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Fracture of crystalline germanium during electrochemical lithium insertion

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ABSTRACT

Germanium is one of the promising alloying anode (Si, Ge, Sn) materials for high capacity lithium ion batteries. Since it is isostructural with crystalline silicon, crystalline Ge is expected to show intriguing lithiation-induced phenomena similar to Si, such as anomalous volume expansion and fracture. Here, we present the study of lithiation of Ge micropillars, and we compare the findings to silicon pillar lithiation. The critical pillar diameter ~1.2 μm associated with lithiation-induced fracture of ⟨111⟩ Ge pillars, determined through our statistical investigation, is much greater than the critical dimension for fracture of ⟨111⟩ silicon pillars (~300 nm). This larger critical size for lithiation-induced fracture of Ge likely arises from lower tensile stress concentrations at the surface due to the more inherently isotropic expansion that Ge undergoes during lithiation. Upon lithiation, Ge displays only slight anisotropy in its volume expansion, with the ⟨110⟩ directions exhibiting radial expansion that is only 1.1 times larger than that along ⟨111⟩ directions. Despite its relatively weak anisotropy in volume expansion, however, Ge pillars above the critical dimension still show anisotropic fracture, with favored fracture sites residing between the ⟨110⟩ directions on the pillar sidewall, similar to Si. We believe that this study provides better understanding of lithiation of Ge for designing high-density anode for Li-ion batteries.

Alloying anode materials are considered promising anode electrodes for Li-ion batteries because of their high specific capacity made possible by reformation of chemical bonds and severe structural transformation [1–3]. However, alloying anodes usually suffer from rapid capacity decay due to mechanical fracture and instability of the solid electrolyte interphase (SEI) caused by large volume changes during repeated electrochemical lithium insertion and extraction [4,5]. In light of such shortcomings, a great deal of fundamental research into lithiation/delithiation-induced volume expansion/contraction and consequent fracture of such anode materials has been carried out [6,7]. Especially, silicon has been extensively studied due to its highest specific capacity among alloy anodes and its relative abundance [8–12]. Contradicting the former thought that Si lithiates via isotropic lithium (Li) reaction and diffusion, we recently showed that Si undergoes anisotropic volume expansion, with expansion most significant along ⟨110⟩ directions [13,14]. These were later confirmed by others [15,16]. Furthermore, we and others have found anomalous fracture behavior of crystalline Si nanostructures upon lithiation; fracture has been seen to occur preferentially between neighboring ⟨110⟩ lateral directions due to the concentrated near-surface tensile hoop stresses that develop between these rapidly expanding directions [17–19]. Fracture promotion due to anisotropic expansion produces a relatively small critical pillar diameter

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for lithiation-induced fracture of crystalline Si pillars. Specifically, such Si pillars are found to fracture during lithiation when the initial pillar diameters are greater than as little as ∼300 nm [17].

Although Ge is recognized as another promising anode material with a large theoretical specific capacity (1600 mAh/g), understanding its lithiation behavior is necessary for designing high-density anode electrode for Li-ion batteries [20–23]. Here, we utilize Ge nano/micro pillar structures with various axial crystal orientations for systematic study of the size effect for mechanical fracture as well as the volume expansion behavior of crystalline Ge upon electrochemical lithiation.

The procedures utilized for lithiation of single crystalline Ge pillars are similar to those of previous Si pillar lithiation research [13,24,25]. Ge micropillars were fabricated by dry etching single crystalline Ge wafer of three crystal orientations (⟨100⟩, ⟨110⟩, ⟨111⟩) that ultimately define the etched pillars' axial orientations. Prior to etching, drop-cast Polystyrene (PS) microspheres with diameters of 1 and 2 μm were first distributed on the wafer to be an etch mask and define the diameter of the etched pillar. The diameters of the etched pillars varied from 0.5 μm to 1.7 μm, and the heights varied from 4 μm to 5 μm. After dry etching of the pillar, PS microspheres were removed by gentle sonication, and the samples were then cut to pieces with area of ∼25 mm^2 that could be used as the working electrode in half-cell with Li-foil counter electrode. Next, the Ge micropillar samples were lithiated by sweeping the applied voltage at a specified rate until reaching a cut-off voltage of 10 mV vs. Li/Li^+. The cut-off voltage was held for 10 h as lithiation was allowed to proceed. The sweep rates were 0.1 mV/s and 1 mV/s. After lithiation of Ge micropillars, the samples were washed in acetonitrile in an Ar filled glove box and transferred to a scanning electron microscope (SEM) chamber for observation of pillar morphologies.

