Bend and Precipitate Formation Mechanisms in Epitaxial GeSn Shells on Ge Nanowires

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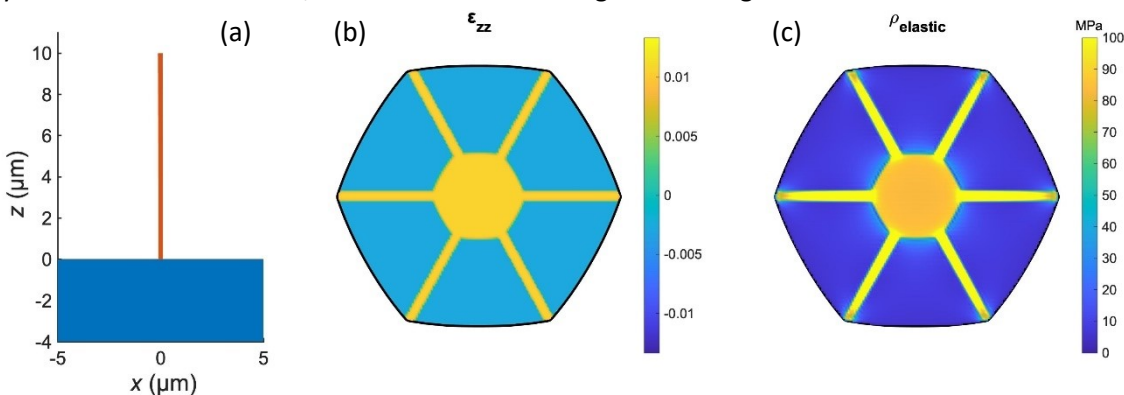Symmetrical Core-Shell Ge/GeSn Nanowire Showing No Bending:

Figure S1 Simulation of symmetrical core-shell Ge/GeSn nanowire with a nominal 10 at% Sn composition in the GeSn shell and no crescent shaped Sn-poor region showing no bending: a) nanowire deflection, b) axial strain, and c) elastic energy density

Axial strain

$$\begin{cases} \epsilon_{yy} = 0, x = 0 \\ \epsilon_{yy} = \pm \dfrac{\Delta L}{L}, x = \pm \dfrac{w}{2} \end{cases}$$

$$R * \theta = L$$

$$\left(R \pm \frac{w}{2}\right) * \theta = L \pm \Delta L$$
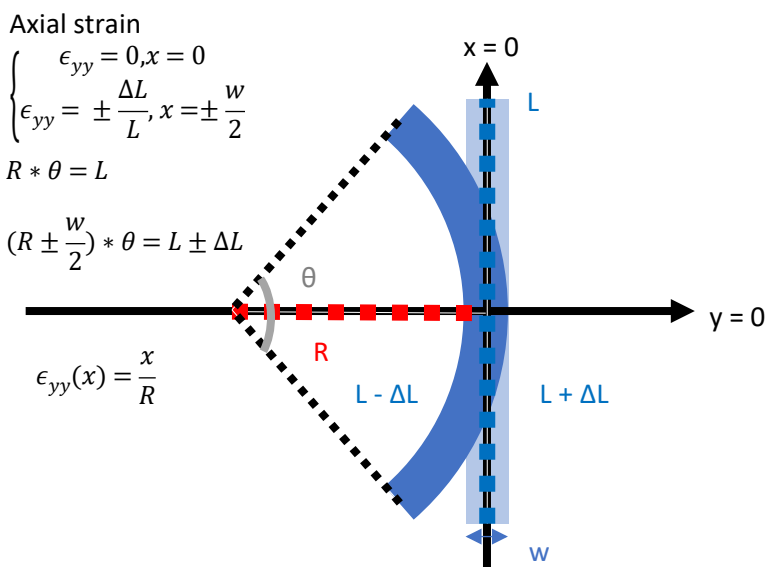
$$\epsilon_{yy}(x) = \frac{x}{R}$$

Figure S2 Schematic for Lattice Parameter Variation due to Bending

The variation of axial lattice parameter due to bending is illustrated in Figure S2. To first order, the increase in length of the nanowire on the outside of the bend is equal to the ratio of the nanowire radius to the bend radius. For a 200 nm diameter nanowire with a 10 μm bend radius, the axial lattice parameter varies linearly from -1% to 1% as a function of radial position from the inside of the bend to the outside of the bend.

