



Mechanical stresses and morphology evolution in germanium thin film electrodes during lithiation and delithiation



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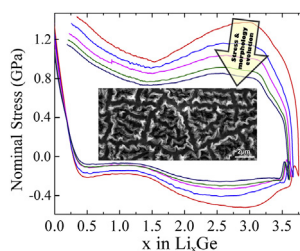
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HIGHLIGHTS

- a-Li_xGe has a lower nominal flow stress than a-Li_xSi.
- The deformation of a-Li_xGe shows a weak dependence on rate.
- Crystallization of a-Li₁₅Ge₄ has a distinct stress signature.
- The stress range of the a-Li_xGe films decreases due to morphological evolution.
- Germanium electrodes decay into island structures but retain capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Germanium and silicon can be used to reversibly store large amounts of lithium, but as a result, suffer from significant volumetric and structural changes during cycling. The mechanical stresses associated with these changes were investigated using *in situ* stress measurements on thin film electrodes. Results for germanium, with its superior transport properties, are compared to silicon, which is structurally similar. The nominal stresses developed in amorphous lithium–germanium (a-Li_xGe) were found to be roughly 30% lower than in a-Li_xSi. When the cycling rate was increased, the germanium electrode showed a smaller loss in capacity than silicon. Crystalline Li₁₅Ge₄ was observed to form below 100 mV and resulted in a distinct tensile bump in nominal stress. During extended cycling, the maximum mechanical stress signal of the film electrodes irreversibly decreased without an apparent loss in capacity. In contrast to silicon films, which typically fracture and lose capacity during cycling, germanium films were capable of reorganizing into three-dimensional structures, thereby improving their mechanical response while minimizing electrochemical energy loss. The reduced nominal flow stresses observed in a-Li_xGe and their weak dependence on charge–discharge rates correlated with the reduced rate sensitivity found in germanium electrodes as compared to silicon.

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1. Introduction

Interest in negative electrodes based on silicon (Si) and germanium (Ge) for next generation lithium-ion batteries has developed as a result of their potential for higher energy and power densities compared to current intercalation electrode materials like graphite. Silicon and germanium offer theoretical capacities of

3579 A h kg⁻¹ for Li₁₅Si₄ and 1384 A h kg⁻¹ for Li₁₅Ge₄ compared to graphite's theoretical capacity of 372 A h kg⁻¹. The low cost and abundance of silicon has made it the main focus of the scientific community despite germanium's superior intrinsic electronic conductivity (three orders of magnitude) and higher diffusivity of lithium (more than one order of magnitude) at room temperature [1,2]. While the gravimetric capacity of germanium is lower than that of silicon, its volumetric capacity (7366 A h l⁻¹) is similar to that of silicon (8334 A h l⁻¹). This makes germanium competitive with silicon in applications where battery size is more critical than weight such as in thin film micro-batteries [3,4].

Several studies have examined the alloying reaction between lithium and amorphous silicon (a-Si) [5–7]. The exact process by which silicon alloys with lithium and whether lithiation proceeds as a single-phase or a multi-phase process are unresolved. The electrochemical lithiation of silicon shows two distinct reaction steps in the cyclic voltammogram (CV). Transmission electron microscopy (TEM) observations and mechanical experiments suggest that lithiation of pristine a-Si results in a distinct amorphous Li_xSi (a-Li_xSi) product with a sharp reaction interface between the newly forming Li_xSi phase and the unreacted a-Si [8]. Other reports concluded that after the first lithiation, subsequent cycles would typically proceed by a single-phase mechanism [9], while *in situ* nuclear magnetic resonance measurements suggest that several phases or mixtures can form and coexist during cycling [8,10,11]. Under certain conditions, a-Li₁₅Si₄ can crystallize into a body-centered cubic crystal structure with space group *I43d* (220) [10,12,13,14]. Only limited understanding of the crystallization process and the factors affecting it exists so far [15]. Like silicon [16], the CV data suggests that germanium forms different alloys with lithium. It is very likely that the peaks that are observed in CV plots for silicon are associated with formation of amorphous phases with distinct ranges of stoichiometry. It is interesting to note that similar peaks are seen for germanium. However, the interpretation of these peaks may be more complex. Baggetto et al. [17] investigated electrochemical lithiation of sputtered and evaporated thin film germanium electrodes and suggested that lithiation proceeds as a series of amorphous lithium–germanium alloys with different distinct compositions, reaching a maximum room temperature composition of 3.75 lithium atoms per germanium atom [17,18]. Just as in silicon, a-Li₁₅Ge₄ can also crystallize [19,20] to form c-Li₁₅Ge₄ [19,20] which has the same crystal structure as c-Li₁₅Si₄ [21]. However, we note that the phases that form during lithiation as well as the sequence and location of formation are still under debate for both silicon and germanium [22].

