Nano Korea 2020
[MF] Materials & Fabrication

Effects of growth condition on the anisotropic growth and stacking behavior of GaAs polar nanowires: *ab initio* thermodynamics

Jul. 2. 2020 (Thu.) 15:30 ~ 15:45

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Computational Materials Design

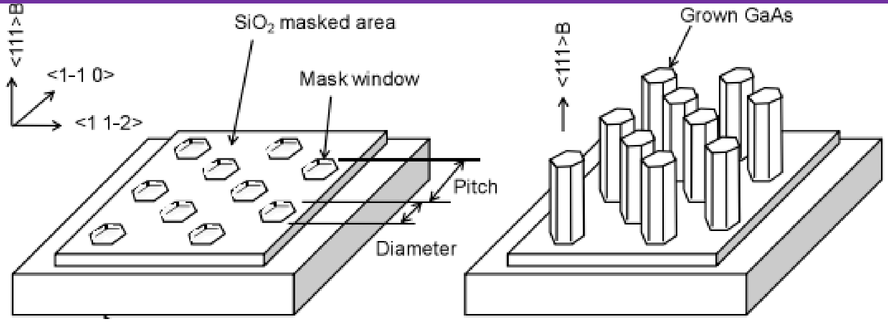
1 Unidirectional growth of GaAs NW

1) Anisotropic VS-growth
2) Theoretical approach to why <111>B ?
3) Ab initio thermodynamics to surface
4) Adsorption on surface reconstruction
5) Adsorption vs. Desorption
6) Preferential adsorption and nucleation

2 Asymmetric stacking of GaAs NW

1) Asymmetric stacking: ANW vs. BNW
2) Energetics of fully formed NW?
3) Nucleation-I: with ZB or SF stacking
4) (111)A & B reconstruction with SF
5) Nucleation-I: ZB vs. SF
6) Asymmetric stacking in nucleation-I

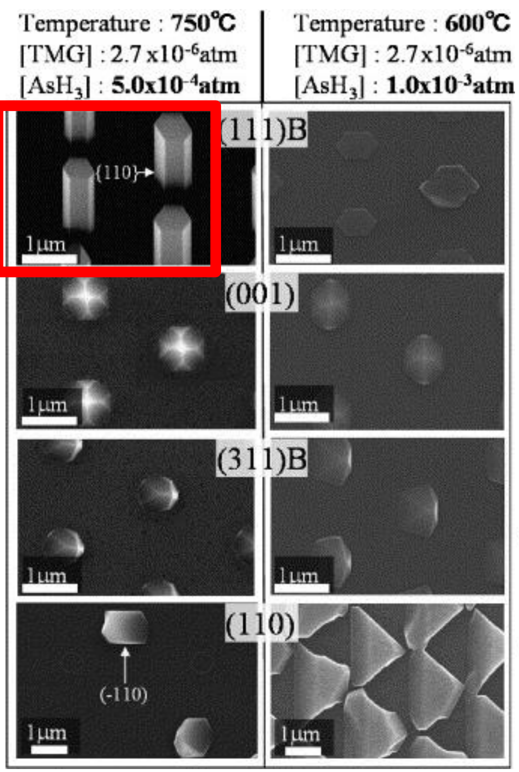
Anisotropic VS-growth of GaAs NW



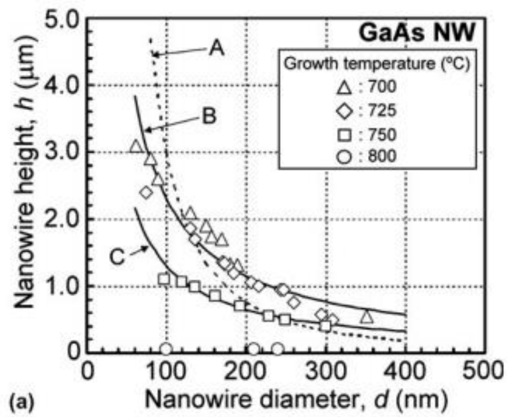
"Catalyst-free VS growth":

