

In-situ Transmission Electron Microscopy (TEM) Study on the Lithium Ion Transport in Si-Ge heterostructured Nanowires

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Controlling the transport of lithium (Li) ions and their reaction with electrodes is critically important in the design of Li-ion batteries for achieving high capacity, high rate capability and long lifetime. One straightforward application is to mitigate the mechanical failure of battery electrode by controlled modification of the volume expansion direction. In the past two decades, it has been shown that ionic transport properties can be dominated by interfaces at the nanoscale [1, 2]. Heterojunctions (namely chemical and structural discontinuities) in nanostructures provide the possibility to control the Li diffusion pathways, resulting in customizing volume expansion behavior. The flexibility in composition and structure enabled by tailoring electrodes at the nanoscale could drastically change the ionic transport and help meet new levels of Li-ion battery performance.

Recently, the in-situ transmission electron microscopy (TEM) electrochemistry technique has emerged as a powerful approach to understand lithiation behaviors and reaction mechanisms during battery operation, attributed to the unique capability of dynamically monitoring the structural evolution, phase transformation, and chemical composition change of electrodes with high resolution [3, 4]. Si-Ge composite anodes have the advantage of integrating a balanced and enhanced performance in Li-ion batteries due to the combination of the high capacity of Si and excellent rate capability of Ge. In this presentation, Li ion transport in Si-Ge heterostructures (i.e. Ge/Si core/shell and Si/Ge core/shell nanowires) was systematically studied inside the TEM in real-time. In sharp contrast to the radial lithiation behavior in pure Ge and pure Si nanowires as well as in Si/Ge core/shell nanowires, pure axial lithiation was observed in Ge/Si core/shell nanowires. These striking observations validate that radial heterostructuring (Si shell on Ge core) can suppress the commonly observed surface insertion of Li ions that has been reported in all nanoscale systems to date, and exclusively induce axial lithiation along the $\langle 111 \rangle$ direction in a layer-by-layer fashion. The deposition of a conformal, epitaxial, and ultrathin Si shell (1~5 nm) on Ge nanowires creates an effective chemical potential barrier for Li ion diffusion through the surface, allowing only axial lithiation and volume expansion. A set of control experiments, such as lithiation of Ge/SiO_x core/shell nanowire, carbon-coated Ge/Si core/shell nanowire and Ge/Si core/shell nanowire after etching of surface Si layer, were also conducted to demonstrate the interface and bandgap engineering effect on ionic transport properties. Our work [5] is the first direct observation of the dramatic interfacial effect on ionic transport at the nanoscale. Specifically, we demonstrate for the first time that interface and bandgap engineering of electrochemical reactions can be utilized to control the nanoscale ionic transport/insertion paths, which provides a powerful additional degree of freedom to define the electrochemical reactions in Li-ion batteries [6].

References:

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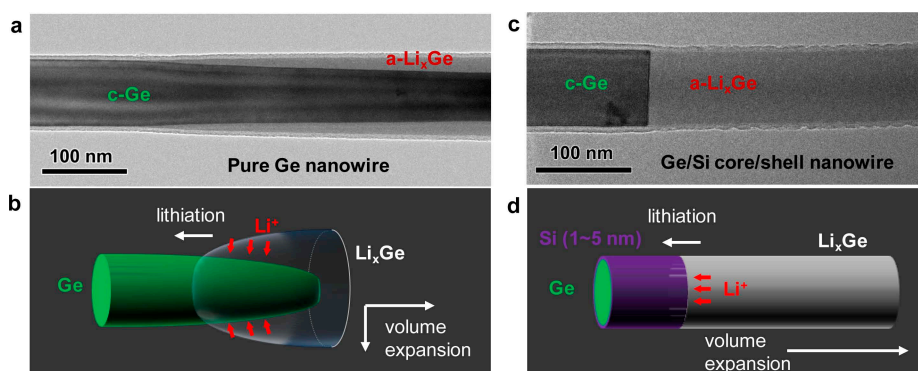


Figure 1. Sharp contrast of radial lithiation of pure Ge nanowire (a, b) and axial lithiation of Ge/Si core/shell nanowire (c, d).

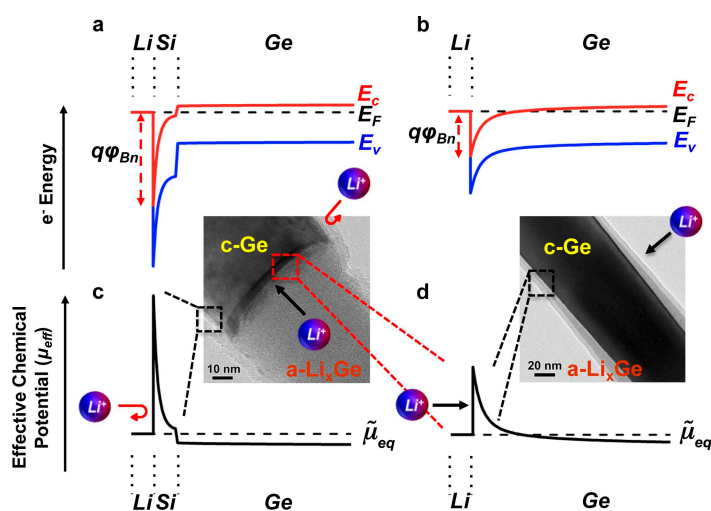


Figure 2. Comparison of band-edge profile and effective Li ion potential in Ge/Si core/shell nanowire (a, c) and pure Ge nanowire (b, d).