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Characterization of Trapped Charge in Ge/Li_xGe Core/Shell Structure during Lithiation using Off-axis Electron Holography

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Lithium ion batteries (LIBs) have important applications as energy-storage systems for portable electronics, electric vehicles, and sources of renewable energy [1,2]. Ge is being considered as a possible alternative to graphite as anode for its theoretically high capacity and high Li^+ diffusivity, despite of its large volume change upon lithiation/delithiation [3]. Knowledge of the charge distribution during lithiation is important to better understand the lithiation mechanism and the associated electrochemistry. Off-axis electron holography (EH) is an interference technique that can effectively measure electrostatic fields with nanoscale spatial resolution [4]. After hologram reconstruction, the projected potential distribution of the object along the electron beam direction can be retrieved from the phase image and compared with calculations. Here, EH has been used to characterize the charge distribution across Ge/Li_xGe core/shell nanowires (NWs) during lithiation. The Ge NWs were grown along [111] directions using the vapor-liquid-solid (VLS) method on Si substrates. The NW was mounted on a Nanofactory holder and attached to Li metal for in-situ lithiation and EH measurement.

Figures 1a, 1d and 1g show sequential holograms of Ge NW taken during lithiation. In Figure 1a and 1d, Ge/Li_xGe core/shell structure was observed, as shown by the darker contrast in the NW center. The Ge core was reduced from 45nm to a faceted one of 16nm in radius, while the outer shell increased from 88nm to 110nm in radius. Li EELS mapping and HAADF image (not shown) taken after Figure 1a confirm the Ge/Li_xGe core/shell structure. In Figure 1g, the Ge core disappeared and the NW radius increased to 125nm, corresponding to a chemical composition of Li_xGe (x~3.75). The reconstructed phase images are shown in Figures 1b, 1e and 1h, respectively, in which pseudo-color is used to show the phase change. Phase profiles along the white arrows are shown on the right. The center part of the NW has higher phase compared to the outer part, due to the greater thickness and higher mean inner potential (MIP) of crystalline Ge, compared to Li_xGe. Both the core and shell parts mimic a cylindrical NW shape. To interpret phase profiles, it is first assumed that there are no trapped charges in the NW and that the phase shift is only due to MIP V_{shell}. Assuming the NW has a cylindrical shape, the phase shift due to the shell can be calculated and compared with the experimental results, as shown by the red curves in the phase profiles. As lithiation continued, V_{shell} changed from 7.6V±0.1V to 6.4V±0.1V and then 5.1V±0.1V. This drop indicates that the Li component has increased during lithiation, because Li is a lighter element and has smaller MIP, compared to Ge. The bias applied to the NW should not affect this conclusion since the bias was fixed at -2V. Similar fitting was applied for the core part in Figure 1c, as shown by the blue curve. However, the best fitted V_{core} is only 10.6±0.1V, compared to the value of 14.3V for crystalline Ge [5]. This difference suggests that charges are trapped in the NW during lithiation. A proposed model, as shown in Figure 2a, assumed that Li^+ ions accumulated in the Li_2O layer on the NW surface, while electrons were uniformly trapped in the Ge NW core. The fitted result is shown in Figure 2b, where the charge density was calculated to be 3×10^{18} electrons/cm^3 and the MIP for the shell was 8.4V. Further investigations are in progress [6].

References:
[1] M. Armand and J. M. Tarascon, Nature **451** (2008) 652.
[2] A. S. Arico, *et al.*, Nature Materials **4** (2005) 366.
[3] D. Larcher, *et al.*, Journal of Materials Chemistry **17** (2007) 3759.
[4] M. R. McCartney and D. J. Smith, Ann. Rev. Mater. Res. **37** (2007) 729.
[5] J. Li, *et al.*, Acta. Crystal. Sec. A **55** (1999) 652.
[6] The electron holography studies have been supported by DoE Grant DE-FG02-04ER46168. We also acknowledge use of the EMSL user facilities.

