제 28회
한국반도체학술대회
The 28th Korean Conference on Semiconductors
"Semiconductor Technology for Untact Era"
2021년 1월 25일(월) - 29일(금)

Ab initio Approach on the Anisotropic Growth of GaAs: from DFT to Growth Kinetics

In Won Yeu[1], Gyuseung Han[1,2], Cheol Seong Hwang[2], and Jung-Hae Choi[1*]

[1]Electronic Materials Research Center, Korea Institute of Science and Technology,
[2]Department of Materials Science and Engineering, and Inter-University Semiconductor ResearchCenter, Seoul National University.

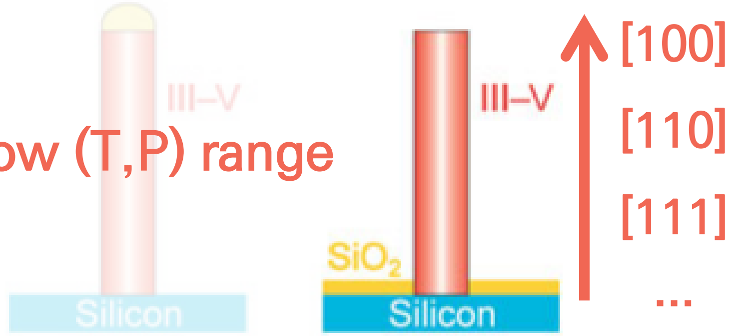
TB1-C-5, 2021. 01. 28, 10:15-10:30

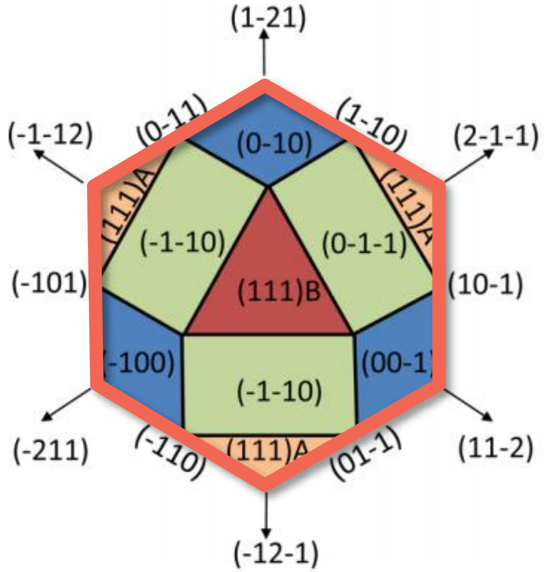
Reference: other works
Reference: our works

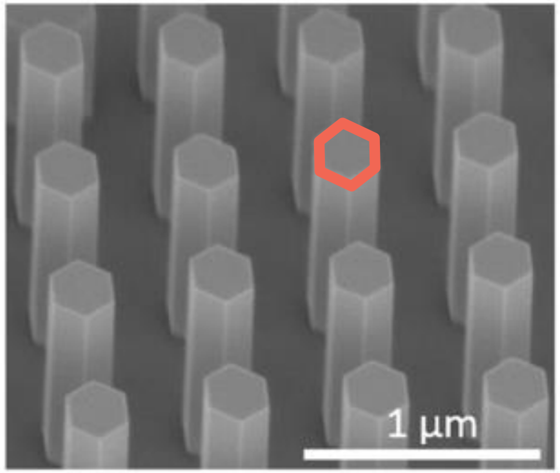
Anisotropic Vapor–Solid (VS) Growth of GaAs NW

Anisotropy of Catalyst-free VS Growth

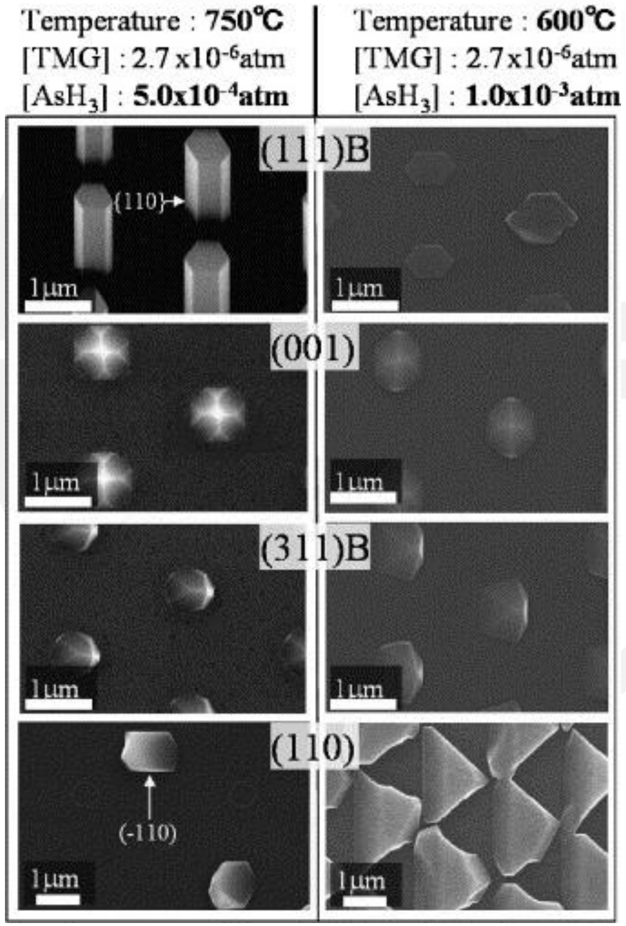
Among various **crystallographic directions**, GaAs NW prefers to grow along **⟨111⟩B** at **narrow (T,P) range**



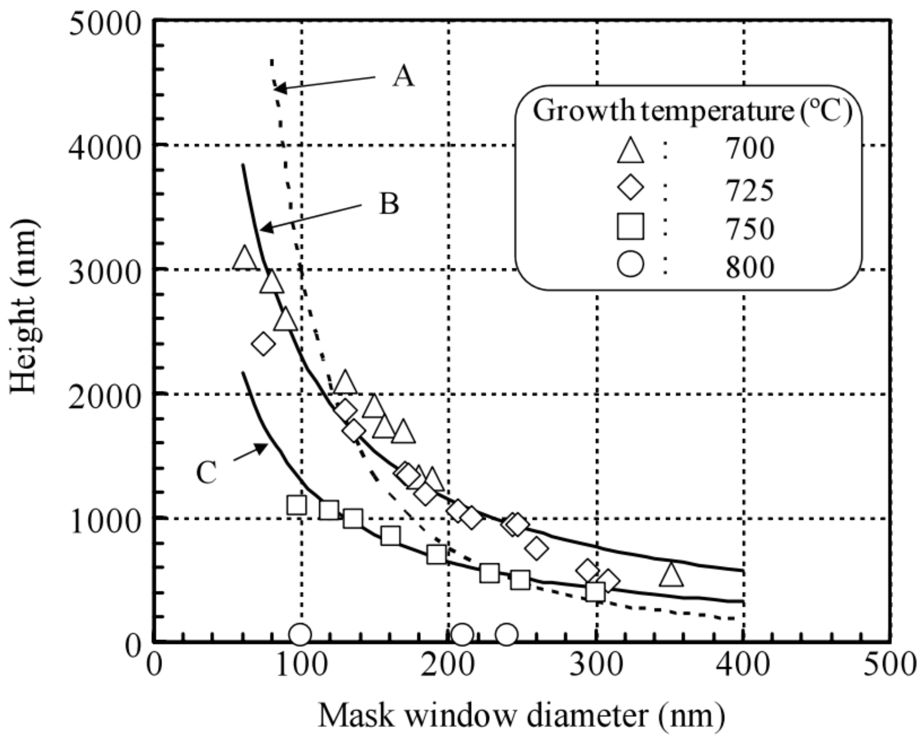




ACS Nano 10, 2424 (2016)



J. Cryst. Growth 298, 616 (2007)

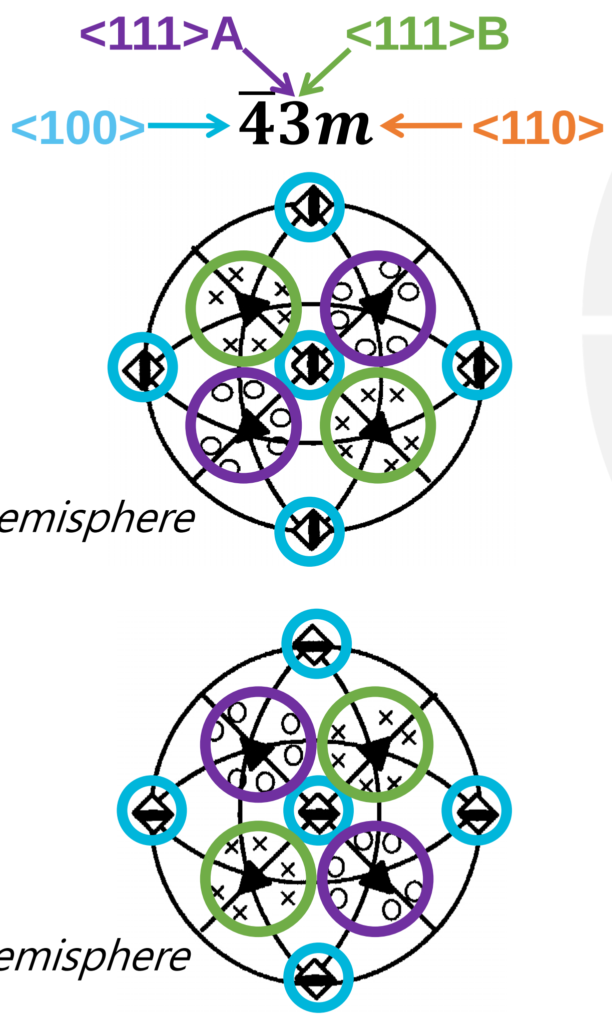


Nanotechnology 19, 265604 (2008)
J. Mater. Res. 26, 2127 (2011)

Crystallographic View Point to Why ⟨111⟩B ?

