Electronic Supplementary Information

Phase-Field Investigation of the Stages in Radial Growth of Core-Shell $Ge/Ge_{1-x}Sn_x$ Nanowires

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FIG. S1: HRTEM image of the cross sections of $Ge/Ge_{0.958}Sn_{0.042}$ nanowires (left). A zoom-in image shows continuous lattice fringes throughout the inset area (right).



FIG. S2: The distributions of the strain components of the grown Ge/Ge_{0.958}Sn_{0.042} core-shell nanowire with a core diameter of 120 nm: (a) ε_{rr} , (b) $\varepsilon_{\theta\theta}$ and (c) ε_{zz} .



FIG. S3: The distributions of the in-plane strain invariants of the grown Ge/Ge_{0.958}Sn_{0.042} core-shell nanowire: (a) $I_1 = \varepsilon_{xx} + \varepsilon_{yy}$, and (b) $I_2 = \varepsilon_{xx}\varepsilon_{yy} - \varepsilon_{xy}^2$.



FIG. S4: The total free energy change of the system ΔF_{tot} , setting the free energy of the initial core configuration as the reference, is decomposed into the contributions from the elastic energy ΔF_{ela} , the interfacial energy ΔF_{int} and the chemical potential related term ΔF_{μ} , and plotted as a function of time. An inset plot is provided to more clearly show the free energy change at the early stage of the growth.



FIG. S5: The minimum vapor chemical potentials for shell growth are plotted as a function of initial core diameter at 0%, 4.2% and 10% Sn respectively.



FIG. S6: A series of SEM images of $\text{Ge}/\text{Ge}_{0.958}\text{Sn}_{0.042}$ nanowires are taken at growth time t = 30s, 1 min, 5 min, 15 min, 30 min and 1 hr respectively.

PHASE FIELD MODEL

Misfit strain

The misfit strain $\varepsilon^{\text{misfit}}$ can be expressed as a function of tin concentration x_{Sn} based on experimental data¹,

$$\varepsilon^{\text{misfit}} = \frac{a_{\text{Sn}} x_{\text{Sn}} + a_{\text{Ge}} (1 - x_{\text{Sn}}) + 0.00882 x_{\text{Sn}} (1 - x_{\text{Sn}}) - a_{\text{Ge}}}{a_{\text{Ge}}}$$
(S1)

where $a_{\text{Ge}} = 5.6579 \text{\AA}$ and $a_{\text{Sn}} = 6.4892 \text{\AA}^2$.

Anisotropy of interfacial energy

To introduce anisotropy of interfacial energy into the model, the parameter $\epsilon(\mathbf{n})$ is designed to depend on the local orientation of the gradient of the ϕ field³, as described in Equation S2,

$$\epsilon(\mathbf{n}) = \epsilon_0 \cdot \left[1 + \epsilon_1 \cdot (n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2) + \epsilon_2 \cdot (n_x^2 n_y^2 n_z^2) + \epsilon_3 \cdot (n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2)^2 \right]$$
(S2)

where ϵ_0 , ϵ_1 , ϵ_2 and ϵ_3 are four constants, and n_x , n_y and n_y are the three components of $\mathbf{n} = \nabla \phi / |\nabla \phi|$.

Variational derivative

The variational derivative of F with respect to the phase field ϕ is given by,

$$\frac{\delta F}{\delta \phi} = 2U\phi(1-\phi)(1-2\phi) - \nabla \cdot \left[\epsilon(\mathbf{n})^2 \nabla \phi\right] - \sum_{n=x,y,z} \frac{\partial}{\partial x_n} \left[(\nabla \phi)^2 \epsilon(\mathbf{n}) \frac{\partial \epsilon(\mathbf{n})}{\partial \phi_{,n}} \right] + \mu \cdot S'(\phi) + \frac{1}{2} C_{ijkl} \left(\varepsilon_{ij} - \varepsilon_{ij}^{\text{eig}} \right) \left(\varepsilon_{kl} - \varepsilon_{kl}^{\text{eig}} \right) \cdot S'(\phi)$$
(S3)

where $S'(\phi) = 5 - 5 \tanh^2(10\phi - 5)$, and i, j, k, l = x, y, z.

