li interface was prepared by stacking a 64-atom *a*-Li bulk model on top of a 64-atom *a*-Si bulk model; after geometry optimization, the dimensions of the supercell are $13.712 \times 12.9569 \times 13.1293$ Å³.

(iii) The model structures for bulk *a*-LiSi (*a*-Li₂Si) alloys consisted of 32 (43) Li and 32 (21) Si atoms were created based on AIMD simulations as previously described in [S6]. (iv) The initial structure for the *a*-Li₄Si/Si(110) interface was prepared by stacking an *a*-Li₄Si bulk model on top of a Si (110) supercell in the *z*-direction ([110] direction). The *a*-Li₄Si model structure consisted of 51 Li and 13 Si atoms has dimensions of $10.914 \times 11.5761 \times 8.5576$ Å³. We used the GGA-optimized lattice constant of 5.457 Å for *c*-Si [S7], and the 96-atom Si (110) supercell considered here has dimensions of $10.914 \times 11.5761 \times 15.5761$ Å³. The *a*-Li₄Si/Si(110) system was fully relaxed and then annealed at 500 K for 1 *ps* to allow sufficient atomic rearrangement, followed by geometry optimization.

2. The spontaneous chemical lithiation process

In our attempt to investigate a SiNW near the onset of lithiation, a model cell consisting of *a*-Si in direct contact with Li in vacuum was constructed, and annealed at 300 K for 8 *ps* and subsequently a slightly higher temperature 500 K for 4 *ps* to speed up the lithiation process. The atomic structures of *a*-Si nanowire at early stages of lithiation are shown in Figure S6 (a). Upon annealing, we notice the preferential Li diffusion along *a*-Si surfaces with some degree of atomic mixing at the Li/Si interface. The more favorable Li incorporation in the surface region than in the bulk is partly attributed to the surface stabilizing effect of Li atoms as discussed in our previous work [S8]. Once the *a*-Si surfaces become nearly saturated with a monolayer of Li atoms, we start to see gradual Li diffusion into the core region, as Si–Si bonds are broken accompanied by slight radial volume expansion. In addition, to elucidate the Li-Si mixing process, an *a*-Li/Si supercell was constructed and annealed at 800 K. Starting from the initial configuration (t = 0 ps), the supercell after different MD time steps (t = 1, 2, 6, 16 and 20 *ps*) resembling different stages of interfacial mixing are shown in Figure S6 (b). Driven by the concentration difference, Li atoms promptly diffuse across the *a*-Li/Si interface

(as indicated by the red dashed-line in the upper panel, t = 0 to 2 *ps*) into the *a*-Si matrix. Upon Li incorporation, the negative heat of formation [S6] leads to favorable mixing/alloying of Li and Si atoms in the subsequent MD time steps. In the process, due to the excess charge transferred from Li, the tetrahedrally bonded *a*-Si is weakened and disintegrates into network of lower-connectivity accompanied by the substantial volume expansion (the *a*-Si network gradually expand across the *a*-Li/Si interface into the space that was originally filled with Li atoms). Around t = 20 ps, Li atoms are fully dispersed while the Si network exhibits typical features (rings, chains, dimers and isolated Si) of a well-mixed *a*-LiSi alloy, as consistent with previous calculations [S6]. Our results clearly demonstrate that the concentration gradient (chemical potential) and the negative heat of formation are sufficient to drive the spontaneous Li-Si mixing.



Figure S6. (a) Atomic structures of *a*-Si nanowire at early stages of lithiation, where *a*-Si is in direct contact with Li in vacuum, and annealed at 300 K for 8 *ps* and subsequently 500 K for 4 *ps* to speed up the lithiation process. (b) Spontaneous mixing between Li and Si atoms at the *a*-Li/Si interface. The system was annealed at 800 K for 20 *ps*, and the red dashed-line indicating the initial position of the *a*-Li/Si interface.

3. Sample calculation to show how D_{Li} at room temperature is derived, and D_{Li} increases with increasing Li contents.

For *a*-Li₂Si and *a*-LiSi alloys, AIMD simulations were performed to estimate D_{Li} at 800, 900, 1000 and 1100 K. For each alloy composition, three samples were averaged to calculate the mean square displacements of Li atoms (MSD = $|R_i(t) - R_i(0)|^2$, where $R_i(t)$ is the position of atom *i* at time *t*). From the MSD profiles shown in the insets of Figure S7, D_{Li} values were obtained using the Einstein relation, D = $\langle MSD \rangle / 6t$; the angular bracket denotes an ensemble average over the AIMD interval. Here, the MD duration of 18 *ps* (12 *ps*) for *a*-Li₂Si (*a*-LiSi) appears to be sufficient to obtain well-converged results; disregarding the first 6 *ps* (4 *ps*),

linear fits over a time interval of the following 12 *ps* (8 *ps*) yield D_{Li} values at the corresponding temperatures. Using these values, an *Arrhenius* plot of $\ln(D_{Li})$ versus 1000/T was constructed based on $D = D_0 \exp(-E_a/kT)$, where D_0 is the prefactor, E_a is the activation energy, *k* is the Boltzmann constant, and *T* is the temperature. By linear extrapolation of the *Arrhenius* plot in Figure S7, the room-temperature D_{Li} in *a*-Li₂Si and *a*-LiSi are estimated to be around $2.32 \times 10^{-8} \text{ cm}^2/\text{s}$ and $5.16 \times 10^{-10} \text{ cm}^2/\text{s}$, respectively.



Figure S7. Arrhenius plot based on the predicated D_{Li} values in amorphous *a*-Li₂Si and *a*-LiSi at 800 K, 900 K, 1000 K and 1100 K. The corresponding mean square displacements (MSD) profiles are shown in the inset.

4. References

- S1. P. E. Blochl, Phys. Rev. B 50 (1994) 17953-17978.
- S2. G. Kresse, J. Hafner, J. Phys. Rev. B 47 (1993) 558-561.
- S3. G. Kresse, J. Furthmuller, Comput. Mater. Sci. 6 (1996) 15-50.

- S4. G. Kresse, J. Furthmuller, J. Phys. Rev. B 54 (1996) 11169-11186.
- S5. H. J. Monkhorst, J. D. Pack, Phys. Rev. B 13 (1976) 5188-5192.
- S6. H. Kim, C. -Y. Chou, J. G. Ekerdt, G. S. Hwang, J. Phys. Chem. C 115 (2011) 2514-2521.
- S7. H. Kim, K. E. Kweon, C. -Y. Chou, J. G. Ekerdt, G. S. Hwang, J. Phys. Chem. C 114 (2010) 17942-17946.
- S8. C. -Y. Chou, G. S. Hwang, Surf. Sci. 612 (2013) 16-23.

Supporting information movie captions

Movie S1: Real time chemical lithiation of a Si [111] nanowire. The SiNW was brought into direct contact with Li metal at room temperature in SEM, without an external electric field. The lithiation speed is around 1082 nm/s, which is extremely faster compared to the previous in-situ tests. The process is controlled by diffusion kinetics.