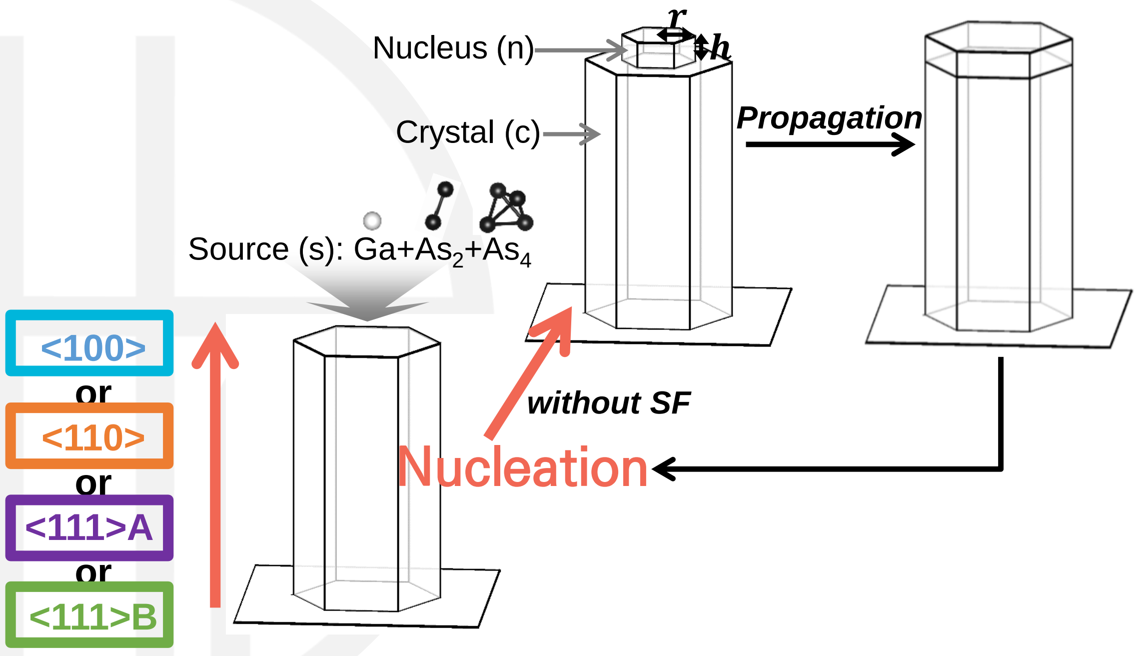
Anisotropy of Nucleation Rate on Surface

Among various crystallographic directions, the distinctive surface structure makes difference in interactions with vapor sources.
In the lattice of zinc−blende (ZB, $F\bar{4}3m$), ⟨111⟩A and ⟨111⟩B are inequivalent and opposite directions of ⟨111⟩



Upper hemisphere

Lower hemisphere



Surface Orientation Dependent Nucleation Rate:

$$\dot{N}_{n|Surf}(T,P) = \underbrace{\dot{C}(Surf,T,P)}_{①} \cdot \exp\left(-\frac{\overbrace{\Delta G^{*}_{sn}(Surf,T,P)}^{②}}{kT}\right)$$

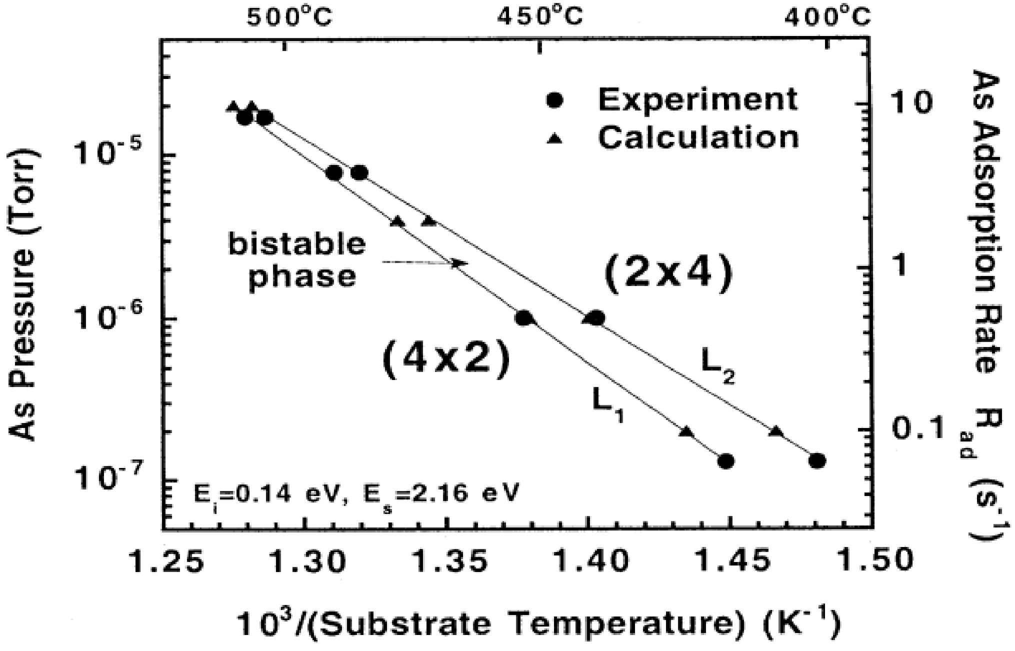
① "Rate of source supply"

② "Nucleation barrier"

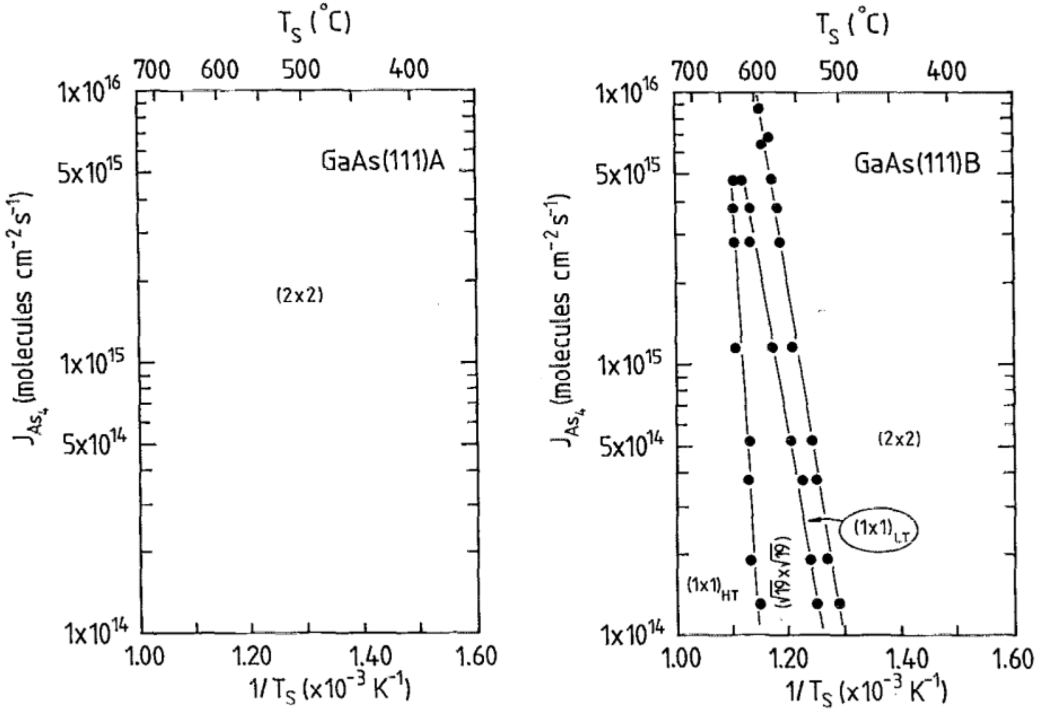
Anisotropy of Surface Structure and its Variations

Each surface shows distinctive bonding geometry and stoichiometry, depending on T−P conditions

Observed by *In situ* RHEED



Phys. Rev. B 51, 9836 (1995)

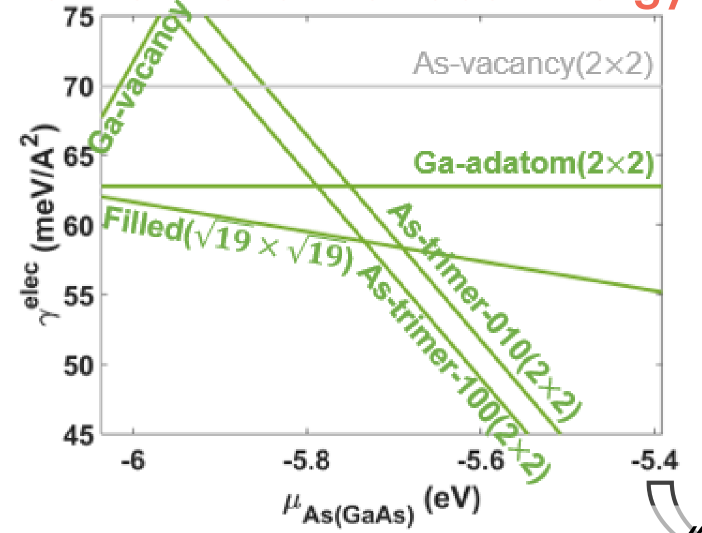


Appl. Phys. Lett. 62, 1370 (1993)

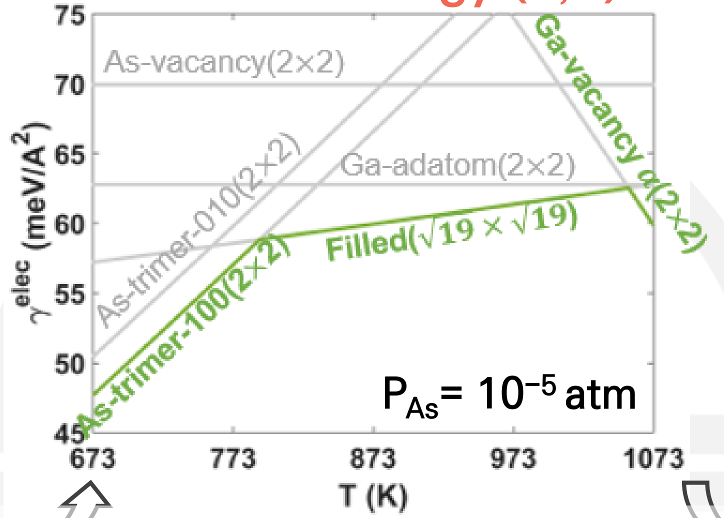
Prediction of Changes in Surface Structure Depending on T, P

Anisotropy of Surface Structure and its Variations: *Ab initio* Thermodynamics

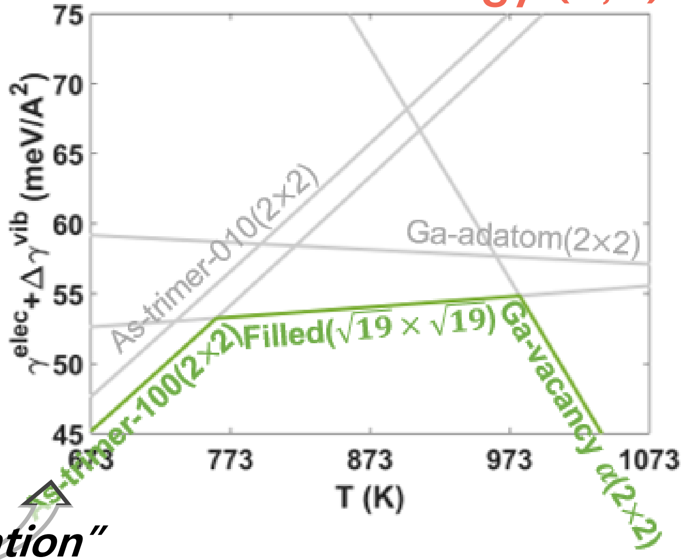
Conventional Surface Energy (μ)



Surface Energy (T,P)



Total Surface Energy (T,P)



"Equilibrium"

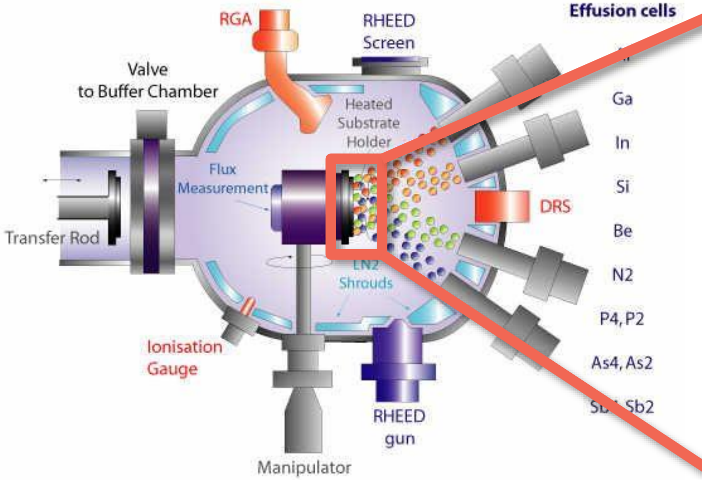
$$\mu_{As(Gas)} = \mu_{As(GaAs)}$$

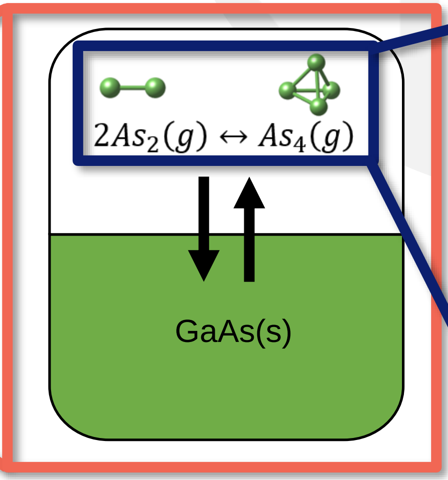
Yeu *et al., Sci. Rep.* 7, 10691 (2017)