And the variational derivative of F with respect to the *i*th component (i = x, y, z) of the displacement field u is given by,

$$\frac{\delta F}{\delta u_i} = -\sum_{j=1,2,3} \frac{\partial \sigma_{ij}}{\partial x_i} \cdot S(\phi) \tag{S4}$$

where $\sigma_{ij} = C_{ijkl} \left(\varepsilon_{kl} - \varepsilon_{kl}^{\text{eig}} \right).$

Interpretation of $\Delta \phi_{\text{max}}$

In Equation 2, the variational derivatives are scaled by $\Delta \phi_{\max}/(-K\Delta t \int \frac{\delta F}{\delta \phi} d^3 \mathbf{x})$ when the total phase volume change of ϕ per step exceeds the pre-set value of $\Delta \phi_{\max}$, to take account for the mass transport limit in the growth. Alternatively, this constraint can be implemented by adding a correction term to the chemical potential,

$$\Delta\phi_{\max} = \int \frac{d\phi}{dt} \cdot \Delta t \ d^3 \mathbf{x} = \int -K\Delta t \left(\frac{\delta F}{\delta \phi} \Big|_{\mu=\mu_0} + \Delta \mu \cdot S'(\phi) \right) \ d^3 \mathbf{x}$$
(S5)

where μ_0 is the unmodified chemical potential, and $\Delta \mu$ is the desired amount of modification on μ_0 (e.g. $-\mu_V$), whose value is determined by,

$$\Delta \mu = -\frac{K\Delta t \int \frac{\delta F}{\delta \phi} \Big|_{\mu=\mu_0} d^3 \mathbf{x} + \Delta \phi_{\text{max}}}{K\Delta t \int S'(\phi) d^3 \mathbf{x}}$$
(S6)

The above equation demonstrates the relationship between $\Delta \mu$ and $\Delta \phi_{\text{max}}$. In the mass transport limited growth, it is expected that the phase volume of the unmodified $\Delta \phi$ is greater than $\Delta \phi_{\text{max}}$, i.e. $-K\Delta t \int \frac{\delta F}{\delta \phi} \Big|_{\mu=\mu_0} d^3 \mathbf{x} - \Delta \phi_{\text{max}} > 0$. Thus, $\Delta \mu$ should be a positive number, leading to a decrease of the true chemical potential driving force $(\mu = -(\mu_V - \Delta \mu))$. If we interpret μ_V as the chemical potential in the vapor reservoir, $\Delta \mu$ may describe the chemical potential drop associated with the material transport from the bulk to the growing interface. In the current model, we can find that when $v_{\text{vol}}^{\text{max}}$ is reached, a sharp modification will be applied on the chemical potential to fix the growth at a constant rate of $v_{\text{vol}}^{\text{max}}$. In a more realistic model, this chemical potential change may be gradual and growth rate dependent.

Model parameters

Table S1 lists the values of all the constant parameters in the phase field model.

TABLE S1: Parameters in the phase field model. $U, \epsilon_0^2, \epsilon_1, \epsilon_2$ and ϵ_3 are interfacial energy associated parameters, whose values are taken to reproduce the surface energies of germanium⁴. h is the grid size. C_{11}, C_{12} and C_{44} are elastic constants of bulk crystalline germanium⁵. M is the kinetic coefficient for the elasticity step. Δt_1 and Δt_2 are the simulation time steps for the phase field evolution step and elasticity step respectively.

$U ~({\rm eV/nm^3})$	$\epsilon_0^2~({\rm eV/nm})$	ϵ_1	ϵ_2	ϵ_3	h (nm)
11.1	90.0	0.6993	-3.6595	-1.7384	1.8
C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	$M (\mathrm{nm}^4/(\mathrm{eV}\cdot\mathrm{s}))$	Δt (s)	Δt_2 (s)
126.0	44.0	67.7	1.0	0.072	0.0036

REFERENCES

- ¹ N. Bhargava, M. Coppinger, J. Prakash Gupta, L. Wielunski, and J. Kolodzey, Applied Physics Letters **103**, 041908 (2013).
- ² M. Oehme, J. Werner, M. Gollhofer, M. Schmid, M. Kaschel, E. Kasper, and J. Schulze, IEEE Photonics Technology Letters 23, 1751 (2011).
- $^3\,$ R. Qin and H. Bhadeshia, Acta Materialia 57, 2210 (2009).
- ⁴ R. Jaccodine, Journal of The Electrochemical Society **110**, 524 (1963).
- ⁵ S. Nikanorov and B. K. Kardashev, Moscow Izdatel Nauka (1985).