To calculate the effect of a change in axial lattice parameter on the 2θ value, we can use Bragg's Law: $\lambda = 2d \sin \theta$. Because the axial lattice parameter variation is linearly distributed from -1% to 1%, we can look at how 2θ values change when the lattice parameter increases or decreases by 0.5%. We consider the (333) GeSn peak: for a 2θ = 88.4850°, if d_{333} increases by 0.5%, then 2θ = 87.9312° (if d_{333} decreases by 0.5%, then 2θ = 89.0473°). Thus, we see that a ±0.5% change in axial lattice parameter results in a 2θ values that differ by about 1.1°. The full width half max for the (333) peak of a 200 nm diameter with a 10 μm bend radius is then about 1°, and this is consistent with the experimental result.
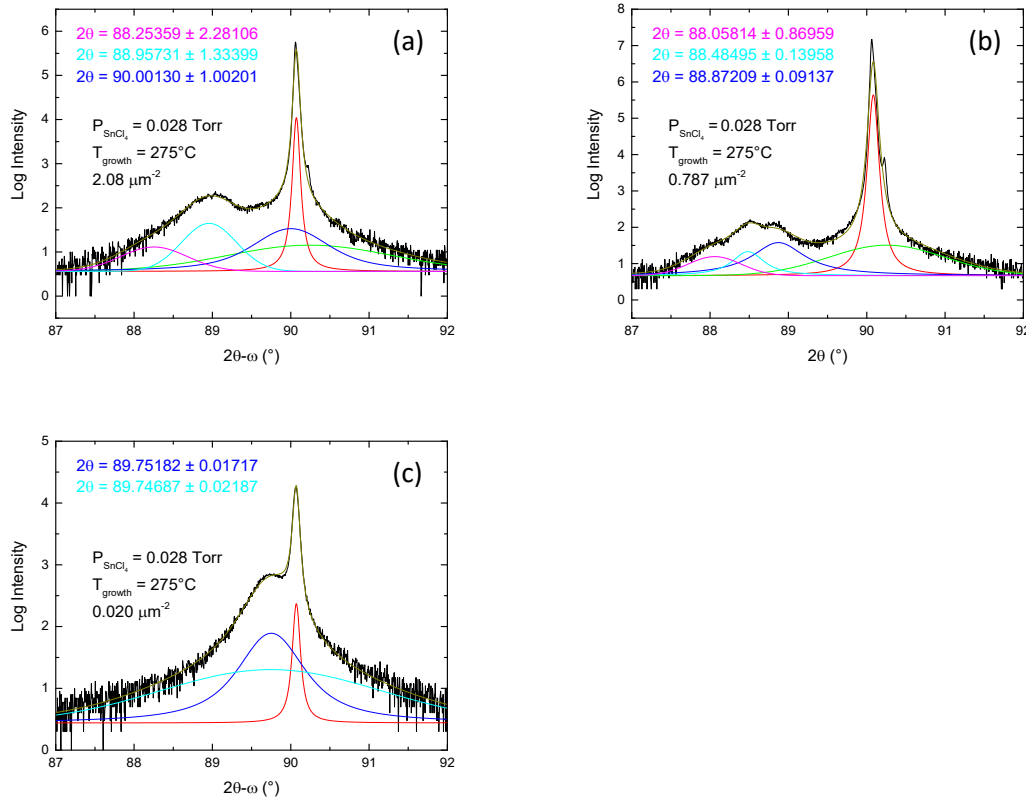

Figure S3 High Resolution XRD Fitting for (333) Peak of Core-shell Ge/Ge$_{1-x}$Sn$_x$ Nanowires grown at decreasing nanowire VLS catalyst loading density from (a)-(c).

In all fits for the XRD data (Figure S3), the contribution from the bulk Ge substrate is fit with a red curve; the blue and magenta curves represent contributions from the core-shell Ge/GeSn nanowires. The green curves are used to fit Ge thin film deposited epitaxially on the Ge (111) substrate (Reference [8]). The XRD scans exhibit multiple (either 2 or 3) contributions from the core-shell Ge/GeSn nanowires (Figures S3a-c); the peaks are also very broad. Because the multiple peaks can be attributed to axial Sn composition variations, we focus on the middle 2θ value, which is the highest maximum intensity peak, to calculate 2θ values for GeSn (333). This peak corresponds to a majority of the GeSn in the shell of the nanowire. As

suggested by reference [20], the highest Sn composition is in the short axial GeSn growth segment, and the lowest Sn composition is in the nanowire base.

