

Investigation of Solid-state Chemical Lithiation of Single Crystalline Silicon Thin Window Anodes by Analytical Scanning and Transmission Electron Microscopy

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Silicon is regarded as one of the most promising anode materials for high-energy density Li-ion batteries because of its exceptional theoretical specific capacity of 4200 mAh g⁻¹, which is more than 10 times the capacity of graphite (372 mAh/g⁻¹) [1,2]. However, alloying silicon with lithium is fundamentally different from classical Li intercalation into graphite. Significant microstructural changes and volume expansion up to 400 % during alloying can cause degradation, pulverization, loss of electrical contact and consequently rapid capacity fading [1,2]. Many studies have attempted to address these issues via nanoscale structural modification of anodes using high surface-to-volume ratio nanostructured Si that better accommodates strain, while allowing shorter diffusion lengths for Li ions and faster charge/discharge rates. In recent years, stable specific capacities over 1200 mAhg⁻¹ for more than 1000 cycles have been realized with nanostructured Si-based anodes, suggesting a great potential for application in batteries [2]. Affirmative description of lithium kinetics and understanding of its evolution mechanisms in Si nanostructures are still quite limited [3]. In this work, we report on the solid-state lithiation of electron transparent single crystalline c-Si anodes by thermal evaporation of metal lithium foil in a vacuum. The average thickness of evaporated films was monitored by controlling evaporation rates of Li. We used p-doped 35 nm-thick window < 100 >-oriented single crystalline planar c-Si membranes as a planar model system suitable for characterization with high-resolution analytical probe-corrected scanning and transmission electron microscopy (S/TEM). Such direct solid-state lithiation is a dry process without complications caused by side reactions under wet electrochemical processing. After lithiation, the membranes were transferred for examination in a S/TEM using a vacuum transfer TEM holder to prevent the samples from being exposed to an ambient environment. Controlled-dose bright/dark-field (BF-/DF)-TEM, selected-area electron diffraction (SAED), high-resolution TEM (HRTEM), STEM, and electron energy-loss spectroscopy (EELS) were employed to characterize the morphology, crystallinity and chemical compositions of the lithiated membranes (Figs. 1 and 2). In the absence of an applied external electric field, lithiation of a < 100 >- single crystalline c-Si membranes is driven primarily by the concentration gradient and occurs as a fast Li-consuming chemical process, closely analogous to diffusive solid-state amorphization [4]. Determining local phase and chemical compositions of the samples from analyses of low-loss and core-loss EEL spectra (Fig. 2), we found highlylithiated metastable Li-Si glass with an atomic ratio of Li/Si ~ 2.2, close to a Li₇Si₃ phase [5], that could coexist with c-Si since the crystallization of equilibrium intermetallic phases is frustrated during lithiation at room temperature.