Fig. 1 shows the size effect of mechanical fracture of ⟨111⟩ Ge pillars upon lithiation. Ge pillars with 0.5 μm diameters expand in a nearly isotropic manner and without observed fracture as shown in Fig. 1(a) while Si pillars larger than about 300 nm in diameter exhibit significant fracture [17]. It agrees with the previous in-situ TEM study of fracture resistance of crystalline Ge particles upon lithiation [26]. Despite their robustness, Ge pillars also exhibit a size effect of fracture upon lithiation, as Si does. Fig. 1(b) clearly shows the fracture of Ge pillars upon lithiation when their initial diameter increases to 1.7 μm. To investigate the size effect and reaction rate effect for fracture, a statistical study was used to measure the fracture ratio for various pillar diameters with the reaction rate controlled by the voltage sweep rate as shown in Fig. 1(c). The examined diameters of the Ge pillars were 0.5 μm, 1.2 μm, and 1.7 μm and voltage sweep rates were 0.1 mV/s and 1 mV/s. When the initial diameter of Ge pillar is 0.5 μm, the fracture is not found regardless of the voltage sweep rate (blue column). When the initial pillar diameter is increased to 1.2 μm (red column) and 1.7 μm (green column), the lithiated pillars exhibit some fracture and the fracture ratios are 4.3% and 11.3% for voltage sweep rates of 0.1 mV/s, respectively. For the faster voltage sweep rate (1 mV/s), the lithiated pillars with initial diameters of 1.2 μm and 1.7 μm show a significant increase of fracture ratio to 46.4% and 81.1%, respectively.

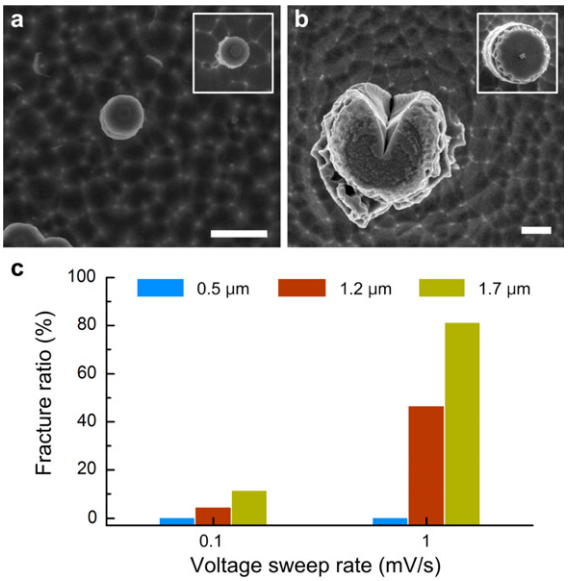

Fig. 1. Size effect for mechanical fracture of crystalline Ge pillar upon electrochemical lithiation. (a) Top-down-view SEM image of an unfractured, lithiated ⟨111⟩ Ge pillar of 0.5 μm initial diameter. The inset is an SEM image of a pristine Ge pillar. (b) Top-down-view SEM image of a fractured, lithiated ⟨111⟩ Ge pillar of 1.7 μm initial diameter. The inset is an SEM image of a pristine Ge pillar. All scale bars are 1 μm. The voltage sweep rates of both lithiated pillars are 1 mV/s. (c) Column chart of the fracture ratio for ⟨111⟩ Ge pillars of various initial diameters and two different lithiation voltage sweep rates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Finite-element-based lithiation simulations explain how isotropic expansion of lithiated Ge enhances fracture resistance (see Movies 1 and 2 in Supplementary Information). The initial diameter of the simulated Ge pillar is 1.0 μm. The artificial moving interface between crystalline Ge and Li_xGe with 270% volume expansion is defined for lithiation of Ge pillar as in our previous study [19]. The mechanical properties of lithiated Ge utilized in formulating the finite element models were obtained from nanoindentation experiments into Li_xGe samples (see Fig. S3 in Supplementary Information). Measured Young's modulus was 57.3 GPa, and the yield strength – taken as the hardness divided by the Tabor factor of 3 – was measured to be 0.84 GPa. The case of isotropic expansion (Fig. 2(a, b)) is simulated by defining a circular interface between the lithiated and unlithiated material that remains circular as it travels radially inward. Fig. 2(a) shows the Li concentration (c_{Li}) profile when the degree of lithiation is 80%. The concentration of Li is zero at the crystalline Ge core and 1 at the Li_xGe shell. There is a steep transition in the concentration profile from 0 to 1 across the interface. Fig. 2(b) shows the hoop stress ($\sigma_{\theta\theta}$) profile for isotropic expansion when the degree of lithiation is 80%. It is evident that isotropic expansion induces uniformly distributed near-surface tensile hoop stresses bounded by the yield strength of lithiated Ge. For comparison, anisotropic expansion of ⟨111⟩ Ge pillar is simulated by hexagonal shape of artificial moving interface. Fig. 2(c) shows Li concentration (c_{Li})