*Among the various crystal directions, GaAs NW tends to grow **along <111>B** at **narrow (T,P) range**"*

SA-MOVPE

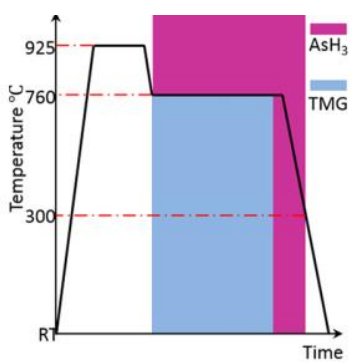


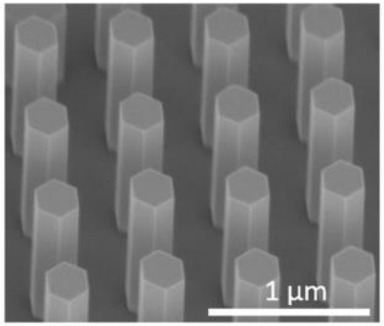
J. Cryst. Growth 298, 616 (2007)



J. Mater. Res. 26, 2127 (2011)

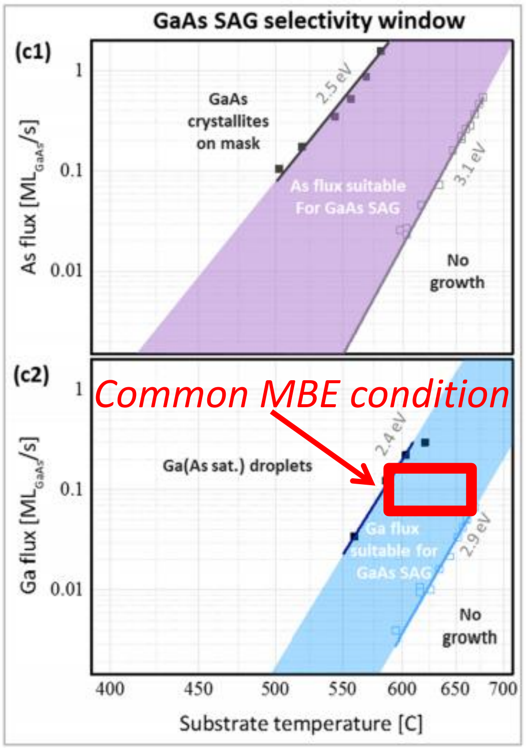
Nanotechnology 19, 265604 (2008)





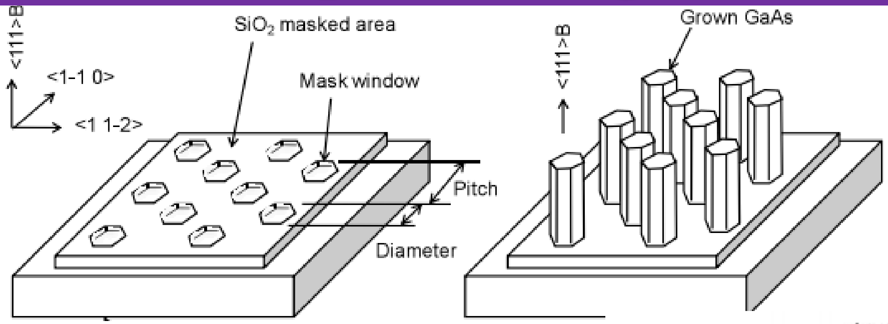
ACS Nano 10, 2424 (2016)

SA-MBE



Nano Lett. 19, 218 (2019)