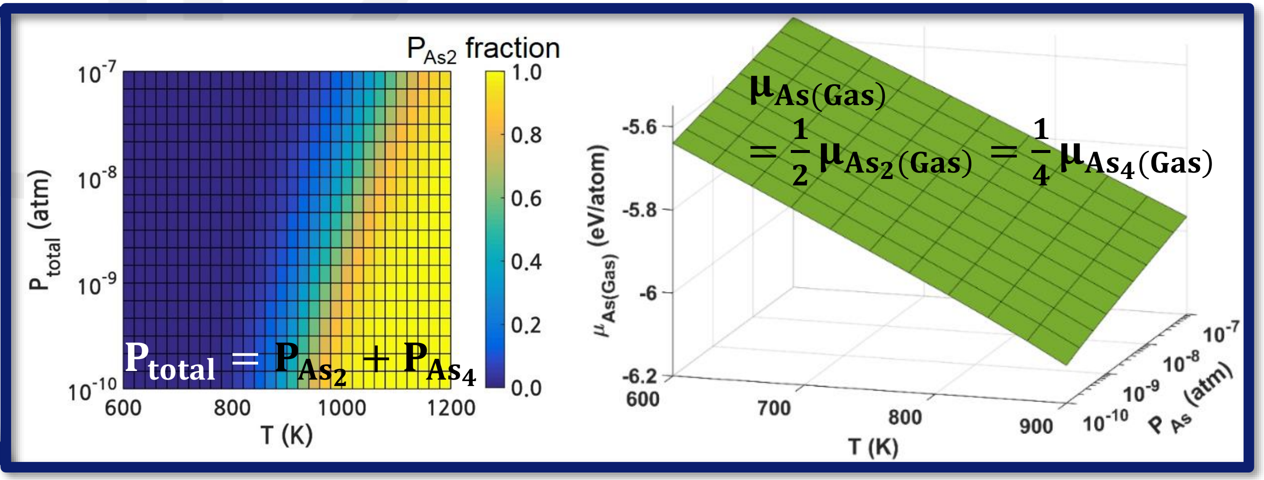
"Surface vibration"

$$\gamma = \gamma^{elec} + \Delta\gamma^{vib}$$

Yeu *et al., Sci. Rep.* 9, 1127 (2019)

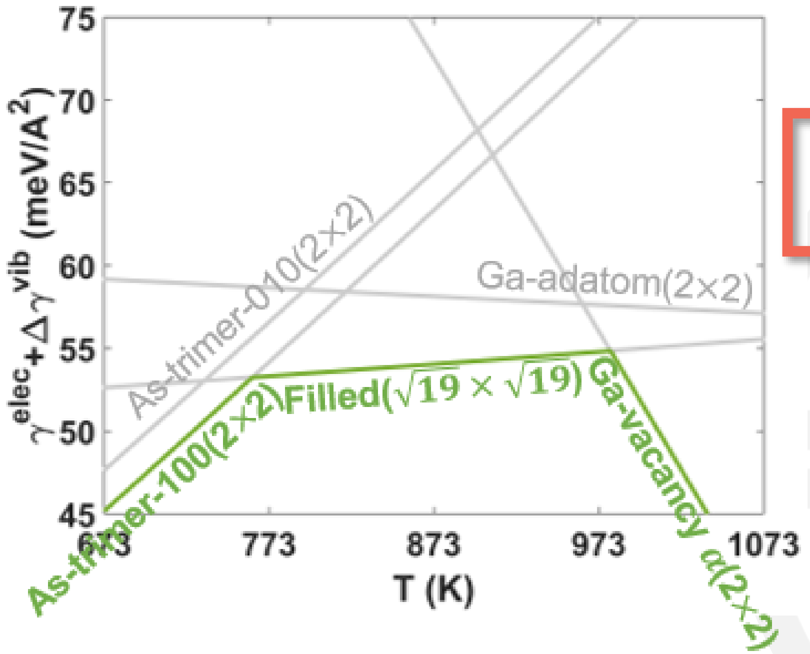




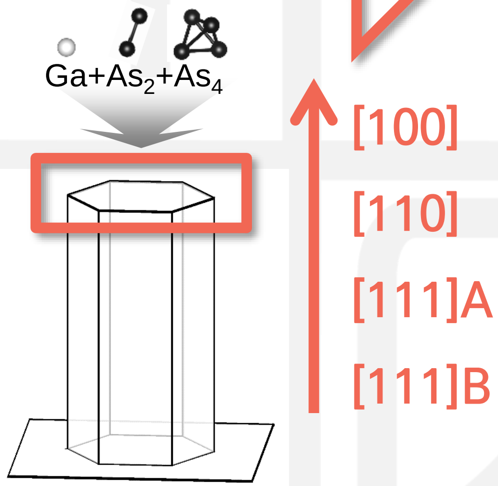


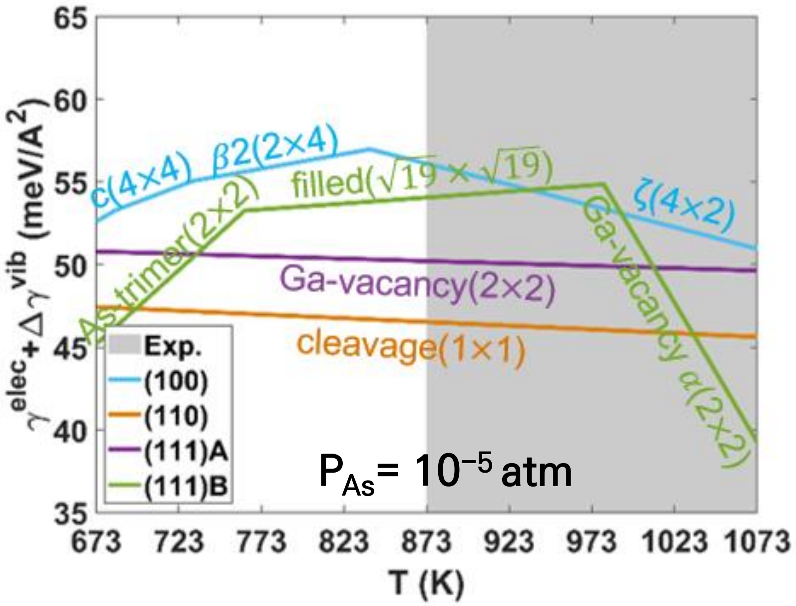
Changes in Adsorption Site Depending on T, P

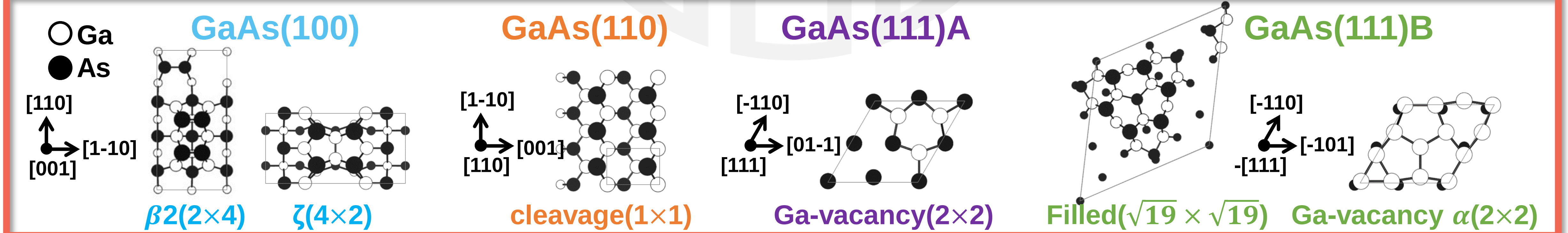
Anisotropy of Surface Structure and Adsorption onto the Surface



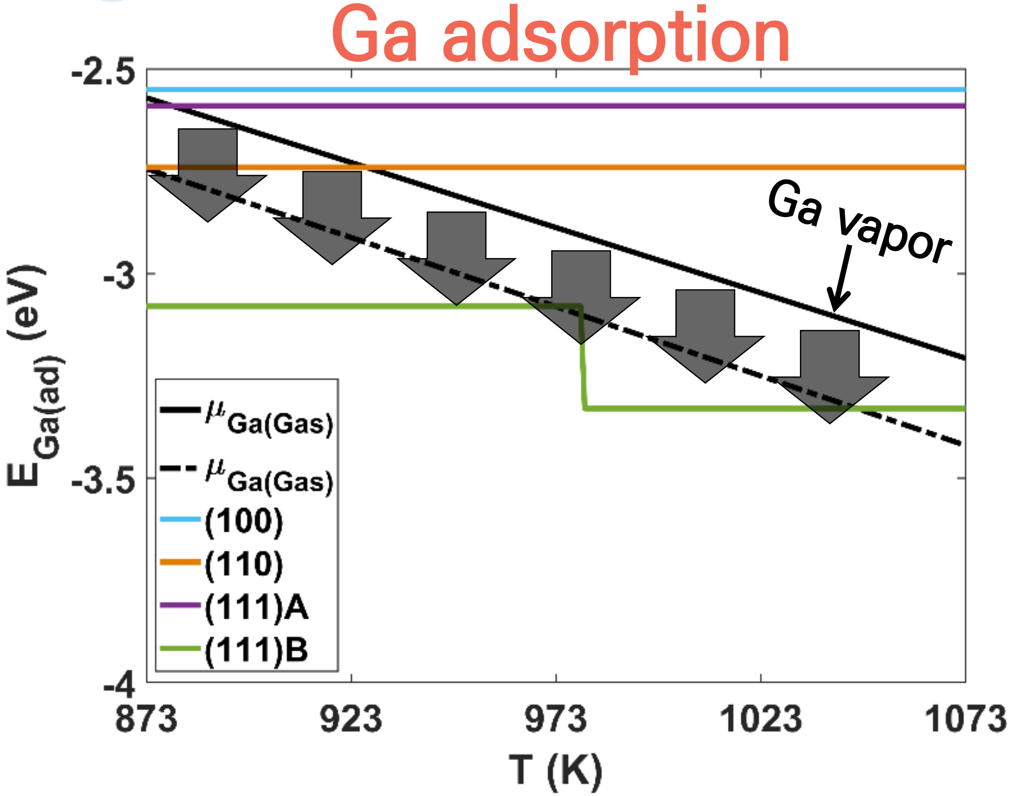
Most stable reconstructions for each surface

