Supporting Information for Strain-induced Structural Defects and Their Effects on Electrochemical Performances of Silicon Core/ Germanium Shell Nanowire Heterostructures

Yung-Chen Lin^{1,*}, Dongheun Kim^{1,*}, Zhen Li², Binh-Minh Nguyen¹, Nan Li¹, Shixiong Zhang², Jinkyoung Yoo^{1,*}

¹Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545

²Department of Physics, Indiana University, Bloomington, IN 47405 *Corresponding author. E-mail: jyoo@lanl.gov

<u>Growth of Si/Ge core/shell nanowire heterostructures</u> The Si/Ge core/shell nanowire (NW) heterostructures were grown by chemical vapor deposition (CVD) assisted with Au catalysts. For the transmission electron microscopy study the core/shell NW heterostructures were prepared on Si substrates. The crystallographic orientations of core Si NWs were controlled by the orientations of Si substrates. Meanwhile the core/shell NW heterostructures for electrochemical characterizations were prepared on 304 stainless steel (SS) disks as current collectors of lithium ion batteries. The crystallographic orientation of Si NWs grown on 304 SS disks is [112] only.

3 nm-thick Au thin films were deposited onto Si and SS disks via *e*-beam evaporation. Subsequently, the Au/Si and Au/SS substrates were loaded into our cold wall low-pressure CVD reactor. The substrates were heated up to ~460°C in the reactor under hydrogen flow. During the ramping up stage the Au thin films formed Au dots, which serve as the nucleation sites of Si NWs. The precursors for the growth of Si NWs were SiH₄ (50% diluted in hydrogen). The growth temperature and reactor pressure were ~460°C and 3 Torr, respectively. After the growth of the core Si NWs *in-situ* growth of Ge shell was performed. The growth temperature and reactor pressure of Ge shell deposition were ~410°C and 0.5 Torr, respectively. The precursor for Ge shell growth was GeH₄ (30% diluted in H₂). The details of growth of Si/Ge core/shell NW heterostructures are described in the reference 1.

<u>Strain Analysis method</u> The strain analysis is operated through two steps, (1) Identify the position of each atomic-column in a HRTEM image with Peak Pairs Analysis (PPA) software² and (2) Calculate strains at the position of each atomic-column. Using a lattice image that is composed of a set of points in a plane, the three local strain components in rectilinear coordinates, ε_{11} , ε_{22} , and ε_{12} , at any point surrounded by 8 neighbors, define the radial strain in the direction of the α^{th} neighbor, $\alpha\varepsilon$, according to the coordinate transformation law³

$${}_{\alpha}\varepsilon = {}_{\alpha}l^{2}\varepsilon_{11} + {}_{\alpha}m^{2}\varepsilon_{22} + {}_{\alpha}l_{\alpha}m\gamma_{12}$$
⁽¹⁾

with $_{\alpha}$ l and $_{\alpha}$ m as direction cosines of the α^{th} neighbor in a perfect (undeformed) lattice in 2D, and higher order terms in strain have been neglected as they are assumed small. In

strain space, Eq. (1) is an ellipse. Thus there are N equations of this form for each lattice point, and the left side of each equation is known since

$$_{\alpha}\varepsilon = \frac{_{\alpha}r}{_{\alpha}R} - 1 \tag{2}$$

where $_{\alpha}$ r and $_{\alpha}$ R are the distances to the α^{th} neighbor in the deformed and perfect lattices, respectively. Referring to Ref. 3, the set of N equations enable the determination of the ε_{ij} components in a least squares sense giving the strains expressed as a column vector

$$\varepsilon = \mathbf{N}^{-1}\mathbf{Q} \,, \tag{3}$$

where the matrix N and column vector Q are given by

$$\mathbf{N} = \begin{bmatrix} \sum_{\alpha} l^{4} & \sum_{\alpha} l^{2}_{\ \alpha} m^{2} & \sum_{\alpha} l^{3}_{\ \alpha} m \\ \sum_{\alpha} l^{2}_{\ \alpha} m^{2} & \sum_{\alpha} m^{4} & \sum_{\alpha} l_{\alpha} m^{3} \\ \sum_{\alpha} l^{3}_{\ \alpha} m & \sum_{\alpha} l_{\alpha} m^{3} & \sum_{\alpha} l^{2}_{\ \alpha} m^{2} \end{bmatrix} \text{ and } \mathbf{Q} = \begin{bmatrix} \sum_{\alpha} \varepsilon_{\alpha} l^{2} \\ \sum_{\alpha} \varepsilon_{\alpha} m^{2} \\ \sum_{\alpha} \varepsilon_{\alpha} l_{\alpha} m \end{bmatrix}$$
(4)

and the sums are over all neighbors. The least squares determination of the strain components, leading to Eq. (3), is necessitated by various uncertainties in the positions of the various lattice points extracted from the HRTEM image.^{4,5}

Meanwhile, the TEM foil is assumed to be under the condition of plane stress. This assumption is reasonable since the thickness of TEM foil along the e-beam direction is \sim 50 nm and the loading is parallel to the TEM foil. Corresponding to plane-stress condition, the stress along the e-beam direction is equal to zero. The strain along the e-beam can be calculated using the measured in-plane strains.

The strain analysis of a single Si [112]/Ge core/shell NW heterostructure



Figure S1. The strain map of a single Si [112]/Ge core/shell NW heterostructure. The PPA analysis was employed to visualize the strain map. The normal strain along axial (ε_{xx}) is cancelled out on average, as shown in (b). The shear strain (ε_{xy}) component

presents different colors in each half of a single Si/Ge core/shell NW heterostructure, which corresponds to the twin orientation. The normal strain along radial (ε_{yy}) direction present the tendency of tensile close to the shell region.

<u>Electrochemical measurements</u> For electrochemical measurements of Si/Ge core/shell nanowire heterostructures and Si nanowires grown on 304 stainless steel disks 2032-type coin half cells were assembled in an Ar-filled glove box using a 25 μ m thick microporous monolayer membrane as a separator (Celgard, 2400), a 1.5 mm thick lithium foil as reference and counter electrodes (Alfa Aesar), and 1 M lithium hexafluorophosphate (LiPF₆) in 1:2 mixture of ethylene carbonate and dimethyl carbonate (Novolyte). Electrochemical performances were carried out using a multichannel potentiostat (Bio-Logic, VMP3) with a constant current mode within the voltage range of 0.01–1.5 V vs. Li/Li⁺. For the formation of smooth solid electrolyte interphase, the samples were cycled at a low rate of 0.05 C in the first cycle and then the cycle rate was increased in the remaining cycles. Galvanostatic intermittent titration Technique (GITT) samples were evaluated between 1.5 and 0.01 V, at a rate equivalent to 0.02 C for 15 min, followed by a relaxation period of 15 min. The chemical diffusion coefficient (*D*) can be calculated at each step, with the following formula

$$D = \left(\frac{4}{\pi}\right) \left(\frac{V_m i}{ZFS}\right)^2 \left(\frac{\frac{dE}{d\delta}}{\frac{dE}{dt^{1/2}}}\right)^2 \text{ for } t \ll L^2/D$$

where, *i*, V_m , *Z*, *F*, *S*, *E*, *t* and δ are the current, the molar volume of electrode, the charge number, the Faraday constant, the electrode area, the electrode potential, the titration time, and the ideal stoichiometry, respectively.

Capacity retention plots of Si nanowires and Si/Ge core/shell nanowire heterostructures



Figure S2. The normalized gravimetric capacities of Si nanowires and Si/Ge core/shell nanowire heterostructures.

References

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