

Supporting Information

Demonstration of hexagonal phase silicon carbide nanowires with vertical alignment

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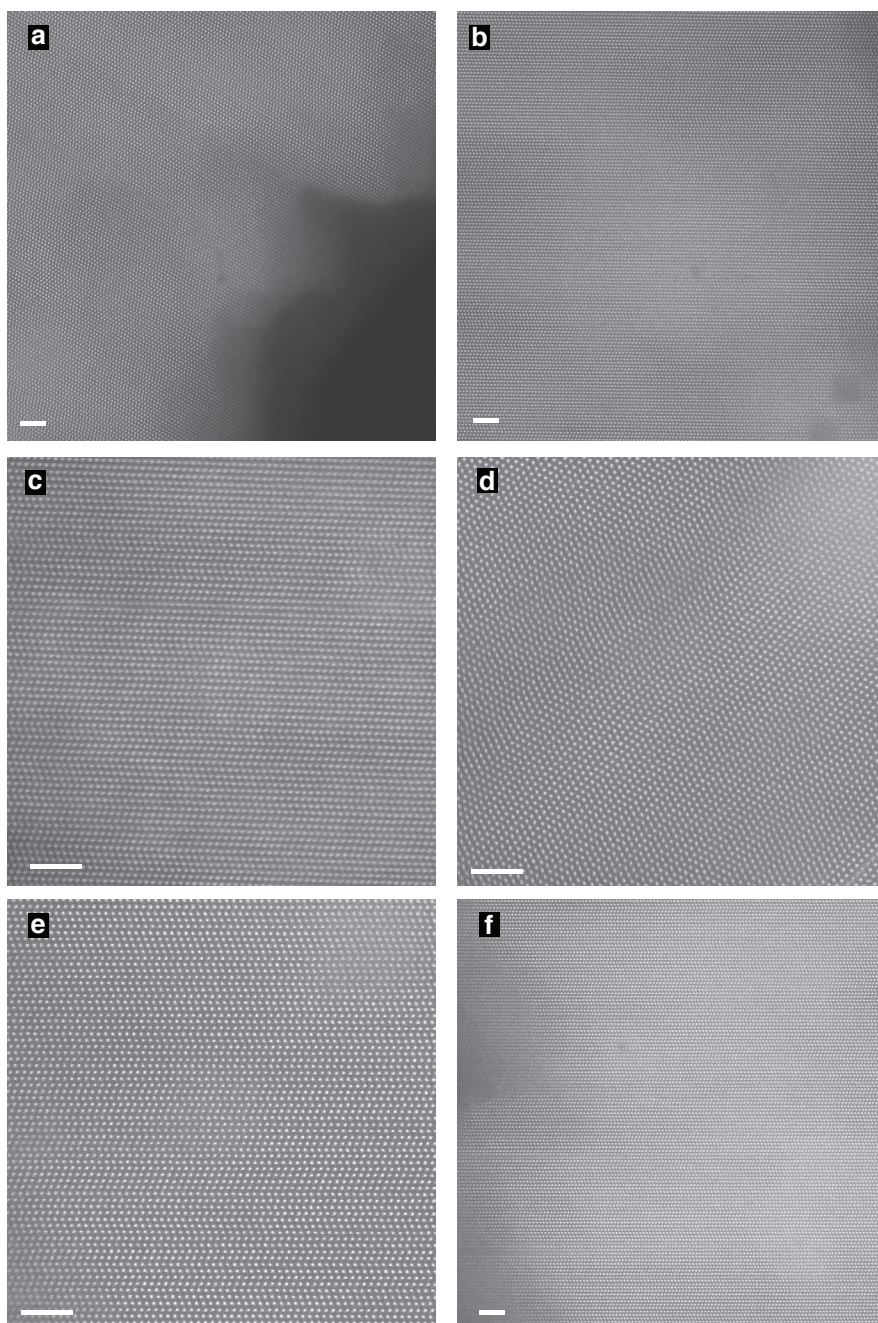


Figure S1. Atomic resolution by high-resolution STEM imaging was used to characterize polytype mixture. (a-f) Original micrographs of 6 different nanowires that were used to determined the combined statistics over 645 Si-C units in Figure 2 of main text. All scale bars are 2 nm.

Table S1. Identification of polytypes and local hexagonal planes.

Image in Supplementary Figure 1	Total No. of planes	No. of 3C planes	No. of 2H planes	No. of 4H planes	No. of locally hexagonal planes
a	172	31	78	70	104
b	128	13	52	67	77
c	64	13	21	29	35
d	92	17	40	23	54
e	65	10	49	19	43
f	124	21	64	44	79
Combined statistic (sum)	645	105	304	252	392
Combined statistic	-	16.3 %	47.1 %	39.1 %	60.8 %

Table S2. Estimated step energy (Γ_i) for SiC.

	Equation	Diamond	Si*	SiC
Lattice constant, a	-	3.57×10^{-8} cm	-	-
Density, ρ	-	3.515 g/cm ³	-	-
Molecular weight, MW	-	12.01 g/mol	-	-
Atomic density, q	$q \times N_A / MW$	1.76×10^{23} cm ⁻³	-	-
Heat of fusion, ΔH^\dagger	-	120 kJ/mol	-	-
		1.99×10^{-12} erg/atom	-	-
Melting temperature, $T_m^{\dagger\dagger}$	-	4100 K	-	-
Excess energy of interfacial bond, W	$0.45 \times \Delta H$	8.96×10^{-13} erg/atom	-	-
Step energy**, γ_{3C}	$1.5^{1/2} q^{2/3} \left\{ \frac{W}{3} - k_B T_m \ln \left[1 + 2 \exp \left(\frac{-W}{k_B T_m} \right) \right] \right\}$	402.6 erg/cm ²	87.6 erg/cm ²	245*** erg/cm ²

* See ref 1.