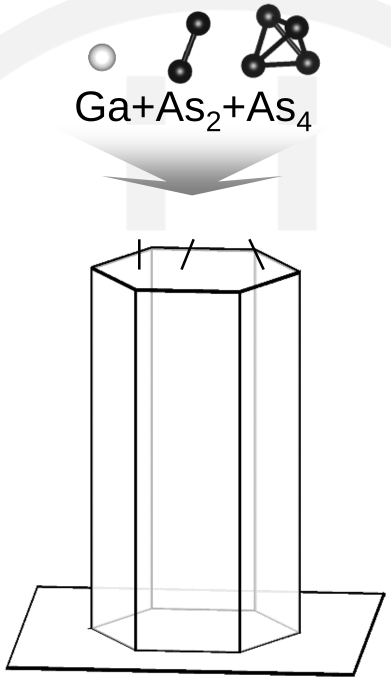


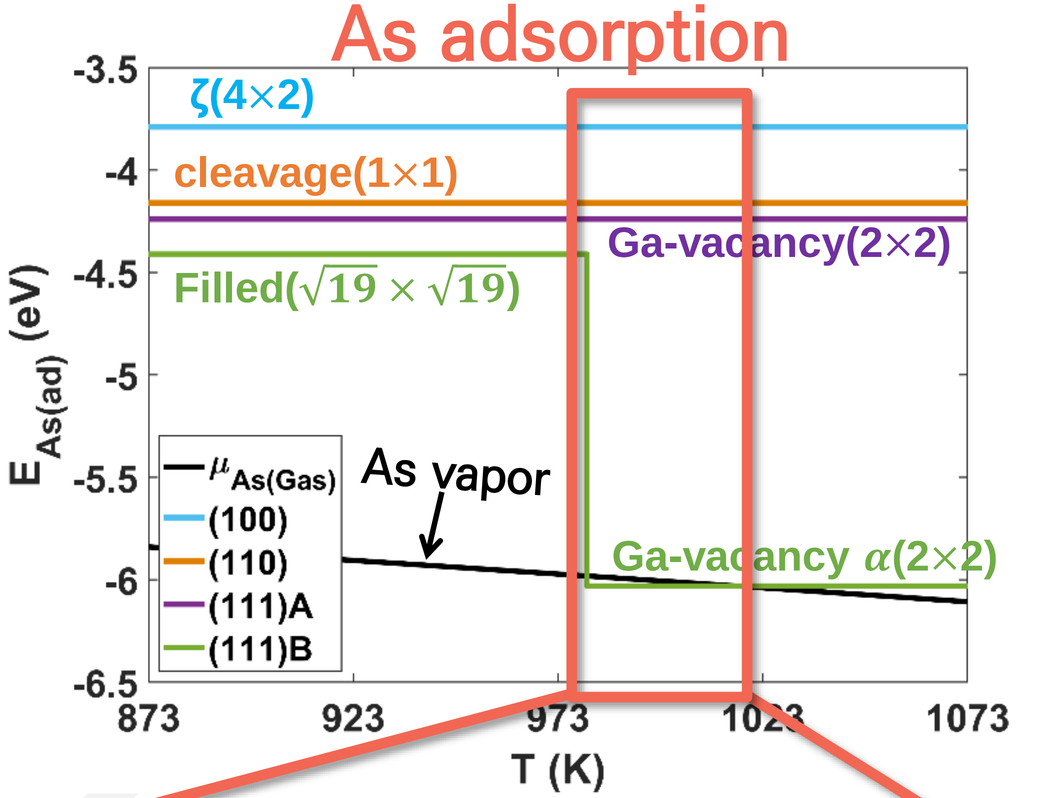




Anisotropy of Surface Structure and Adsorption Energy



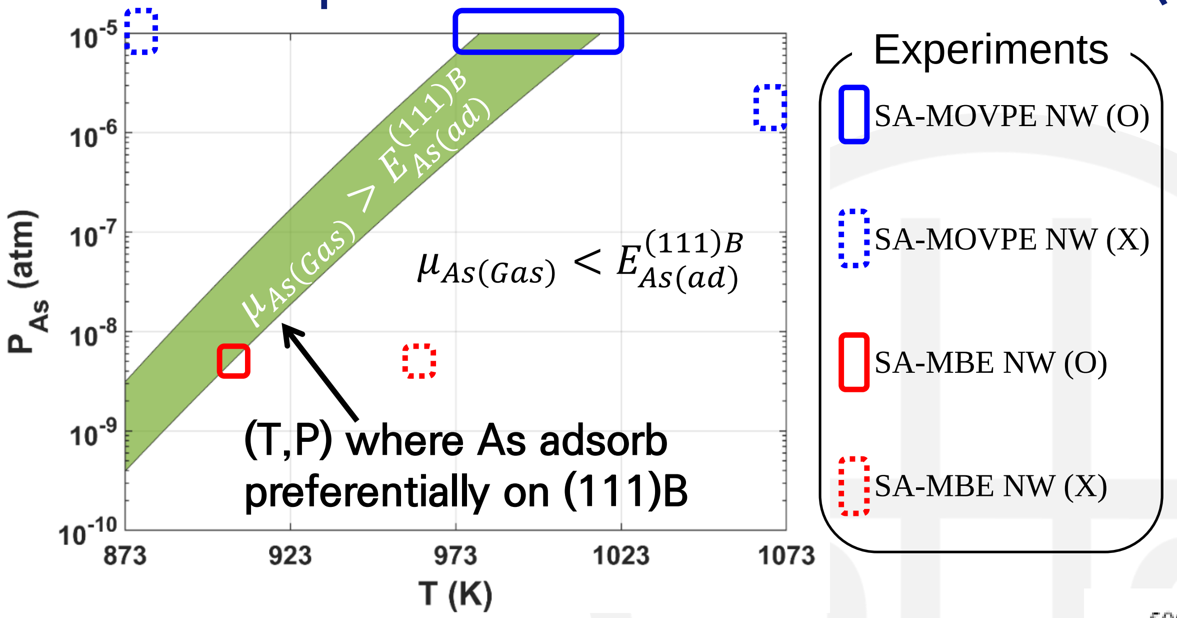


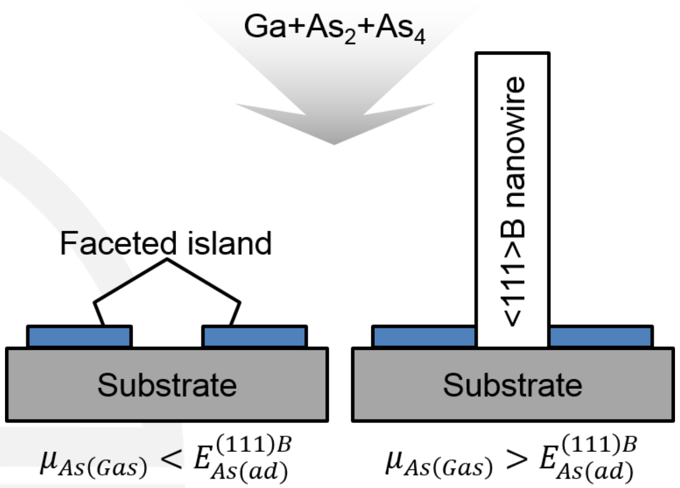


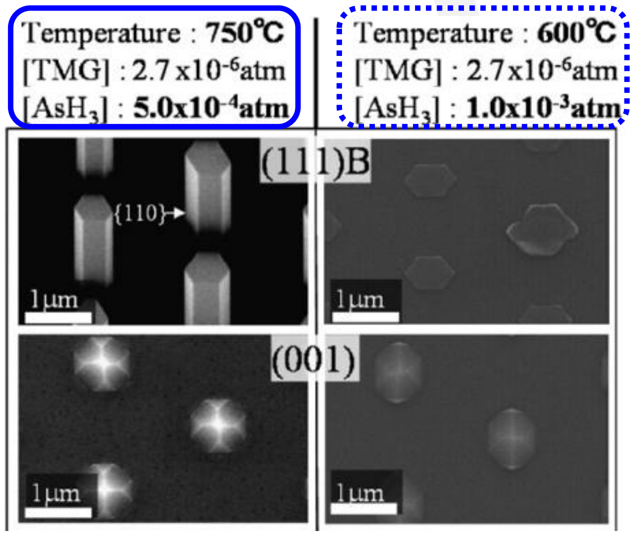
$$\dot{C}(Surf,T,P): (111)B \gg (111)A \cong (110) > (100)$$

$$\dot{N}_{n|Surf}(T,P) = \dot{C}(Surf,T,P) \cdot exp\left(-\frac{\Delta G^*_{sn}(Surf,T,P)}{kT}\right)$$

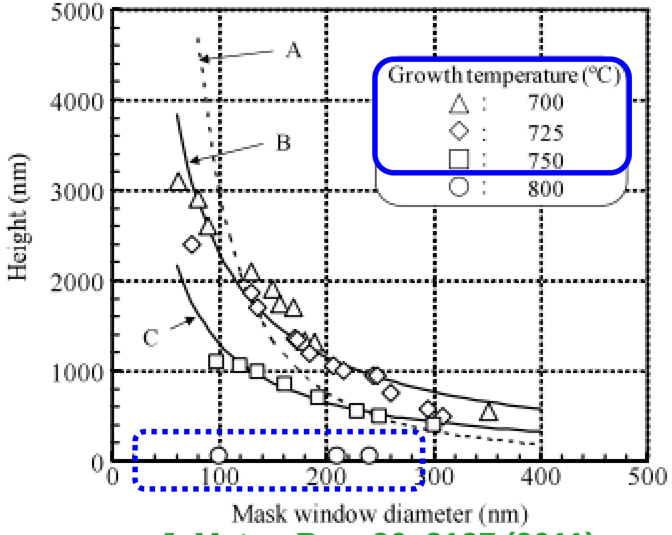
Preferential Adsorption → Preferential Nucleation → ⟨111⟩B NW Growth







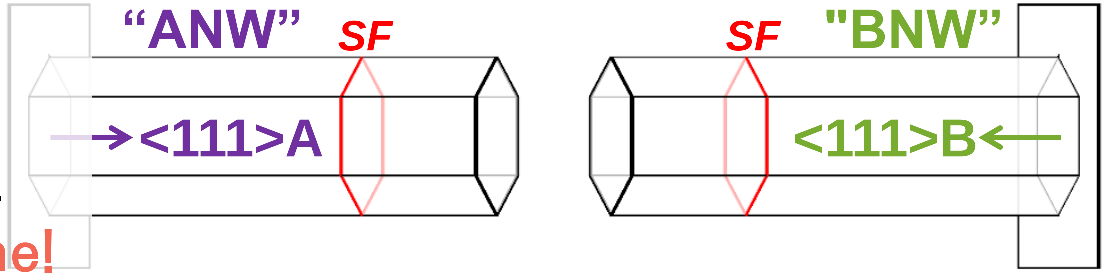
J. Cryst. Growth 298, 616 (2007)

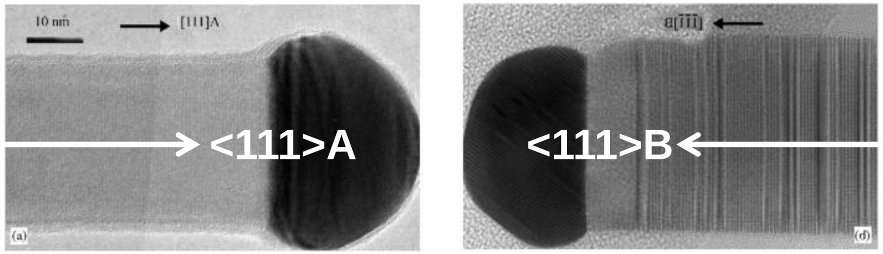


J. Mater. Res. 26, 2127 (2011)
Nanotechnology 19, 265604 (2008)

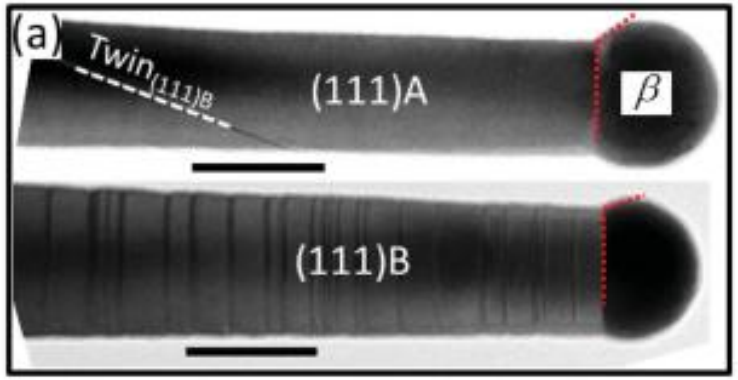
Asymmetric Formation of Stacking Sequence