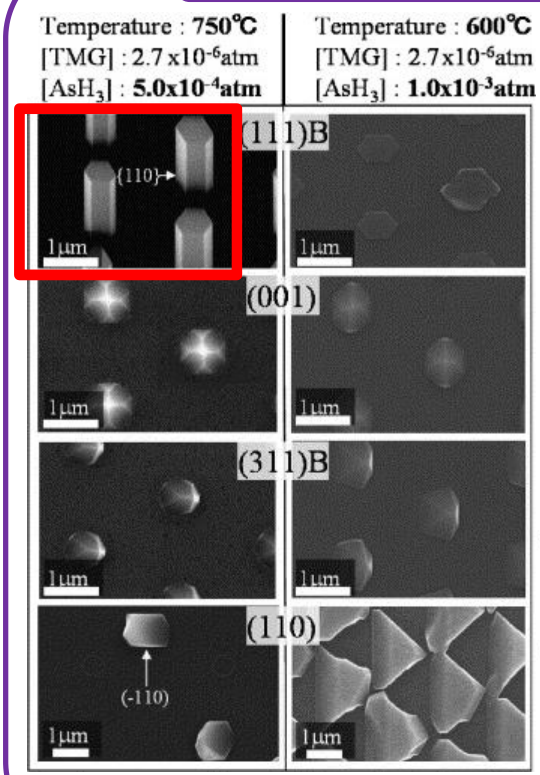
Anisotropic VS-growth of GaAs NW



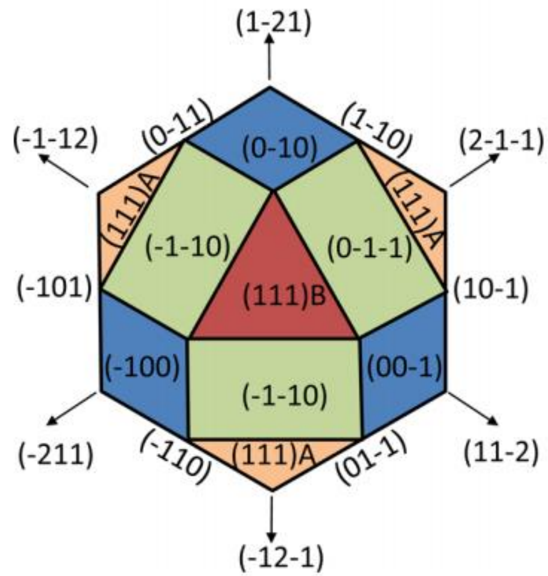
"Catalyst-free VS growth":

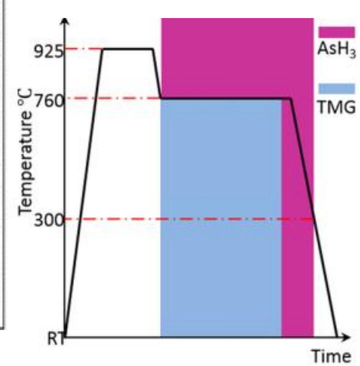
*Among the various crystal directions, GaAs NW tends to grow **along <111>B** at **narrow (T,P) range**"*

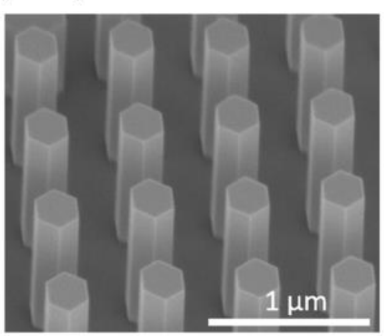
SA-MOVPE



J. Cryst. Growth 298, 616 (2007)







ACS Nano 10, 2424 (2016)