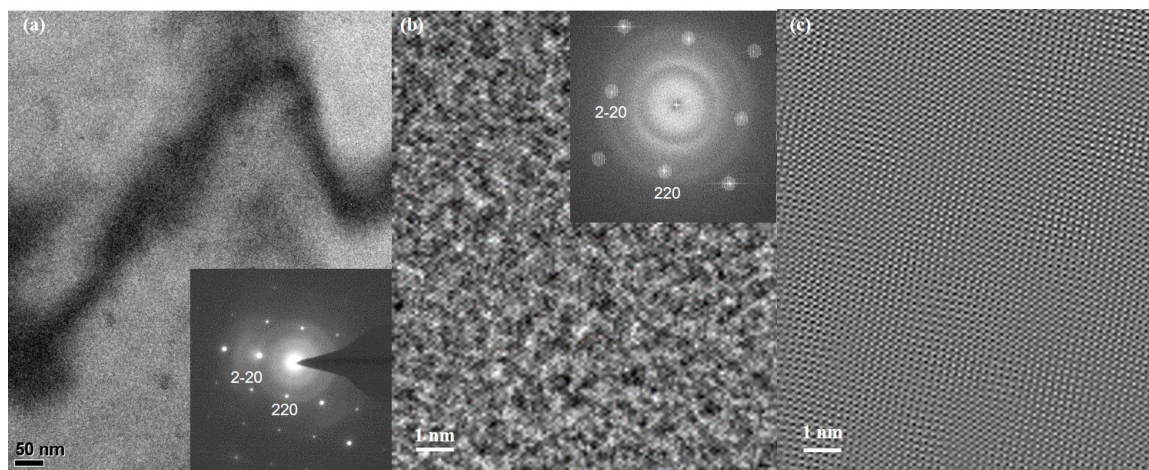


Figure 1. Chemically lithiated 35 nm-thick window Si membrane with a 38 nm evaporated Li film: (a) BF-TEM, bending contours from the remaining c-Si phase. SAED pattern (bottom inset) shows diffuse rings from a Li-Si glass and point Bragg reflections from c-Si, near zone axis $B = [001]$. (b) HRTEM, barely visible lattice fringes through predominantly amorphous Li-Si glass. FFT pattern (top inset) reveals diffuse rings and point (220) reflections. (c) (220) c-Si lattice fringes distorted due to local strain were derived by Fourier-filtering from image (b) using spot reflections selected in the inset.

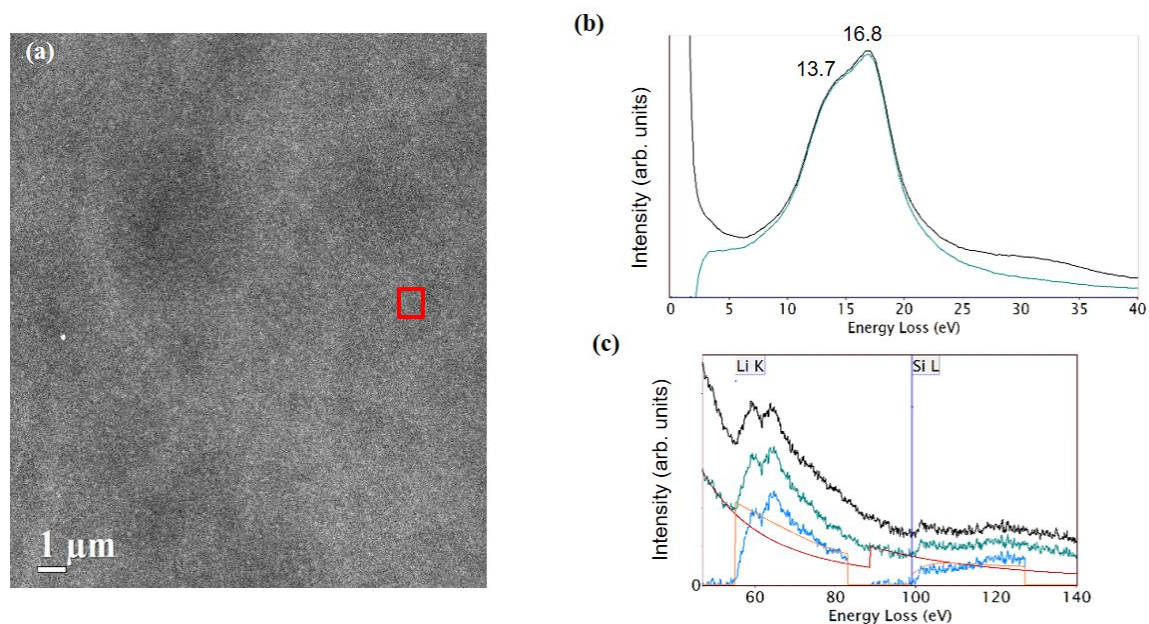


Figure 2. STEM-EELS of a lithiated Si membrane. (a) High-angle annular DF (HAADF) STEM, large-area view reveals weak contrast variations over a randomly distributed Li-Si glass film. (b) Low-loss EEL spectrum (black) acquired from the area marked by red box in (a) shows a shoulder at 13.7 eV assigned to a Li_7Si_3 glass in addition to the bulk Si plasmon at 16.8 eV. A single scattering distribution (green) is derived by a Fourier-log deconvolution of the initial spectrum. (c) Core-loss spectrum from the same region with an estimated atomic ratio $\text{Li}/\text{Si} = 2.2$. Fitted extrapolated power law backgrounds for the LiK and the SiL_{2,3} edges shown in red were used to extract the net edges (blue). The calculated Hartree-Slater scattering cross-sections for Li and Si are shown in orange.

References

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