Fracture of Crystalline Silicone Nonopillars during Electrochemical Lithium Insertion

Understanding the insertion of lithium into silicon electrodes for high capacity lithium-ion batteries is likely to have benefits for mobile energy storage, for both electronics and transportation. Silicon nanostructures have proven to be attractive candidates for electrodes because they provide less constraint on the volume changes that occur and more resistance to fracture during lithium insertion. But still, fracture can occur even in silicon nanostructures. Here, we consider the fracture of Si nanopillars during lithiation and find surprising results. We find that fracture is initiated at the surfaces of the nanopillars and not in the interior, as had been predicted by analyses based on diffusion-induced stresses. In situ transmission electron microscopy observations of initially crystalline Si nanoparticle-clusters shows that lithiation occurs by the growth of an amorphous lithiated shell, subjected to tension, at the expense of a crystalline Si core, subjected to compression. We also show that the expansion of the nanopillars is highly anisotropic and that the fracture locations are also anisotropic. In addition, we find a critical fracture diameter of about 300 nm that appears to depend on the electrochemical reaction rate. Modeling the stress evolution in Si nanopillars during lithiation provides a way to understand and control these failure processes. Also, we show that initially amorphous Si nanopillars are much more resistant to failure because the stresses at the surface are largely compressive in this situation compared to tension in the case of initially crystalline nanopillars.