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An atomistic perspective on lithiation-induced stress in silicon nanopillars

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ABSTRACT

We present reactive force field simulations that provide an atomistic understanding of lithiation-induced stress generation in silicon nanopillars. We investigate two-phase lithiation by developing a new protocol for simulation of formation and movement of an atomically sharp phase boundary. This protocol involves the layer-by-layer insertion of lithium atoms in the silicon lattice. The simulation results show the development of compressive stresses at the phase boundary and hoop tension near the surface of a Si nanopillar, thereby highlighting the atomistic underpinning of lithiation-induced stress. The work enables a direct mapping between atomistic and continuum modeling of lithiation-induced stress in large-volume-change electrodes.

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As a promising anode material for high-performance lithium-ion batteries, silicon (Si) has the highest known theoretical specific capacity of lithium (Li) [1,2]. During lithiation, this high capacity results in dramatic volume changes, ~300%, causing stress generation and fracture in Si anodes [1,3,4]. The problems of lithiation-induced stress and fracture have attracted considerable attention in recent years. *In situ* transmission electron microscopy (TEM) and scanning electron microscopy (SEM) experiments have revealed the lithiation process [5] and lithiation-induced fracture in *c*-Si nanomaterials [3,6]. These experiments show that the lithiation of crystalline Si (*c*-Si) nanopillars and nanoparticles features a two-phase mechanism [5]. During the two-phase lithiation, the lithiated (Li_xSi) and pristine (*c*-Si) phases are separated by an atomistically sharp phase boundary with a thickness of ~1 nm [5,7], and the chemical reaction at the phase boundary is the rate-limiting step that controls the lithiation kinetics [5]. This mechanism results in a core-shell structure, in which an amorphous Li_xSi (*a*-Li_xSi) shell encloses a *c*-Si core [4,6]. As the lithiation proceeds, surface cracks form in the lithiated shell, leading to fracture and pulverization of the anodes [3,4,8].

While continuum modeling based on the classical finite strain theory and nonlinear diffusion approximation has provided some interpretation of stress generation in lithiated *c*-Si anodes [9–13], bridging the gap between the atomic-scale physics and the continuum-level mechanical behavior still presents major challenges. Particularly, the mechanisms of dynamic lithiation and associated stress generation in *c*-Si remains elusive, due to a multitude of concurrent processes involved, including anisotropic chemical reactions, crystalline to amorphous phase transformation, species diffusion, irreversible and non-affine deformation, stress generation, as well as cracking and fracture. These processes depend sensitively on the atomic-scale physics, making modeling at the atomic scale well suited for studying lithiated *c*-Si nanomaterials. For example, first principles calculations have been performed to investigate the thermodynamic and the kinetic aspects of lithiation with high accuracy [14–16], but they are limited to small systems and short timescales. Other atomistic approaches such as interatomic-potential-based molecular dynamics simulations enable studies in larger systems and at longer timescales. They have shown the peeling of {111} atomic facets and amorphization processes at the interface [17–19]. Kinetic Monte Carlo simulations have revealed morphological evolutions of electrodes with the required prior knowledge of elementary reaction mechanisms [20].

In this work, we report an atomistic simulation study of the mechanical response of a ⟨111⟩-oriented *c*-Si nanopillar during lithiation. We perform the simulations using LAMMPS and employ a recently developed reactive force field (ReaxFF) to describe the atomic interaction in Li—Si systems [21–23]. The ReaxFF has demonstrated the capability of describing chemo-mechanical processes, such as lithiation-induced stress generation in Si films [23] and the formation of phase boundaries between pristine and lithiated Si at high temperatures [17,24]. The molecular dynamics simulations in Refs. [17, 24] focused on *flat* phase boundaries in Si films and thus could not address an important effect of the *curvature* of phase boundary on the stress generation and ensuing

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degradation in lithiated Si nanopillars and nanowires. Here we focus our work on understanding the stress evolution during lithiation of the nanopillar. Simulation results elucidate the atomistic origin of lithiation-induced stresses and provide atomistic insight into the mapping between atomistic and continuum modeling.

The lithiation of a ⟨111⟩-oriented *c*-Si nanopillar has been shown with no elongation in the axial direction [25], but nearly isotropic expansion within the cross section where six equivalent ⟨110⟩ directions are present (Fig. 1a). To construct the initial structure, we create a thin slice of a cylindrical nanopillar containing 14,216 Si atoms (Fig. 1a) and impose the periodic boundary condition in the cylinder axial direction (*z* direction). The cylinder has a diameter of ~10 nm and a thickness of ~4 nm. The dimensions are sufficiently large for capturing the variation of different stress components as a function of radial distance, *r*. Before lithiation, we perform an energy minimization of the initial system using the conjugate-gradient method. Since lithiation induces negligible axial expansion in *c*-Si nanopillars [26], we apply the plane strain condition by fixing the thickness of the system during the entire lithiation process.

In situ TEM experiments have shown that the chemical reaction of Li and Si at the phase boundary leads to solid-state amorphization, which occurs through layer-by-layer disruption of the *c*-Si lattice [5]. At the reaction interface between the *c*-Si and the amorphous product of Li_xSi, inserted Li atoms break Si—Si covalent bonds and cause the *c*-Si lattice to dissociate into single Si atoms and Si—Si pairs surrounded by Li atoms [5]. Based on these TEM results, we develop a Li-insertion protocol to simulate the two-phase lithiation in the ⟨111⟩-oriented *c*-Si nanopillar. This protocol allows layer-by-layer insertions of Li atoms into a *c*-Si lattice near the two-phase interface, as schematically illustrated in Fig. 1b. The protocol enhances the computational efficiency of simulating phase boundary migration and avoids the long-time diffusion dynamics that is nearly impossible to simulate by direct molecular dynamics simulations. The protocol has the following steps (with details given in Supplementary Fig. S1).