Accompanying the high volumetric expansion of both materials (≥280%) are problems due to mechanical stresses that lead to plastic deformation, cracking, poor cyclability, and low coulombic efficiency [5,7,16]. *In situ* curvature measurements have been performed in a number of studies to investigate the evolution of stress in silicon thin film electrodes to better understand how the mechanical stresses are associated with lithiation. By tracking the mechanical loading of films during cell operation, fundamental processes such as the formation of phases can be investigated. Experiments on amorphous silicon films [23–26] showed the development of compressive and tensile stresses in excess of 1 GPa during lithiation and delithiation. High stresses are strong driving forces for lithium transport and thereby can affect the electrochemical behavior [26–28]. Conversely, changes in the electrochemical conditions such as in voltage or current density can influence the evolution of mechanical stress. Knowledge of the mechanical stresses and their relaxation mechanisms may therefore prove useful in better understanding the electrochemical behavior. The effect of different lithiation rates on time-dependent mechanical behavior was recently investigated in silicon [26].

These results suggested that time-dependent deformation processes can relax stress and that high stresses occur under high charging rates. Mechanical aspects associated with silicon lithiation such as film thickness [25], fracture [24,28], and physical properties [27,29] have also been previously investigated. However, the mechanical behavior of germanium has not been investigated so far. Investigation of germanium is of interest due to its applicability as an anode material in lithium-ion batteries but also due to its similarity to silicon. Both materials react and alloy with lithium, with germanium–lithium alloys showing improved kinetics over those of silicon. A detailed investigation of the mechanical response of germanium electrodes may help in understanding the fundamental mechanisms by which these electrodes operate.

2. Experimental procedures

Double-side polished aluminum oxide (99.6% Al₂O₃, 250 μm thick, Stellar Ceramics) was used to fabricate cantilever electrodes. The aluminum oxide was cut into 16 mm by 6 mm pieces and was cleaned using a 5:1:1 mixture of deionized water, ammonium hydroxide, and hydrogen peroxide at 85 °C for 30 min. After this step, the aluminum oxide substrate was rinsed with deionized water and dried by nitrogen. A thin, 100 nm thick tungsten film was sputter deposited (CMS-18, Kurt Lesker) using argon at a pressure of 3 mTorr and a power of 50 W DC. A shadow mask exposing only 10 mm by 6 mm of the cantilever area was used to deposit either silicon or germanium. Room temperature deposition of both silicon and germanium was performed by argon sputtering at a pressure of 2.5 mTorr and a power of 90 W RF to a thickness of about 90 nm or 170 nm. The thickness of the electrode films was measured by spectral reflectance (Filmetric F20) and by cross-sectional SEM. The as-deposited films were amorphous based on X-ray diffraction and Raman spectroscopy. Samples were dried under vacuum at 80 °C for 12 h before being assembled into cells. Curvature experiments were performed on more than ten samples. In this report, representative samples of the following three electrode types are presented: a 100 nm silicon film, a 90 nm germanium film, and a 170 nm germanium film.

Cell assembly was done in an argon glovebox. Curvature measurements were conducted using a home-built setup using a dedicated three-electrode cell for stress measurements [30]. The cantilever served as the working electrode and was electrically contacted by clamping the exposed 4 mm by 6 mm region of the tungsten underlayer to nickel foil. Lithium metal pieces were pressed onto nickel strips and served as counter and reference electrodes in the cell. A tailored electrolyte [31] was mixed in the glovebox by adding bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, Sigma Aldrich) to 1,3-Dioxolane (DOL, Sigma Aldrich) to make a 1 M solution. The electrolyte had a water content of 19 ppm as determined by Karl Fischer titration and a refractive index of 1.4165 as determined by a refractometer. A sapphire window in front of the cantilever allowed two laser beams to enter and exit the electrochemical cell. The deflection of these cantilever beams from the backside of the electrode was tracked by a large sensor CMOS camera. Once the cell was mounted in the curvature measurement setup, the spacing of the two laser spots and their positions with respect to the clamped and free ends of the cantilever were recorded with a scale marker in a digital image. These images were then analyzed using ImageJ (National Institutes of Health). The spot spacing was always around 4–4.5 mm and the first spot was at least 4.75 mm away from the clamped end of the cantilever. The stress inhomogeneities resulting from the clamp were minimized by the fact that the cantilever was clamped onto a compliant polyethylene layer that lay beneath the nickel electrical contact. This way the anticlastic curvature was restrained only minimally. The entire test

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