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Enhanced lithiation and fracture behavior of silicon mesoscale pillars via atomic layer coatings and geometry design

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HIGHLIGHTS

- Atomic layer deposition (ALD) of metal oxides is found to enhance the Li transport.
- The volume expansion and fracture of silicon micropillars are improved by ALD.
- Square geometry is more beneficial for large lithium storage without fracture.
- Extrapolation of anisotropic behavior from nano- to micro-sized region is cautioned.
- Models are developed to address expansion behavior of silicon micropillars after ALD.

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ABSTRACT

Crystalline silicon nanostructures are commonly known to exhibit anisotropic expansion behavior during the lithiation that leads to grooving and fracture. Here we report surprisingly relatively uniform volume expansion behavior of large aspect-ratio (~25), well-patterned, n-type (100) silicon micropillars (~2 μm diameter) during the initial lithiation. The comparison results with and without atomic layer metal oxides (Al_2O_3 and TiO_2) coatings reveal drastically enhanced solid electrolyte interphase (SEI) formation, higher volume expansion, and increased anisotropy. Square-pillars are found to exhibit nearly twice volume expansion without fracture compared to circular-pillars. Models are invoked to qualitatively address these beneficial or detrimental properties of silicon for lithium ion battery. Our experiments and computer simulations point at the critical relevance of SEI and pristine geometry in regulating volume expansion and failure. ALD-coated ultrathin metal oxides can act as an ion channel gate that helps promote fast Li^+ transport into the bulk by changing the surface kinetics, suggesting new ways of designing electrodes for high-performance lithium ion battery applications.

1. Introduction

The large lithium storage capacity (~3579 mAh g^{-1}) and industry scalable manufacturing capability of various silicon materials (including micro- and nano-scale structures) have inspired intense research in these materials as anodes for lithium-ion batteries (LIBs) [1,2]. The enormous potential of silicon as energy storage materials has however been counteracted by several known challenges, including a rather large volume expansion (VE ~300%) during lithiation that inevitably degrades the structural integrity of silicon electrodes during the cycling, highly anisotropic lithiation/delithiation behavior witnessed in single crystalline silicon, and poor solid electrolyte interphase (SEI) layer formation. To overcome the first two shortcomings, a wide variety of nanostructures or amorphous silicon (e.g., nanowires, nanotubes, nanoparticles, and nanoporous structures) have been intensively investigated where much valuable information has been garnered [3–7]. Unfortunately nanostructured silicon is expensive to scale-up and also suffers from intrinsically low tap density (leading to low volumetric capacity). Furthermore, high surface area nanostructures inevitably induce worse SEI layers that are known to degrade the performance of LIBs [8]. In comparison, the electrochemical and electromechanical behavior of mesoscale (e.g., micrometer-sized) silicon is less well understood. To date a limited amount of experiments have

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been conducted [9,10]. Because of the clear size, stress and subsequent phase boundary curvature differences, the lithiation kinetics of microsized silicon is expected to be different from that of nanostructures. Such information could bear critical relevance to the commercial applications due to the high energy density needs that call for thick electrodes (e.g., commercial electrodes are typically over 100 μm thick).

Another critical challenge yet little understood to the long cycle life of silicon-based LIBs is to overcome the poor SEI layers that are intrinsically associated with large volume change electrodes. Such SEI layers are unstable both mechanically and thermally as the SEI layer is an organic/inorganic composite (e.g., containing Li_2CO_3, LiF, $(CH_2OCO_2Li)_2$, polycarbonates) [8,11] that could decompose at a relatively low temperature. The continuous re-exposure of fresh silicon to electrolyte due to the instability of SEI leads to low Coulombic efficiency and may promote subsequent exothermal reactions that lead to "thermal runaway" and cause fire and explosion of LIBs due to the chain reactions of oxidative cathode materials (if a full cell configuration is used). As such, the thermal and mechanical stability of SEI layers on anodes is of importance to the safety of LIBs. To this end, few studies have been performed to address these SEI issues, with existing effort focused on carbon or silicon oxide coatings as the potential front-runner solutions. The former is electrically conductive such that it may not be able to impede the growth of SEI at low potentials [10], while the latter has low fracture toughness, Table 1 [12–18], and can be reactive to fluoride species, and thus requires strict structural designs [1]. Another important class of coating materials is metal oxides, which can not only offer high thermal stability, but also possess other beneficial properties such as high mechanical strength and fracture toughness, low electrical conductivity, and high lithium diffusivity (Table 1 [19]). These unique properties render them as excellent surface protection materials for anodes (as well as cathodes). Enhanced cycling performance and high Coulombic efficiency have indeed been reported in Al_2O_3-coated silicon nanostructures [20,21]. Nonetheless, there exists limited understanding of the impact of metal oxide coatings on the lithiation and fracture/failure behavior of silicon materials.