Between the **two opposite directions** of NW growth,
density of **planar defects** is **much higher in ⟨111⟩B** than **⟨111⟩A**.
However, the **stacking fault energy (SFE)** in ANW and BNW is the **same!**

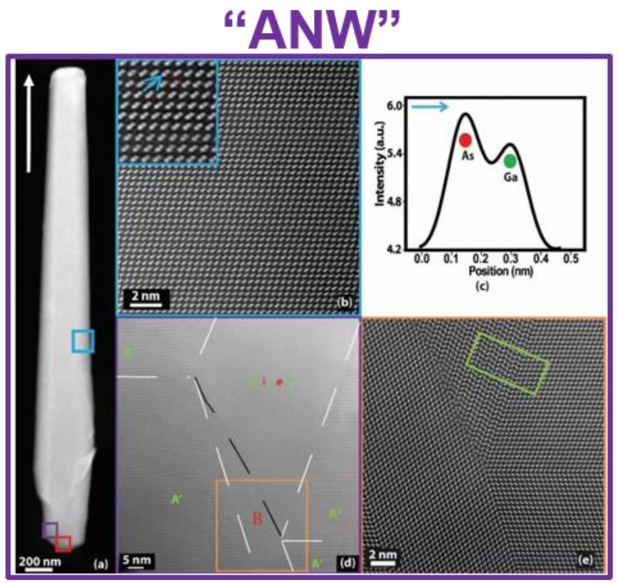


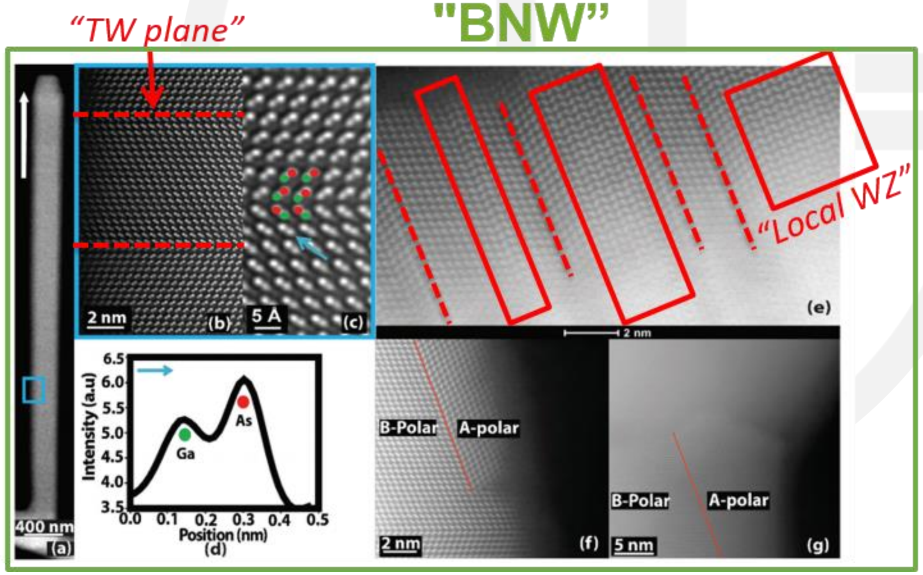


J. Cryst. Growth 287, 5004 (2006)



Adv. Mater. 27, 6096 (2015)



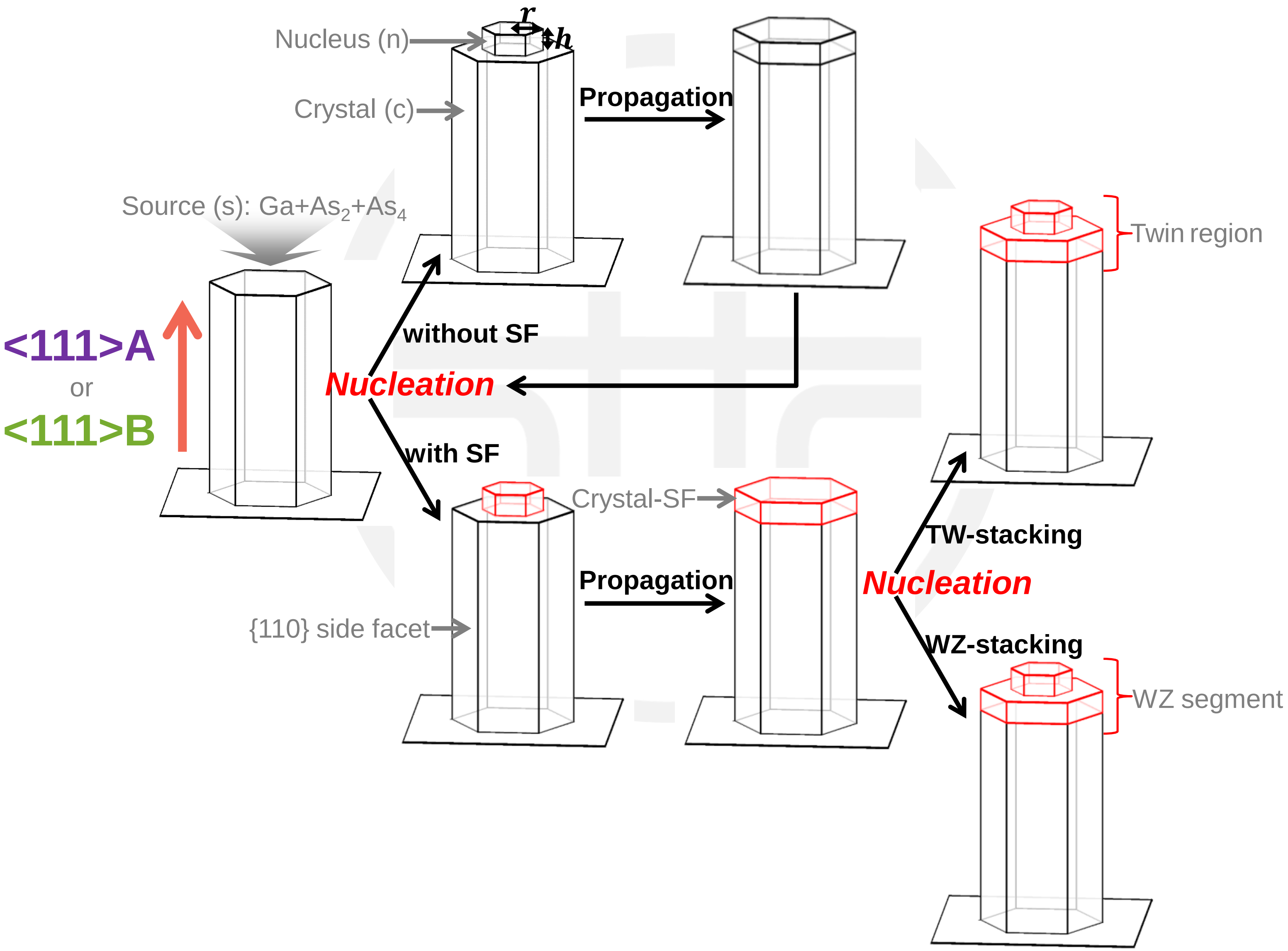


Nanoscale 10, 17080 (2018)

Kinetics Approach to Asymmetric Stacking

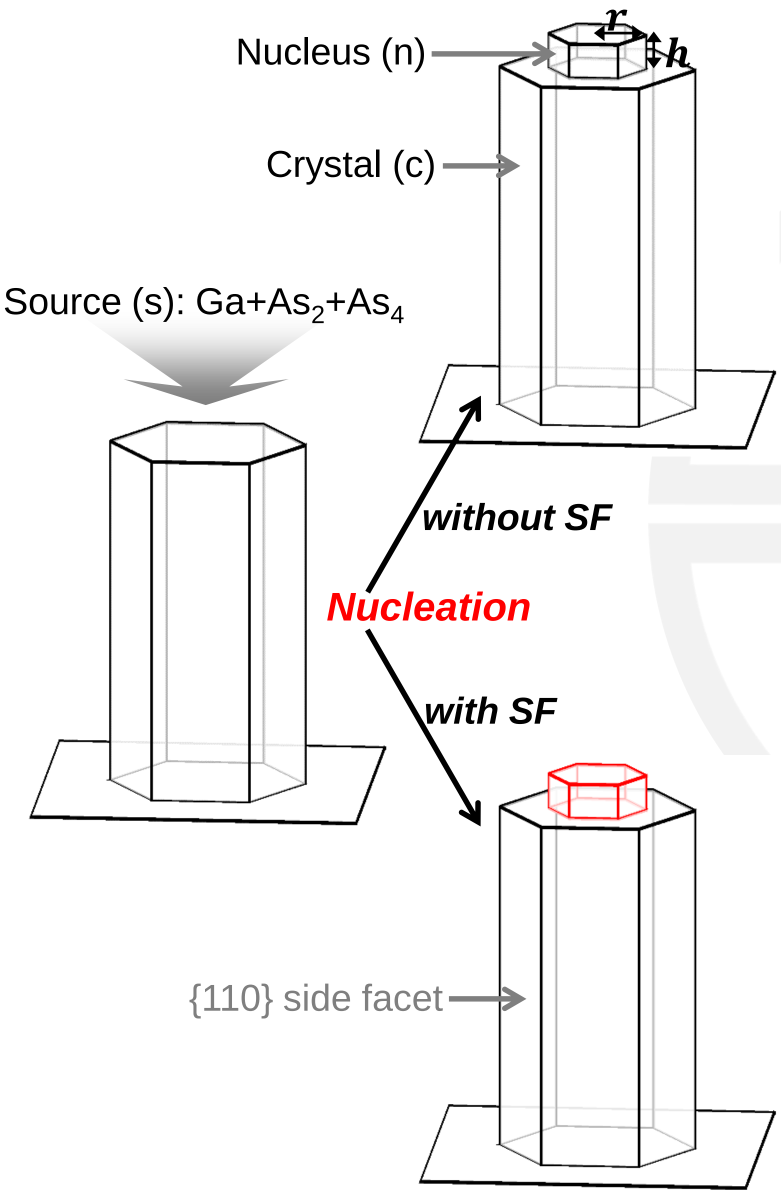
The SF Formation must be Stochastic during $\dot{N}_{n|Surf}(T,P) = \dot{C}(Surf,T,P) \cdot \exp\left(-\frac{\Delta G^{*}_{sn}(Surf,T,P)}{kT}\right)$