X-ray Diffraction Sn Composition Calculation

As an example, we calculate the Sn composition from nanowires with (333) peak at $2\theta = 88.4850°$.
We know Bragg's Law: $\lambda = 2d \sin \theta$ and that for Cu Kα1, $\lambda = 1.5406$ Å.
This allows us to calculate $d_{333} = 1.10406 \times 10^{-10}$ m and lattice parameter, $a = 5.73687$ Å.
If we assume the $Ge_{1-x}Sn_x$ shell is relaxed as in reference [13], we need to compare $a = 5.73687$ Å to $a_{Ge} = 5.658$ Å and $a_{Sn}/a_{Ge} = 1.14$, which gives a Sn composition of 10%. If we assume the core-shell interface is coherent, then the $Ge_{1-x}Sn_x$ shell is in a slightly compressed state and the actual lattice parameter is a little greater than 5.73687 Å, making the Sn composition slightly greater than 10 at%. Furthermore, based on reference [13], the Sn composition is not very sensitive to the assumption on the shell strain state because the shell is close to relaxed.

Phase Field Simulations

Adopting the parameters in Table I, the total free energy of the core-shell nanowire system can be expressed as a functional of the phase field $\phi(x)$ and the displacement field $u(x)$ in the following form,

$$F[\phi(x),u(x)] = \int U\phi^2(1-\phi)^2 + \frac{1}{2}\epsilon(n)^2(\nabla\phi)^2 + \frac{1}{2}C_{ijkl}(x)\left(\varepsilon_{ij} - \varepsilon_{ij}^{eig}\right)\left(\varepsilon_{kl} - \varepsilon_{kl}^{eig}\right)d^3x$$

More specifically, $\epsilon(n)$ is a function of the local orientation of the phase field, in order to introduce the anisotropy of the interfacial energy,

$$\epsilon(n) = \epsilon_0 \cdot \left[1 + \epsilon_1 \cdot \left(n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2\right) + \epsilon_2 \cdot \left(n_x^2 n_y^2 n_z^2\right) + \epsilon_3 \cdot \left(n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2\right)^2\right]$$

where n_x, n_y and n_z are the x, y and z components of $n = \dfrac{\nabla\phi}{|\nabla\phi|}$ respectively.

$$C_{ijkl} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$$

which is the stiffness tensor for the simplest anisotropic case.

ε_{ij} is the i-j component of the elastic strain, which can be linked to displacement field u by $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, and ε_{ij}^{eig} is an eigen-strain field (if $i = j$, $\varepsilon_{ij}^{eig} = \varepsilon^{misfit}$, otherwise, $\varepsilon_{ij}^{eig} = 0$) designed to represent the lattice misfit between the core and shell, depending on the Sn concentration,

$$\varepsilon^{misfit} = \frac{a_{Sn}x_{Sn} + a_{Ge}(1 - x_{Sn}) + 0.0082 x_{Sn}(1 - x_{Sn}) - a_{Ge}}{a_{Ge}}$$

where $a_{Ge} = 5.6579$ Å and $a_{Sn} = 6.4892$ Å

In the phase field model, the parameters M, Δt and Δt_2 are used in the Cahn-Hilliard (C-H) type equation of motion,

$$\phi(t + \Delta t) = \phi(t) + K\nabla^2\left(\frac{\delta F}{\delta\phi}\right)\Delta t$$

$$u(t + \Delta t_2) = u(t) - M \frac{\delta F}{\delta u} \Delta t_2$$

where $K = M$ is the kinetic coefficient, $\frac{\delta F}{\delta \phi}$ and $\frac{\delta F}{\delta u}$ are the variational derivatives of F with respect to ϕ and u, respectively. The value of Δt_2 is set to a much smaller value than that of Δt, with the assumption that the local relaxation of the atoms in response to the mechanical stress is much faster than the long-distance diffusion for shaping the interface.

In addition, the values of M, h and Δt are determined from the reference [12] such that the nanowire growth curve predicted by the model is comparable with the experimental data. However, it should be noted that in this study since the C-H equation of motion is applied, there is no net growth of the nanowire.