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Thickness effects on the lithiation of amorphous silicon thin films

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The lithiation of thin film Si was investigated in an electrochemical cell, using in situ wafer curvature to monitor the evolution of in-plane stresses. Increasing the initial film thickness from 50 to 250 nm led to decreases in both the nominal flow stress and the Li capacity. These observations are consistent with relatively slow Li diffusion. The corresponding concentration gradients should have a substantial effect on the deformation and viscous flow that occur in lithiated Si.

Keywords: Thin films; Electrochemistry; Internal stresses; Lithium-ion batteries

To improve the capacity of lithium ion batteries, a variety of new electrode materials have been investigated. Many of these materials undergo significant volume changes when Li is added and removed during charging and discharging. Significant stresses will result when this expansion is physically constrained, and reducing the material dimensions to the nanoscale has been widely discussed as a general strategy for improving the damage tolerance of electrodes [1–4]. One difficulty in understanding the stresses that occur during Li insertion and removal is the complex porous microstructure of most electrodes. With this in mind, we investigated lithium-induced changes in thin films where the stress response is more easily interpreted. Silicon was selected for these investigations because it has a large Li capacity that is accompanied by an extremely large volume expansion (>300% for full lithiation). When a mechanical constraint confines this expansion, previous experimental investigations clearly demonstrate that significant Si flow occurs (i.e., the stress due to lithiation reaches the flow stress) [5–9]. This behavior has a substantial impact on the performance and degradation of Si-containing negative electrodes, thus further understanding of the flow characteristics is essential.

The stress response in amorphous Si films was measured during Li cycling with a multibeam optical stress sensor (MOSS) [10,11]. With this configuration, the effects of moving to the nanoscale were explored in one dimension by varying the initial film thickness, h_0. Several key differences were observed, and interpreted in terms of relatively slow Li diffusion. Ideally, one would also measure Li concentration profiles directly; however, these measurements are difficult because Li reacts vigorously with air. Thus the thickness effects reported here are a useful way to probe the effects of diffusion limitations.

All of the Si electrodes were fabricated on one inch diameter 250 μm thick, high-purity SiO_2 substrates. E-beam evaporation was used to produce bilayered films with a 200 nm thick Ti current collector, followed by an amorphous Si film. The deposition rate for both materials was 0.1 nm s^{-1}.

The experiments were conducted in a custom electrochemical cell. The contents were assembled in a dry box filled with ultrapure argon, beginning with lithium metal that was placed at the bottom of the cell. This electrode was covered by a Celgard membrane with 45% porosity (to separate Li from the Si electrode), then the liquid electrolyte was introduced (a 50:50 mol% mixture of ethylene carbonate/dimethylecarbonate containing 1 M $LiPF_6$ salt). The specimen was then positioned with the Si film in contact with the separator and electrolyte. The back surface of the wafer was visible through a quartz window on top of the sealed cell, which made it possible to monitor bending of the thin film specimen with the MOSS. Because the SiO_2 substrate deforms elastically (unlike metal current collectors), the stress in the film is proportional to the curvature, κ, via a modified Stoney equation [12]:

$$\langle\sigma\rangle h = \int_0^h \sigma(z)dz \cong \frac{B_s h_s^2 \kappa}{6}\left[1 + 4\frac{Bh}{B_s h_s}\right] \tag{1}$$

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where z is the dimension normal to the film surface, and h and B are the thickness and biaxial modulus for the film (no subscript) and the substrate (subscript s). The film thickness, h, varies considerably in these experiments because of the large expansion and contraction of the solid. Because both $\langle\sigma\rangle h$ and h_0 can be measured directly, the data is reported as nominal stress: $\sigma^{NOM} = [\langle\sigma\rangle h]/h_0$.

Lithium insertion and removal was conducted by running the cell galvanostatically for multiple cycles between 2.2 and 0.05 V vs. Li/Li$^+$. The constant C/10 rate was calculated using the theoretical capacity of Li in Si (3600 mA h g^{-1}). The lower limit of 0.05 V vs. Li/Li$^+$ was chosen to avoid crystalline phase ($Li_{15}Si_4$) formation below this critical voltage [13]. Several films of each thickness were cycled in this manner. Data during the first cycle are not reported, because the voltage response is strongly influenced by the formation of a stable SEI layer on the film surface. After electrochemical cycling the samples were rinsed thoroughly in dimethyl carbonate solution to remove condensed salt. The films were then examined with scanning electron microscopy, and no cracking was observed.