** The step energy for diamond was calculated using equation given in ref 1, adapted from ref 2.

*** Taken as the average value of diamond and Si.

† Heat of fusion of diamond is estimated as graphite's heat of fusion, measured by ref 3.

†† Melting temperature of diamond is estimated as the diamond/graphite/liquid triple point at 125 kbar, given in ref 4.

Gibbs free energy for nucleation, ΔG_i :

$$\Delta G_i = -\frac{\pi}{2s} r^2 \Delta \mu + \frac{\pi}{2} r^2 \sigma_i + r \Gamma_i$$

Energy barrier for nucleation, ΔG_i^* : \downarrow nucleus orientation
i = h (hexagonal) or k (cubic)

$$\Delta G_i^* = \frac{\Gamma_i^2}{2\pi \left(\frac{\Delta \mu}{s} - \sigma_i \right)}$$

\downarrow
Nucleation rate $\propto \exp(-\Delta G_i^*/k_B T)$. Probability of stacking nucleus with orientation i :

$$p_i = \frac{\exp\left(-\Delta G_i^*/k_B T\right)}{\sum_i \exp\left(-\Delta G_i^*/k_B T\right)}$$

\downarrow
Polytype formation probability ρ_{3C} , ρ_{4H} , and ρ_{2H}

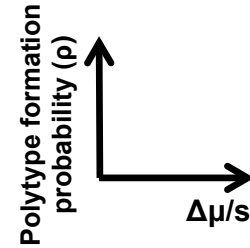


Figure S2. Flow diagram of how Figure 3a in the main text is generated for a nucleus with semicircular geometry. The free variable is $\Delta \mu/s$ and is plotted on the x-axis. See Figure S3 for a description of how interface energy (σ_i) is estimated. Table S2 shows how the step energy (Γ_i) is estimated. The probability factors for stacking a nucleus with orientation i is defined as p_i . The polytype formation probability is then given ρ_i , which is a function of p_i as detailed in ref 5.

$$\sigma_i = \sigma_o - J_1 s_1 s_2 - J_2 s_1 s_3$$

i = denotes polytype

σ = estimated interface energy

σ_o = reference value (no interaction)

J = interaction parameter between the nucleating layer and its nearest (1) and next nearest (2) neighbor

s = layer orientation: '+' is ABC stacking (forward) and '-' is CBA stacking (reverse)

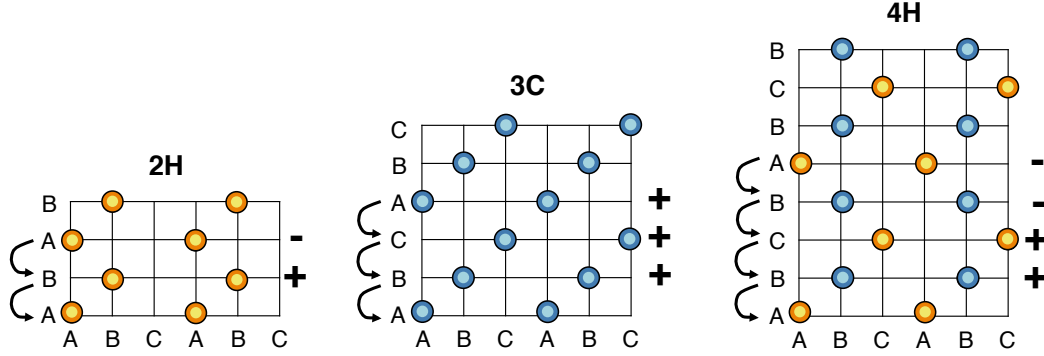


Figure S3. The axial next nearest neighbor Ising (ANNNI) model is used to estimate the interface energies (σ_i) of the 2H, 3C, and 4H polytypes. Table S2 shows how the step energy (Γ_i) is estimated. The twin plane energy (σ_t) is related to the interaction parameters J_1 and J_2 by the following relationship: $\sigma_t = 2(J_1 + 2J_2)$. Using this relationship, the interface energy σ_i can be rearranged in terms of σ_t (estimated as half the stacking fault energy or 17.5 mJ/m² for SiC) and $\eta = -J_1/J_2$.^{1,5,6}

References

1. Hurle, D.T.J. A mechanism for twin formation during Czochralski and encapsulated vertical Bridgman growth of III-V compound semiconductors. *J. Cryst. Growth* **1995**, *147*, 239-250.
2. Voronkov, V.V. Supercooling at the face developing on a rounded crystallization front. *Sov. Phys.-Crystallogr.* **1973**, *17*, 807-813.
3. Heremans, J.; Olk, C.H.; Eesley, G.L.; Steinbeck, J.; Dresselhaus, G. Observation of metallic conductivity in liquid carbon. *Phys. Rev. Lett.* **1988**, *60*, 452-455.
4. Bundy, F.P. Direct conversion of graphite to diamonds in static pressure apparatus. *J. Chem. Phys.* **1963**, *38*, 631-643.
5. Johansson, J.; Bolinsson, J.; Ek, M.; Caroff, P.; Dick, K.A. Combinatorial approaches to understanding polytypism in III-V nanowires. *ACS Nano* **2012**, *6*, 6142-6149.
6. Ning, X.G.; Ye, H.Q. Experimental determination of the intrinsic stacking-fault energy of SiC crystals. *J. Phys.: Condens. Mat.* **1990**, *2*, 10223-10225.