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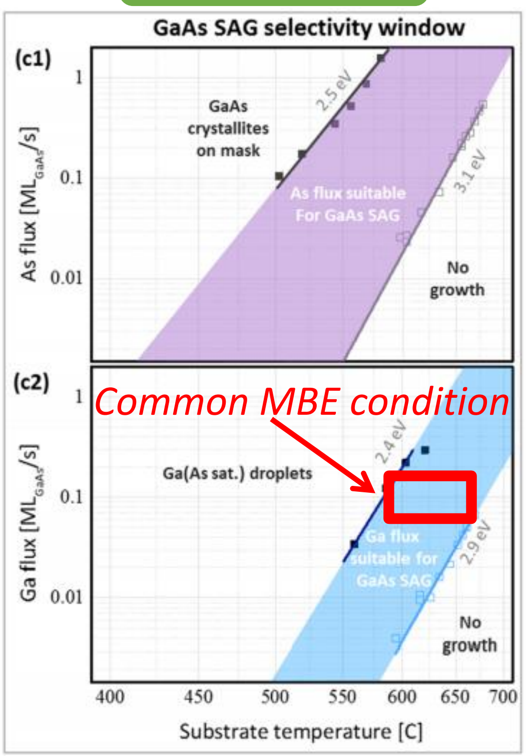
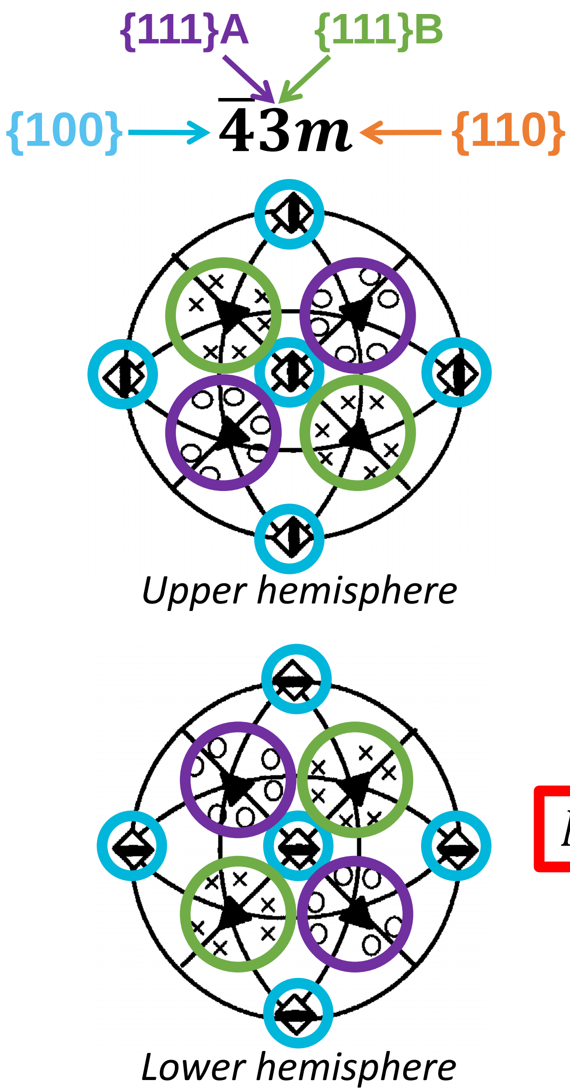
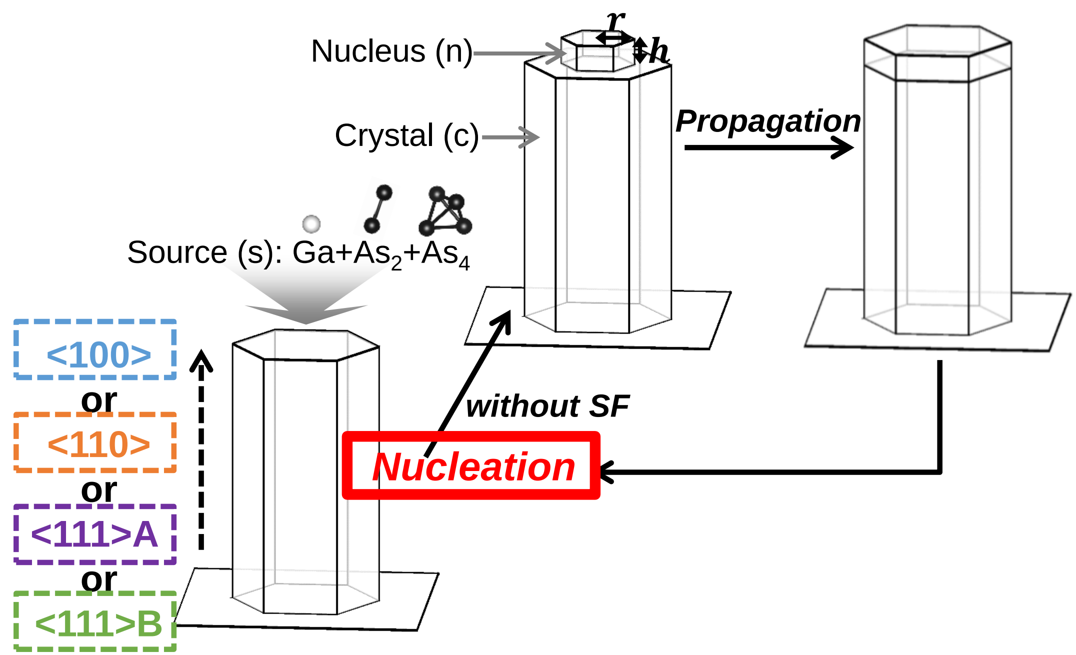