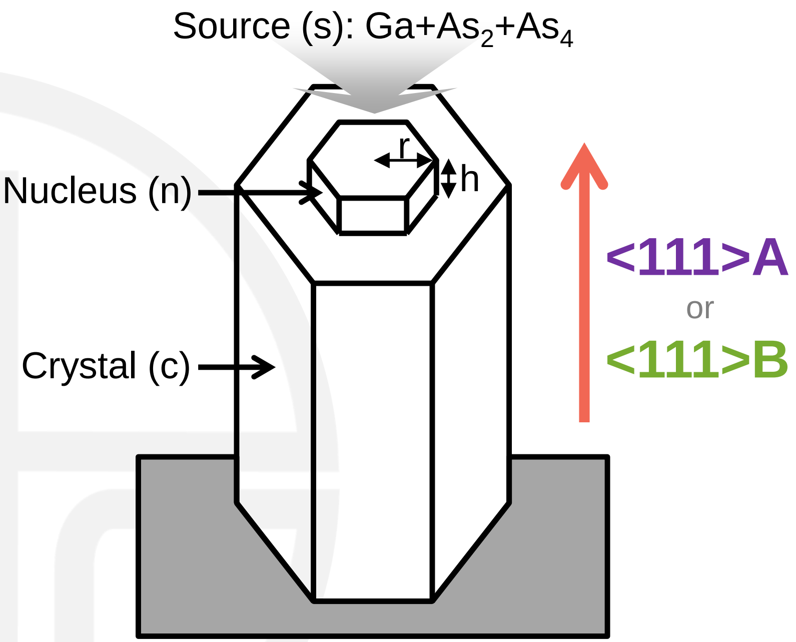
① $\dot{C}(Surf,T,P)$ ② $\Delta G^{*}_{sn}(Surf,T,P)$



Ab Initio Calculation for Nucleation Gibbs Free Energy

Change in Gibbs Free Energy during Nucleation





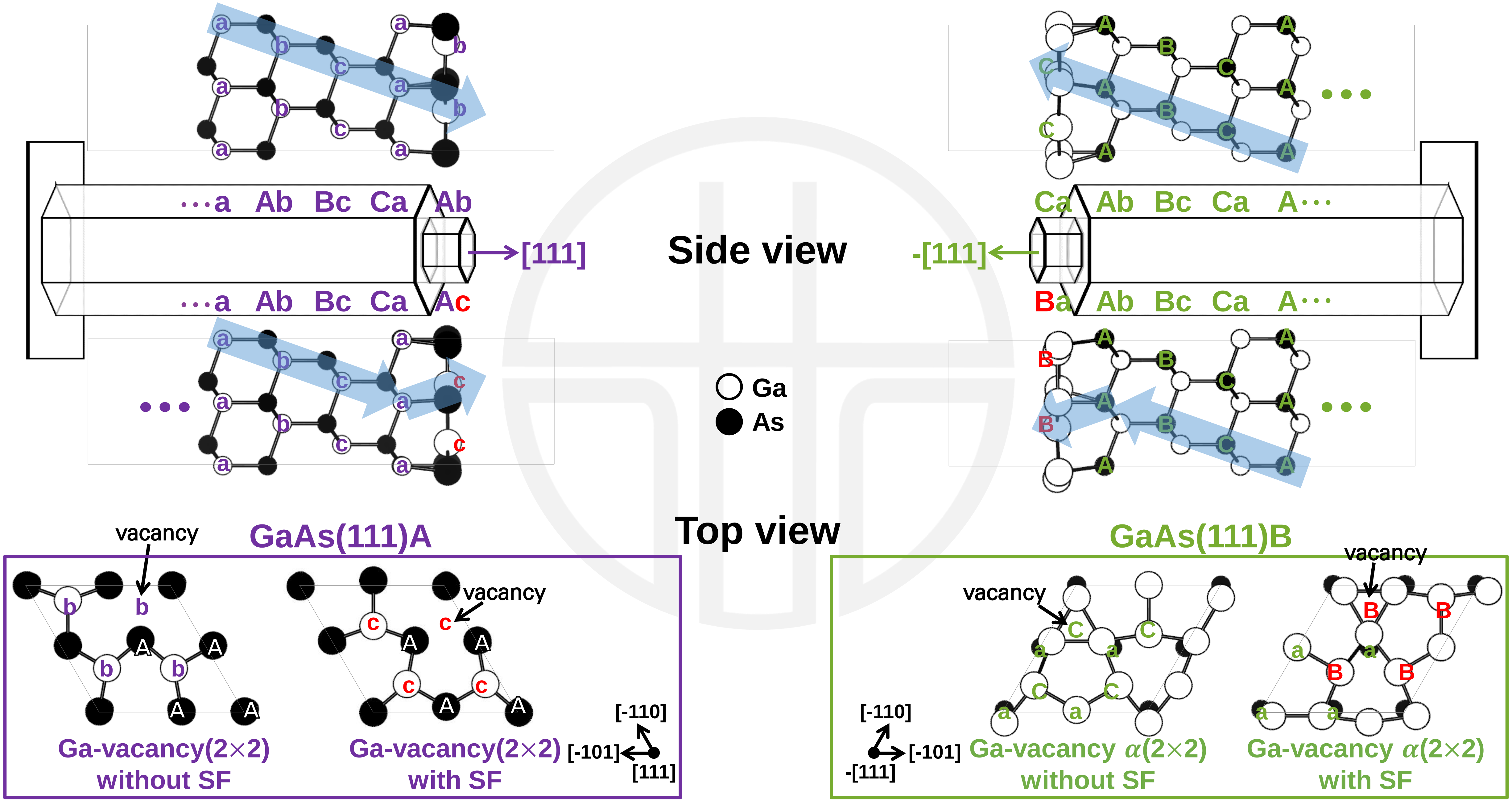
$$\Delta G_{sn} =$$

"Incorporation Energy" $V\Delta\mu_{sn}$

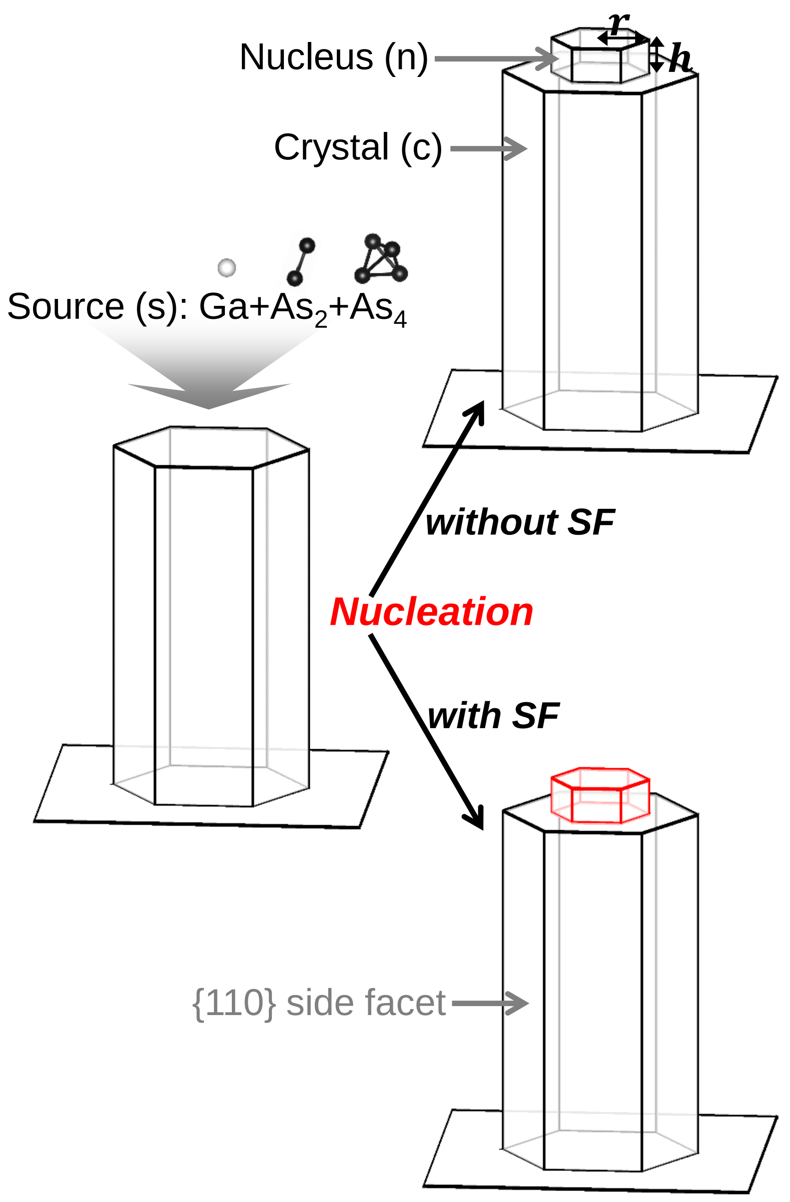
"Side Surface Energy" $+A_{side}\gamma_{sn(110)}$

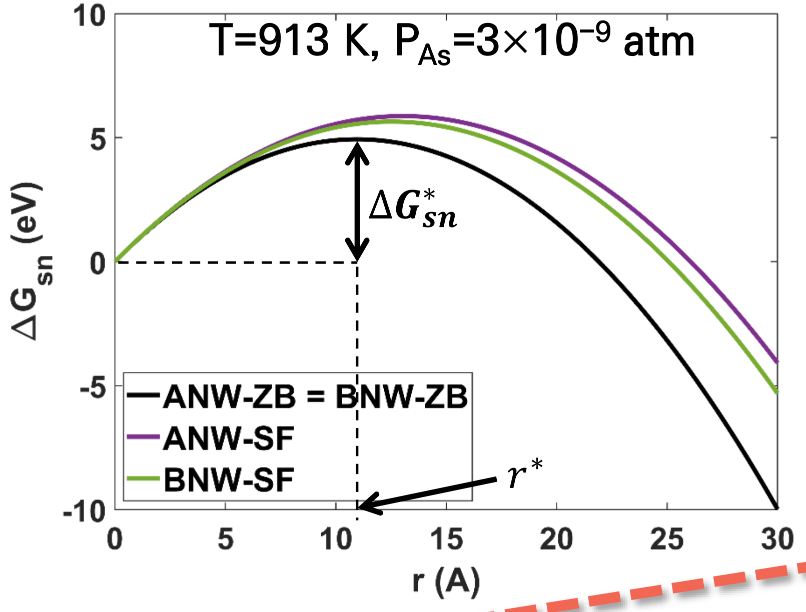
"Top Surface Energy" $+A_{top}\left(\gamma_{sn(111)} - \gamma_{sc(111)}\right)$