i) Identify the position of the moving phase boundary in the cross section of the nanopillar. The phase boundary can be determined by calculating the Li concentration profile in the simulation cell. At the beginning of a simulation, lithiation starts from the nanopillar surface, producing *a*-$Li_{3.75}Si$ in the surface layer. As lithiation proceeds, the phase boundary moves radially toward the center of the nanopillar, and this boundary involves an abrupt change of Li concentration, *x*, from 0 and 3.75.

ii) Insert new Li atoms into the identified phase boundary layer. To simulate the disruption of the *c*-Si lattice due to reaction with inserted Li atoms, we search for largest voids in the phase boundary layer and add a Li atom at the center of each of these voids. We also check the coordination number of the surrounding atoms of each void to ensure the local bonding environment in our *a*-$Li_{3.75}Si$ is similar to the *a*-$Li_{3.75}Si$ generated by the melt-quenching method in our previous work [23].

iii) Relax the structure and accordingly lithiation-induced stresses for the atomic configuration obtained in step ii). With the newly added Li atoms, the local stresses are built up. We relax the system using the conjugate-gradient energy minimization method. The ReaxFF enables the simulations of atomic relaxation processes through bond breaking, formation, stretching and compression. During relaxation, the layer with the newly inserted Li atoms expands in the radial direction, and the resulting change in the Li concentration profile indicates the migration of the phase boundary.

iv) Return to step i) with the new configuration until the desired state of lithiation is achieved in the nanopillar.

By following the above protocol, we are able to simulate the solid-state amorphization from *c*-Si to *a*-$Li_{3.75}Si$ and the migration of the phase boundary in between. The protocol enables selective Li insertions and provides the flexibility of simulating isotropic and anisotropic migration of the phase boundary. Therefore, the protocol is also applicable to simulations of highly anisotropic lithiation, for example, in ⟨100⟩-, ⟨110⟩-, and ⟨112⟩-oriented *c*-Si nanopillars.

Fig. 2a shows the simulation results of morphological evolution in a *c*-Si nanopillar. Movie S1 shows the simulated lithiation process of the nanopillar. The *c*-Si to *a*-$Li_{3.75}Si$ solid-state amorphization starts from the lateral surface of the nanopillar and the phase boundary migrates inward, forming a *c*-Si/*a*-$Li_{3.75}Si$ core-shell structure. The nanopillar dramatically expands, as the *c*-Si core shrinks and the *a*-$Li_{3.75}Si$ shell thickens. As the lithiation proceeds, the phase boundary migrates toward the center of the nanopillar. Particularly, the material in the phase boundary undergoes a large volume expansion, ~300%, due to Li insertion, and the phase boundary relaxes to accommodate a strain mismatch between *c*-Si and *a*-$Li_{3.75}Si$. Fig. 2b plots the Si atoms and the Si—Si bonds in the partially lithiated nanopillar, showing the separated Si atoms in both the phase boundary layer and *a*-Li_xSi shell. Fig. 2c shows Li concentration profiles corresponding to the atomic configurations in Fig. 2a. These concentration profiles show that the phase boundary between the *a*-Li_xSi (x~3.75) shell and the *c*-Si core has a thickness of ~1 nm, consistent with previous TEM observations. The results in Fig. 2 demonstrate the effectiveness of the Li-insertion protocol and ReaxFF simulations for modeling the two-phase lithiation of *c*-Si.

To investigate the stress evolution during lithiation, we examine the distribution of local stress components in the nanopillar by computing the Virial stress tensor in a finite volume. First, we define equal finite volumes by dividing the system into through-thickness bins. Each bin has in-plane (x-y plane) dimensions of $6Å \times 6Å$. The bin size is appropriate for computing the local stress with reasonable statistical fluctuations. Then we calculate the local stress components in each bin and transform stresses from the Cartesian (x,y,z) coordinate system into the cylindrical (r,θ,z) coordinate system; the z axis is aligned with the axis of the nanopillar. This transformation gives the hoop ($\sigma_{\theta\theta}$) and

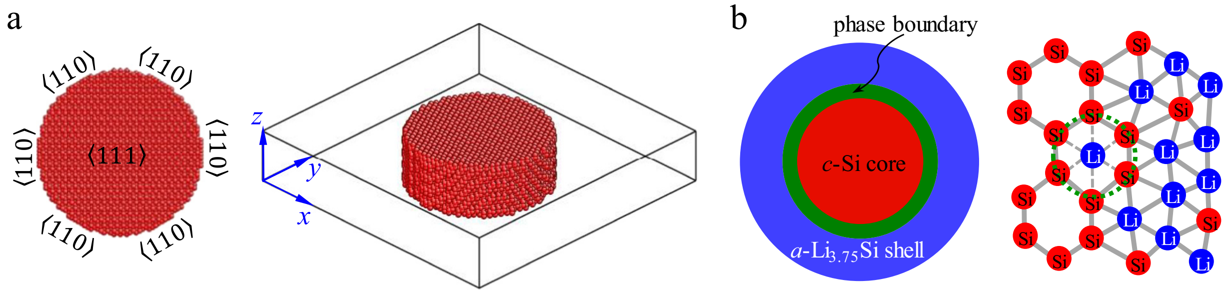

Fig. 1. (a) Atomic structure of the ⟨111⟩-oriented *c*-Si nanopillar. Left: cross-sectional view showing the characteristic crystallographic orientations of the nanopillar. Right: perspective view of the structure in a simulation box. (b) Schematic two-dimensional representation of Li insertions in the phase boundary layer. Red and blue spheres represent Si and Li atoms, respectively. The dashed green circle represents the largest void. A Li atom is added at the center of the void. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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