By using atomic layer deposition (ALD), here we report on the substantially enhanced lithiation and fracture behavior of silicon micropillar arrays that are ALD-ed with an ultrathin layer (<1 nm) of Al_2O_3 and TiO_2, respectively. Silicon micropillars for this study were directly fabricated from (100) n-type silicon wafers with a diameter of 2 μm and a height of 50 μm, yielding a height/diameter aspect ratio of 25:1. To our knowledge, this is the highest aspect ratio silicon micropillars reported so far for investigation of lithiation behavior, which mechanistically ensures plane strain condition near the pillar top without having to take into account the substrate confinement effect. Similar pillars have been popularly used as thermal neutron detector materials with excellent performance [22]. The penetration ability of ALD technique to very high aspect ratio structures further makes these studies possible. We investigate two types of conformal coatings; i.e., 0.43-nm-thick Al_2O_3 and 0.75-nm-thick TiO_2, respectively (both thicknesses are nominal). To explore the initial pillar geometry effect on the lithiation/fracture behavior, square micropillars were also fabricated. Systematic and comparison experiments were performed on the bare silicon circular micropillars (bare-Circular-Si), Al_2O_3-coated (Al_2O_3-ALD-Circular-Si) and TiO_2-coated (TiO_2-ALD-Circular-Si) silicon circular micropillars, and TiO_2-coated square micropillars (TiO_2-ALD-Square-Si). For the square-shaped pillars, the orientation of four sides is oriented along {110} crystallographic planes, which is considered as the fastest Li diffusion direction in silicon. Earlier studies have generally revealed that circular shape nanowires exhibit strong anisotropic expansion, leading to grooving and fracture. It is thus interesting and of technological importance whether similar behavior occurs in mesoscale pillars and whether one can take advantage of geometrical design to mitigate or even completely annihilate such anisotropic failure behavior.

Table 1
Selected properties of silicon, SiO_2 and metal oxides.

Materials	Fracture toughness (MPa m$^{1/2}$)	Electrical conductivity (S cm^{-1})	Li ion conductivity (S cm^{-1})
Al_2O_3	2.7–4.2 [17]	10^{-14} (Crystalline) [16]	10^{-6} (Amorphous) [12]
TiO_2	2.38 [17]	10^{-6} [14]	10^{-5} to 10^{-7} (Rutile) [15]
SiO_2	0.79 [19]	10^{-14} [16]	–
Si	<110>: 0.73 <100>: 0.89 [18]	2 (Our data)	$\sim 3 \times 10^{-7}$ [13]

2. Experimental details

2.1. Preparation of Si micropillars

Bulk n-type (100) silicon wafers with the conductivity of 2 S cm^{-1} (determined by a four point probe method) were selected for micropillar fabrication. The pillar diameter and spacing were defined lithographically, followed by inductively coupled plasma etching. The etching process used a Bosch Process (also known as pulsed or time-multiplexed etching), alternating repeatedly between two modes to achieve vertical structures. This was accomplished by alternating between isotropically etching the silicon with a short duration of 25 sccm SF_6 plasma, and a short duration of polymerization using 80 sccm C_4F_8. The passivation layer protected the entire substrate from further chemical attack and protected further etching. Circular- and square-shaped pillars were fabricated according to the applied mask. The diameter, spacing and height of the pillars were 2 μm, 2 μm and 50 μm, respectively. The high quality and well-patterned nature of all as-fabricated pillars can be seen in Fig. 1a–c scanning electron microscopic (SEM) images.

2.2. TiO_2 and Al_2O_3 ALD coatings

To investigate the coating effect, silicon micropillars were coated with sub-nanometer-thick Al_2O_3 or TiO_2 films using the well-established trimethyl-aluminum ($AlMe_3/H_2O$) [23] and titanium tetrachloride ($TiCl_4/H_2O$) [24] atomic layer deposition (ALD) processes in a warm wall reactor with the wall temperature of 100 °C and the sample stage temperature of 125 °C for Al_2O_3 and 110 °C for TiO_2. Long pump, pulse and purge times (20 s/50 s/50 s) were used to ensure uniform coatings throughout the material. The nominal film thicknesses using 15 cycles for TiO_2 and 3 cycles for Al_2O_3 are 0.75 nm and 0.43 nm based upon the ALD rates reported in Refs. [25] and [26], respectively.

2.3. Transmission electron microscopy (TEM) sample preparation

The TEM samples of TiO_2 ALD coated silicon micropillars were prepared by using a focused-ion-beam (FIB) (FEI, Nova 600) liftout method, where the target pillar arrays were first coated with a thin protection layer of e-beam Pt, followed by the further deposition of ion-beam Pt which helps to "weld" several pillars together, Fig. 1d. The cross-sectional samples were examined in a FEG Philips CM300 TEM with traditional bright-field (BF) and high-resolution (HR) imaging conditions. The BF TEM in Fig. 1e suggests that the side