Nano Lett. 19, 218 (2019)

Theoretical approach to why <111>B ?





Surface orientation dependent nucleation rate:

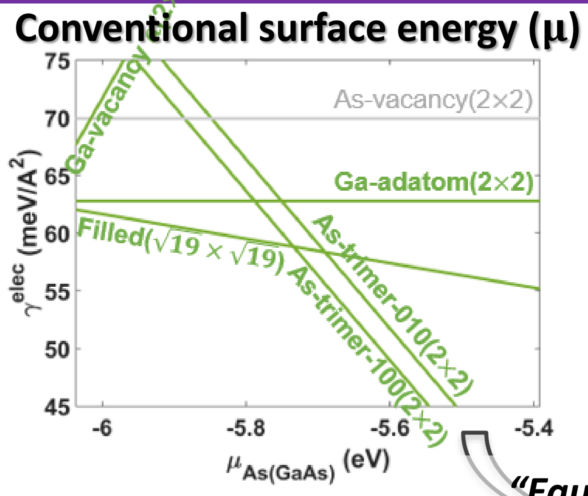
$$\dot{N}_{n|Surf}(T,P) = \dot{C}(Surf,T,P) \cdot \exp\left(-\frac{\Delta G^{*}_{sn}(Surf,T,P)}{kT}\right)$$

① *"Rate of source supply" onto each surface*

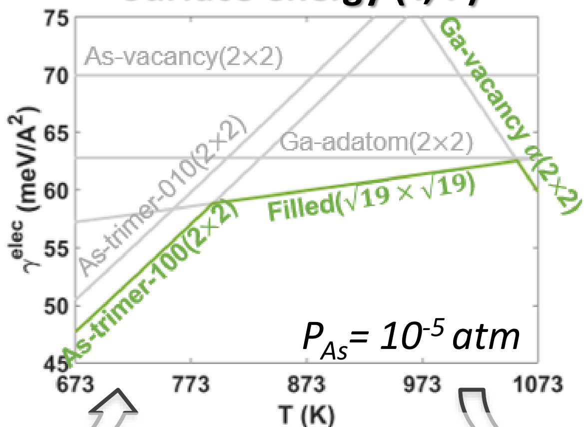
② *"Nucleation barrier" on each surface*

Ab initio thermodynamics to surface

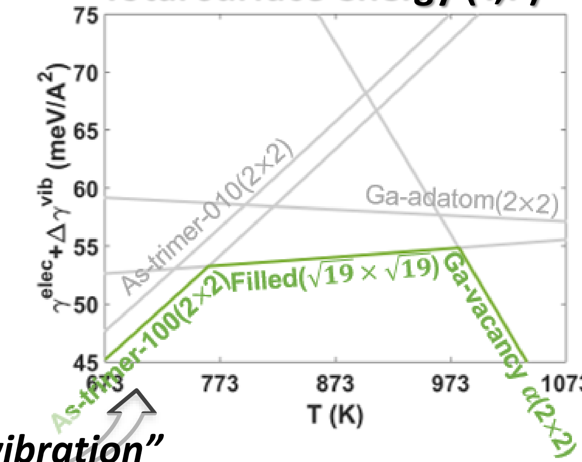
Conventional surface energy (μ)



Surface energy (T, P)



Total surface energy (T,P)