The stress and voltage responses for a 50 nm thick film are shown in Figure 1. The basic trends seen here were observed in all of the films that were investigated. As Li is first added, the Si expands and substantial compressive stress develops. As previous researchers have observed, the large volume expansion during the lithiation of Si invariably leads to flow when the material is constrained by a substrate [5–9]. This is consistent with Figure 1, where an initial elastic response corresponds to a sharp increase in the magnitude of σ^{NOM}, followed by flow after σ^{NOM} levels off. After flow begins, the volume expansion due to continuing lithiation presumably leads to a significant expansion normal to the substrate. As this occurs, the in-plane stress should continue to be limited by the flow stress. Then, when the charge cycle begins, Li removal first leads to an elastic response that first reduces the compressive stress. As this process continues, tensile stress evolves and eventually becomes large enough to induce flow in the other direction (i.e., as the film volume decreases). Figure 2 shows schematics of this complete cycle. With the proposed Li concentration gradients, the onset of flow occurs incrementally during both lithiation and delithiation, as shown in Figure 2. During Li insertion the concentration, c_{fl}^0, corresponds to the point where the initial elastic stress due to expansion causes the material to first reach the flow stress, σ_{fl}. While c_{fl}^0 is determined by the properties of the material (i.e., Si here), note that its specific value will also vary with the initial residual stress in the film. The biaxial stress in the film is then determined by the elastic expansion of the material at $c \leqslant c_{fl}^0$ and equal to the flow stress at $c \geqslant c_{fl}^0$. If diffusion is relatively fast, the boundary at c_{fl}^0 will move through the film quickly; however, with slower diffusion this intermediate state will correspond to a significant portion of the cycle.

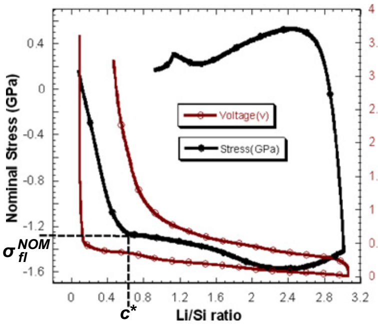

Figure 1. Stress (in situ MOSS data) and voltage vs. Li content for 50 nm thick film.

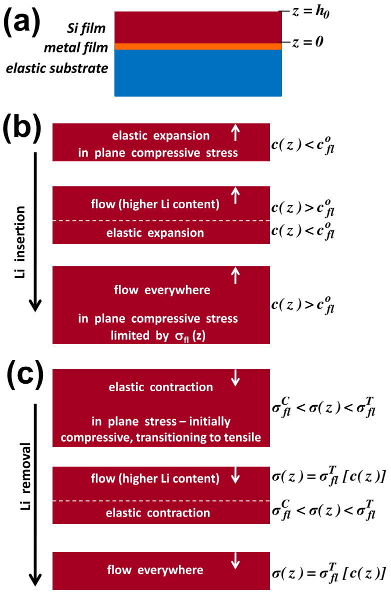

Figure 2. (a) Specimen configuration; (b) film changes during Li insertion; (c) film changes during Li removal. In parts (b) and (c), the film is still fully constrained by the substrate, as shown in part (a).

The schematics in Figure 2 are based on maintaining the thin film geometry with no surface roughening and with substantial expansion and contraction in the z direction after the flow stress is reached. Assuming a flat surface is questionable without experimental verification, since stress relaxation due to surface roughening has been widely documented in many strained thin films [12]. However, the AFM measurements in Table 1 indicate that the film surfaces remain essentially flat after full Li cycles. Based on these observations, a one-dimensional view of deformation and concentration profiles in the z direction is reasonable. The question of whether significant gradients occur is then based on the kinetics during Li insertion/removal, which can be interpreted as a basic competition between surface reactions and Li diffusion. In theory, silicon bulk diffusion can also lead to stress relaxation. However, self-diffusion in pure Si is known to be nonexistent at room temperature, and Si diffusion in $SiLi_X$ is expected to be significantly slower than Li diffusion.

Table 1. Surface roughness from atomic force microscopy (performed in tapping mode on 20 μm × 20 μm scan areas).

h_0 (nm)	Initial rms roughness (nm)	Roughness (nm) after three complete lithiation cycles
50	1.35	1.45
100	1.11	1.27
150	1.17	1.68
250	1.24	1.32