Surface Reconstruction with SF



Energy Cost on Top Surface by SF



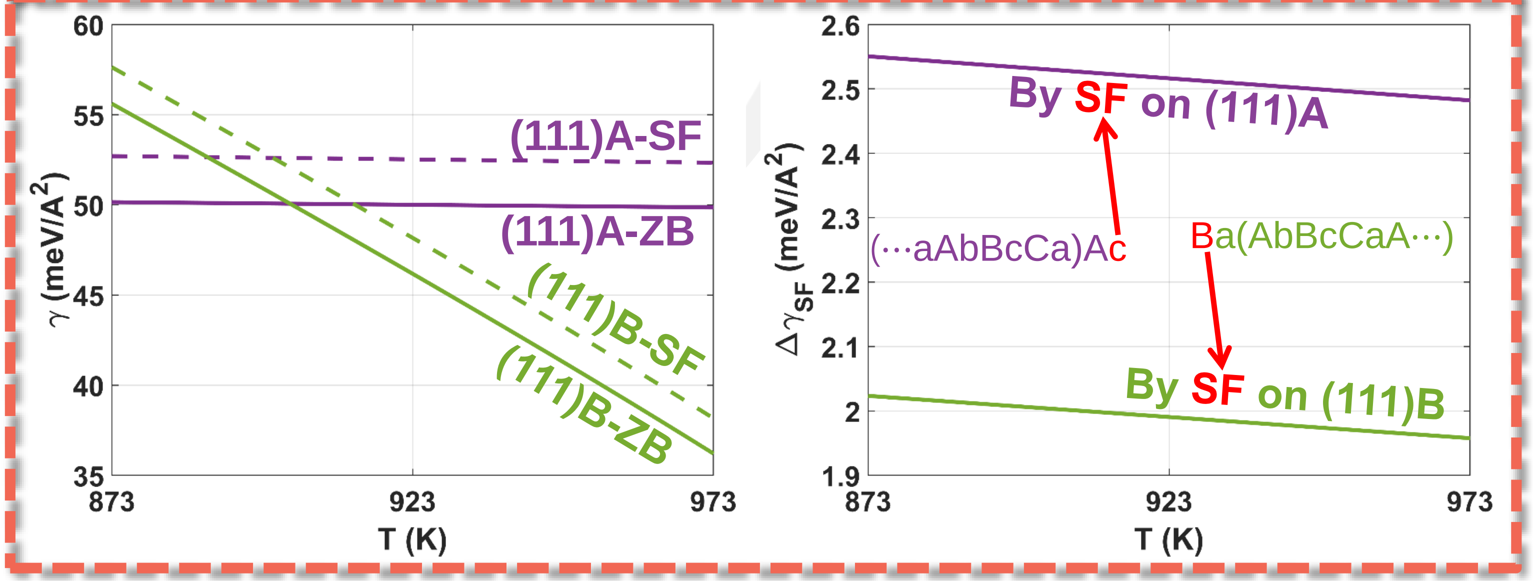


$$\Delta G_{sn} =$$

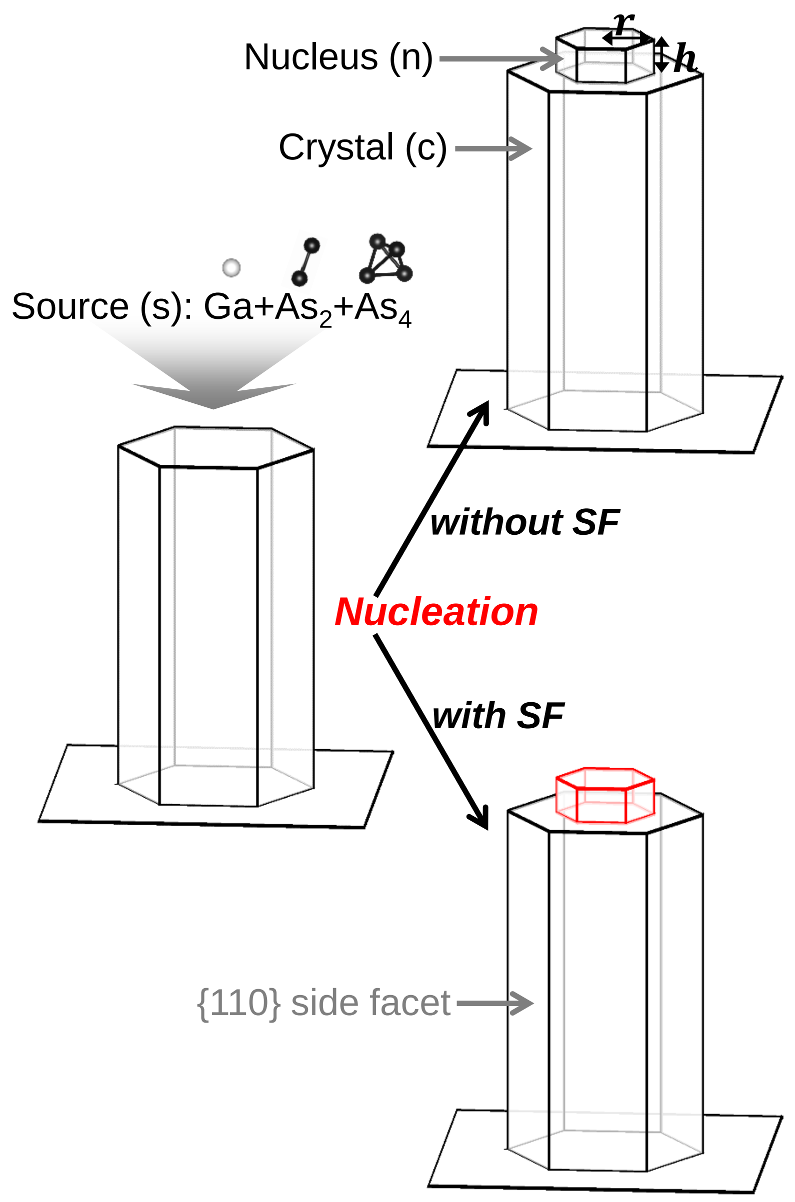
$$V\Delta\mu_{sn}$$

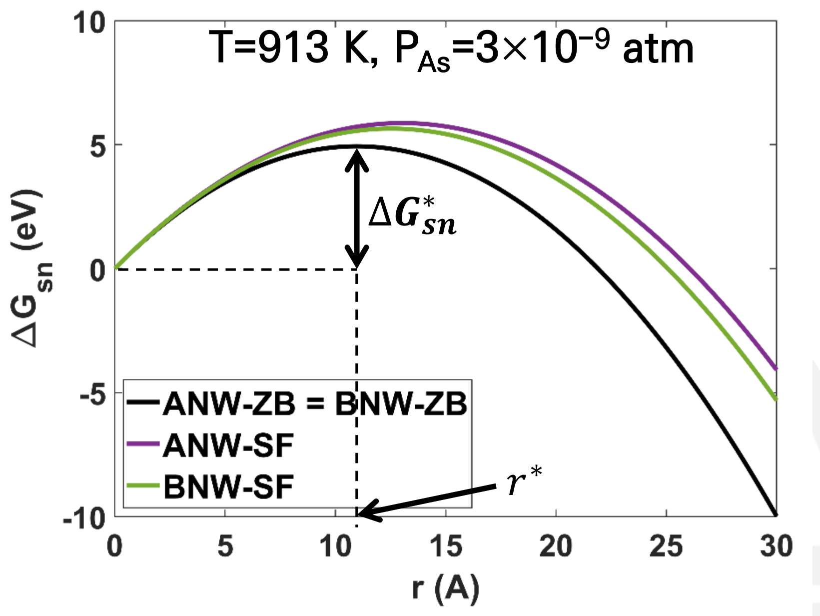
$$+A_{side}\gamma_{sn(110)}$$

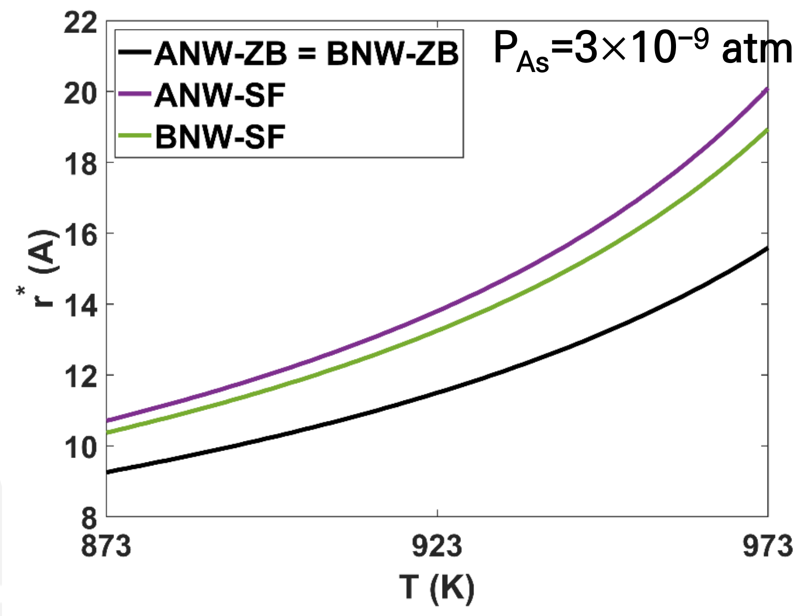
$$+A_{top}\left(\gamma_{sn(111)} - \gamma_{sc(111)}\right)$$

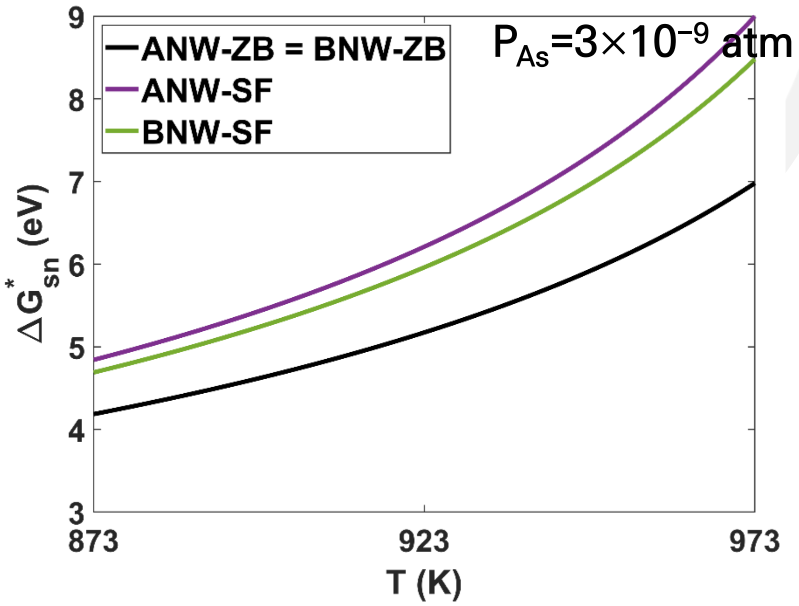


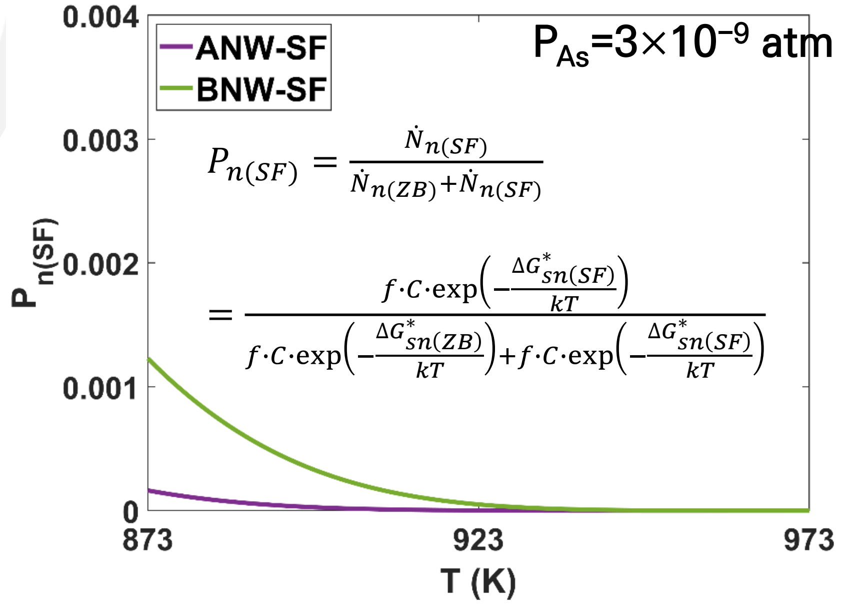
Stacking Sequence of Nucleation: ZB vs. SF