"Equilibrium"

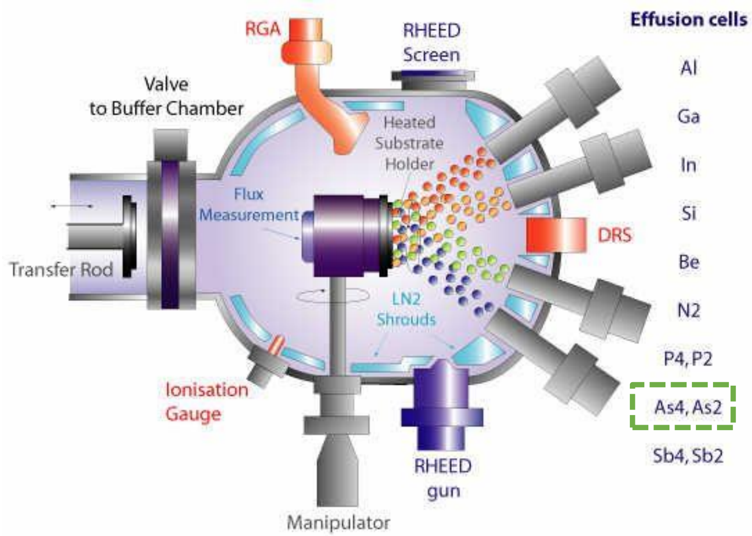
$$\mu_{As(Gas)} = \mu_{As(GaAs)}$$

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

"Surface vibration"

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

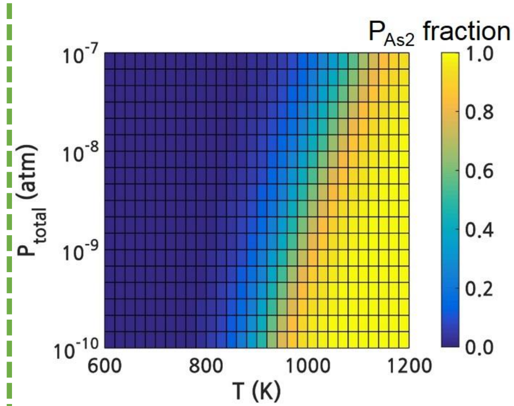
Yeu *et al.*, *Sci. Rep.* 9, 1127 (2019)