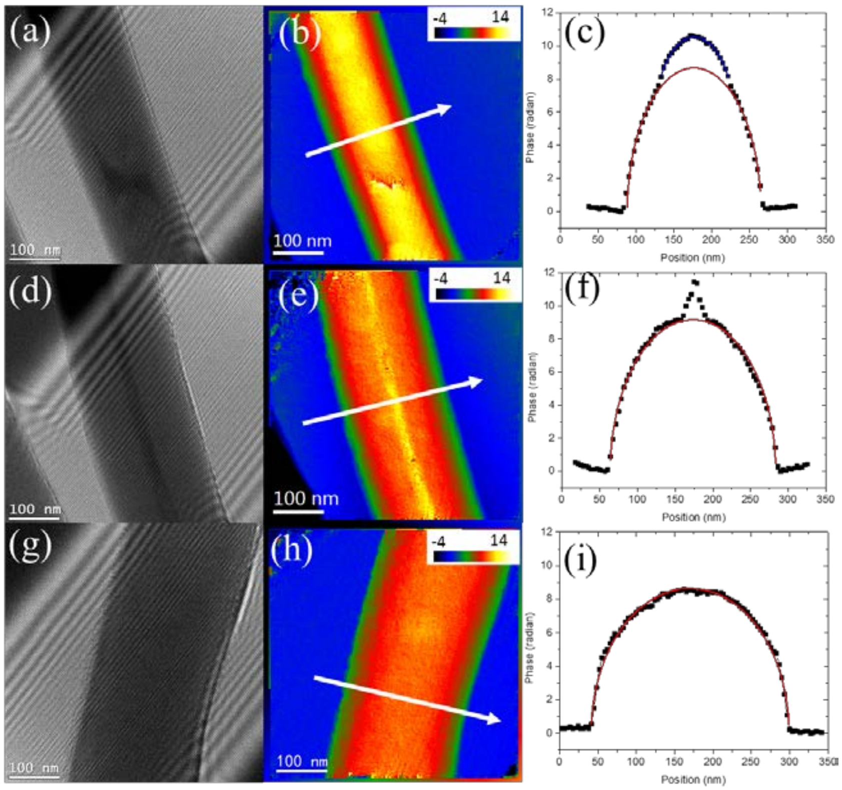

Figure 1. (a), (d) and (g) Holograms of Ge/Li_xGe core/shell NW structure during lithiation; (b), (e) and (h) Corresponding reconstructed phase images, shown in pseudo-color (scale bar shown at top right is in units of radian); (c), (f) and (i) Phase profiles along the white arrows in (b), (e) and (h), respectively.

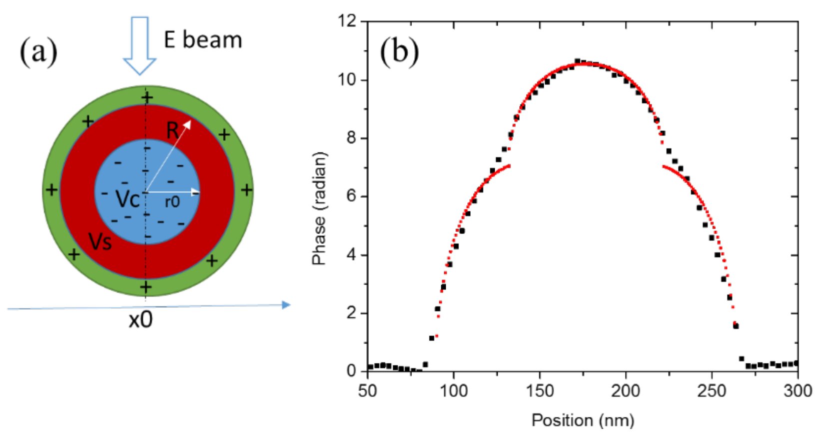

Figure 2. (a) Schematic diagram of the model for trapped charges in Ge/Li_xGe core/shell NW structure; (b) Experimental data (black) and best fitted results (red).