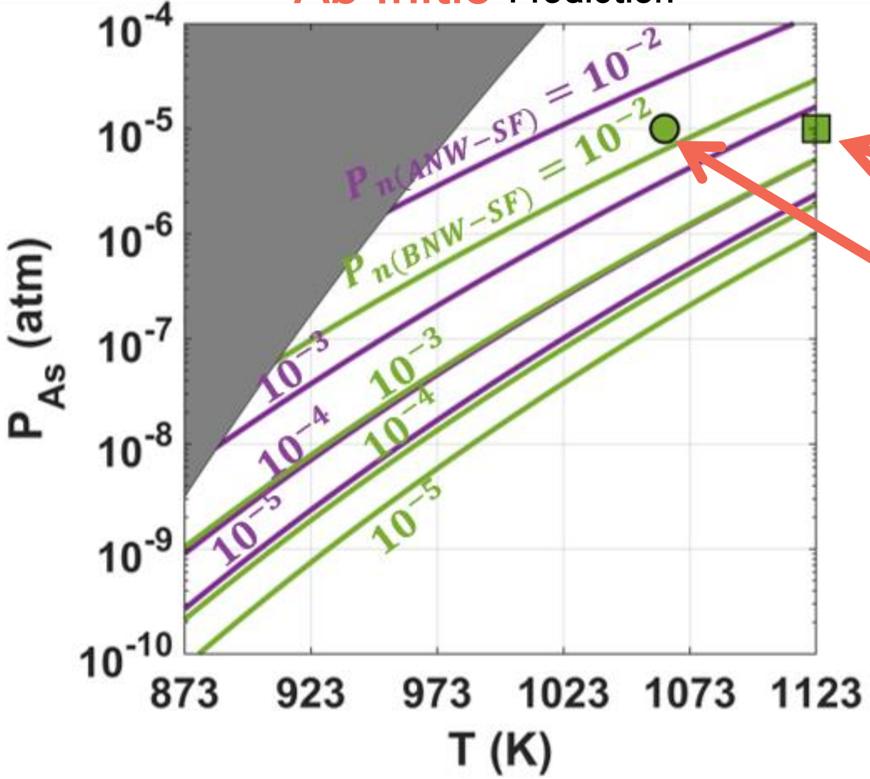




$$P_{n(SF)} = \frac{\dot{N}_{n(SF)}}{\dot{N}_{n(ZB)}+\dot{N}_{n(SF)}} = \frac{f\cdot C\cdot\exp\left(-\frac{\Delta G^*_{sn(SF)}}{kT}\right)}{f\cdot C\cdot\exp\left(-\frac{\Delta G^*_{sn(ZB)}}{kT}\right)+f\cdot C\cdot\exp\left(-\frac{\Delta G^*_{sn(SF)}}{kT}\right)}$$

Asymmetric Stacking: Calculation vs. Experiment

Ab Initio Prediction



P_{SF} ~ 0.006 at 1123 K

P_{SF} = 0.03 at 1063 K

"SF Probability"

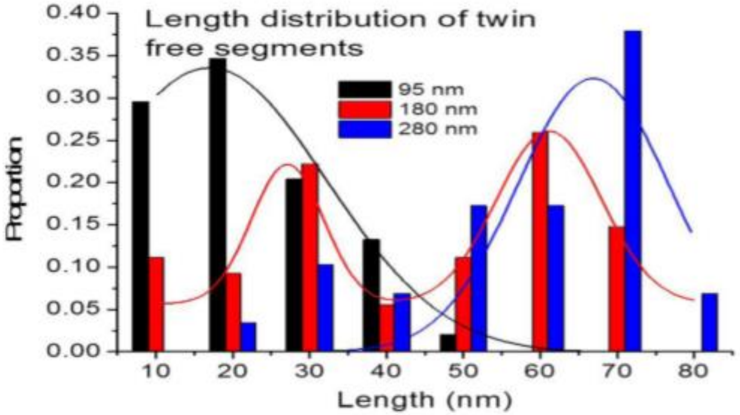
Polarity dependence: **ANW < BNW**

T dependence: **high T < low T**

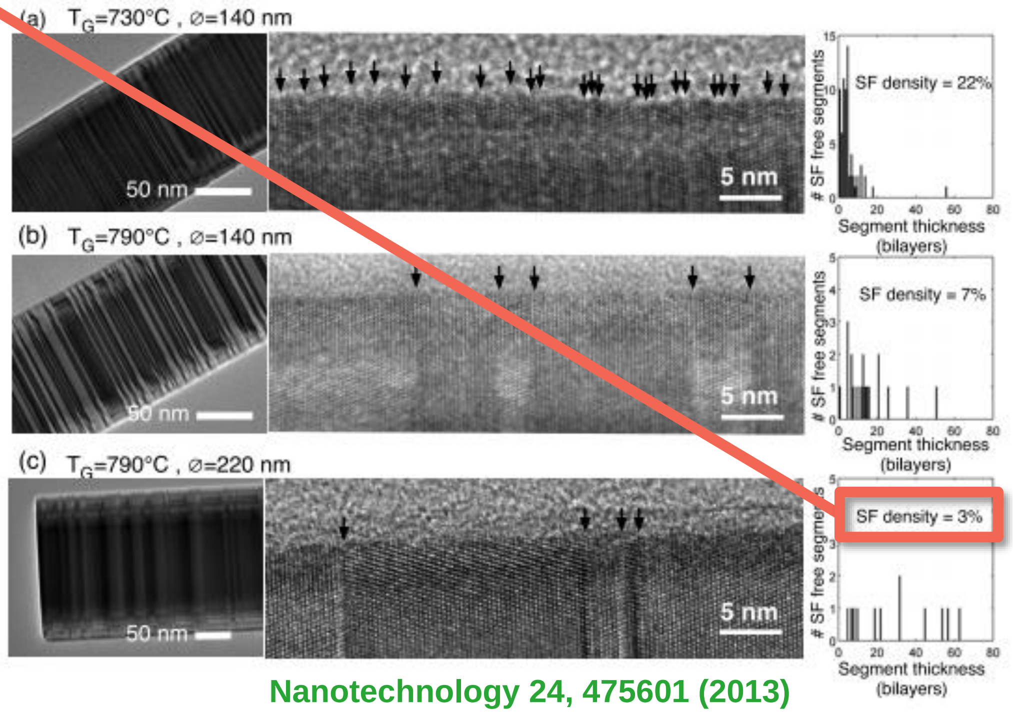
P dependence: **low P < high P**

Measured by TEM for Grown BNWs

The average twin−free length = 531 Å

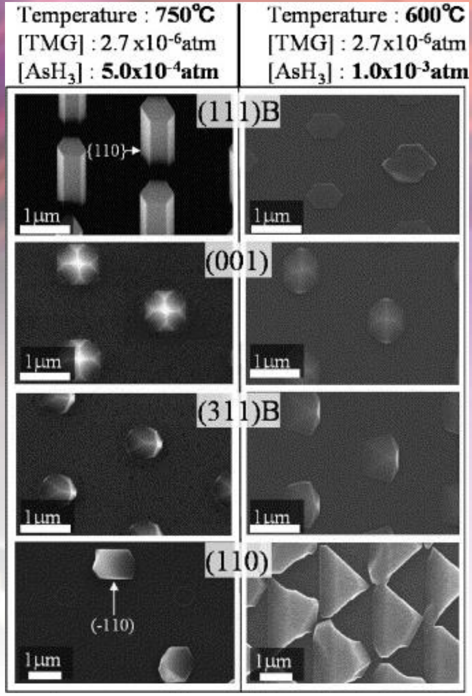


ACS Nano 10, 2424 (2016)



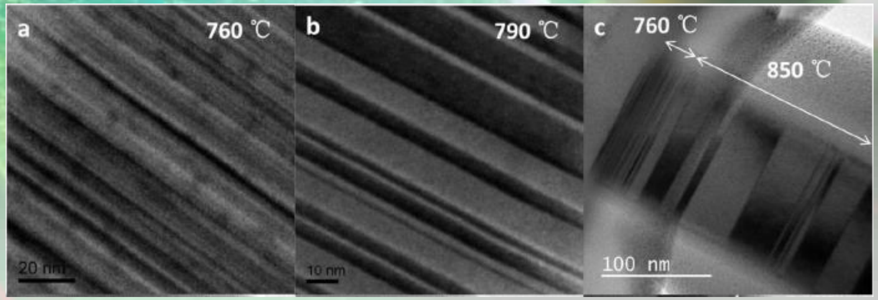
Nanotechnology 24, 475601 (2013)

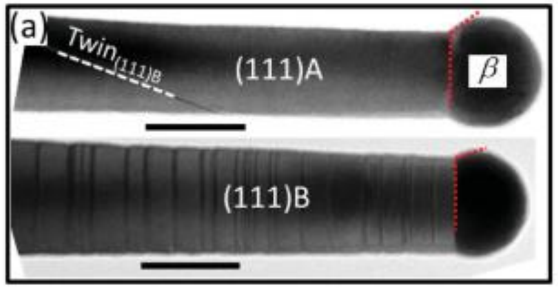
Summary



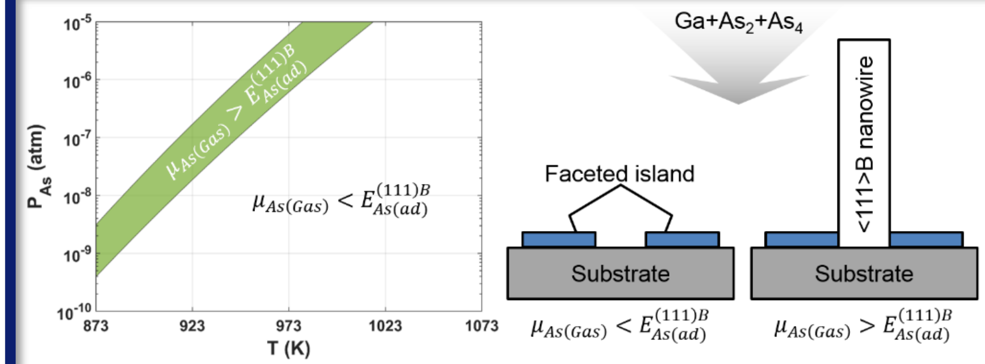
Anisotropic Growth

$$\dot{N}_n = f \cdot C \cdot \exp\left(-\frac{\Delta G^*_{sn}}{kT}\right)$$

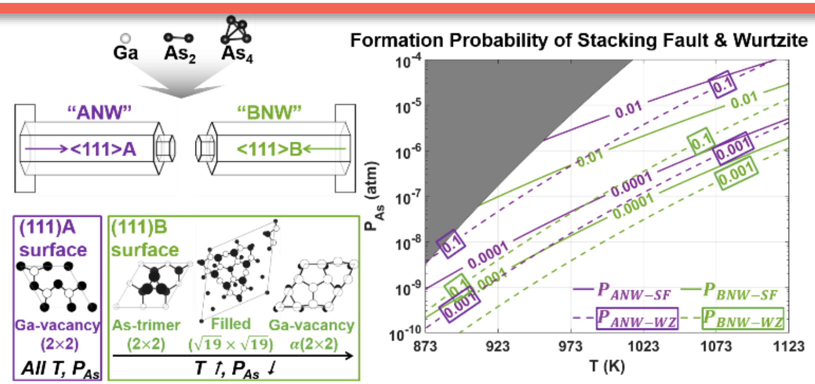




Asymmetric Stacking



Yeu *et al.*, *Appl. Surf. Sci.* 497, 143740 (2019)



Yeu *et al.*, *Nanoscale* 12, 17703 (2020), Outside Front Cover