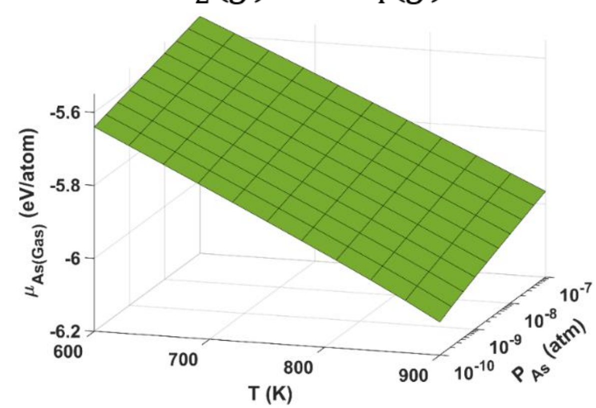


Vapor environment of GaAs

$$\mu_{As(Gas)} = \frac{1}{2}\mu_{As_2(Gas)} = \frac{1}{4}\mu_{As_4(Gas)}$$

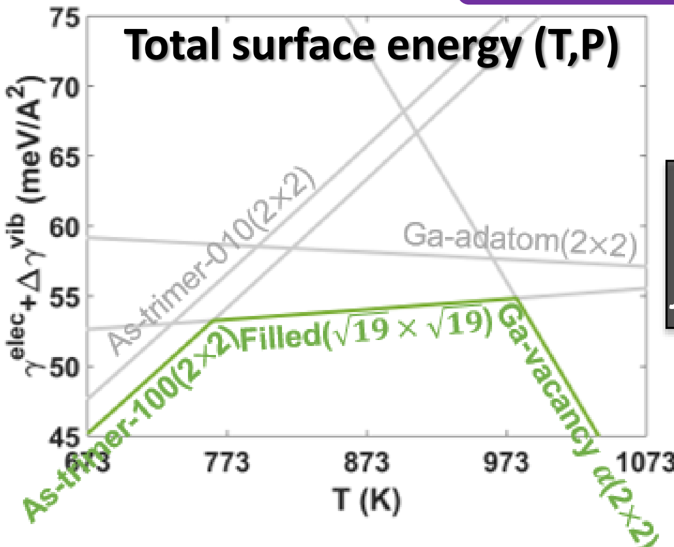
$$2As_2(g) \leftrightarrow As_4(g)$$



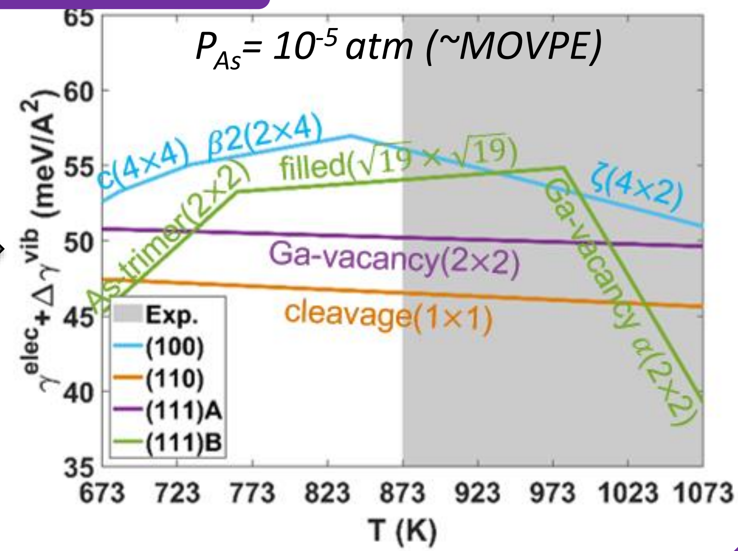


Adsorption on surface reconstruction

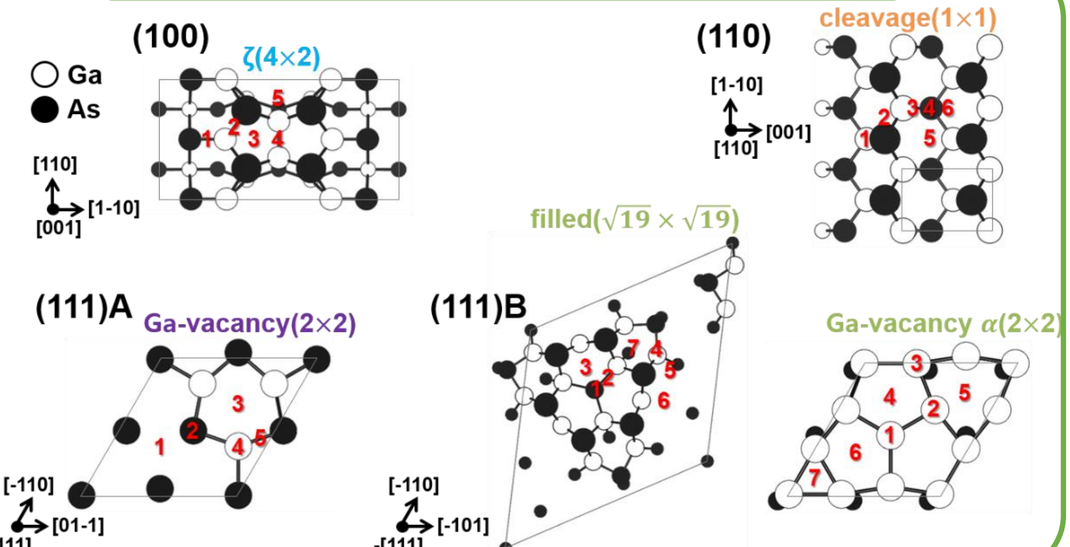
Stable surface structures



Most stable reconstructions for each surface

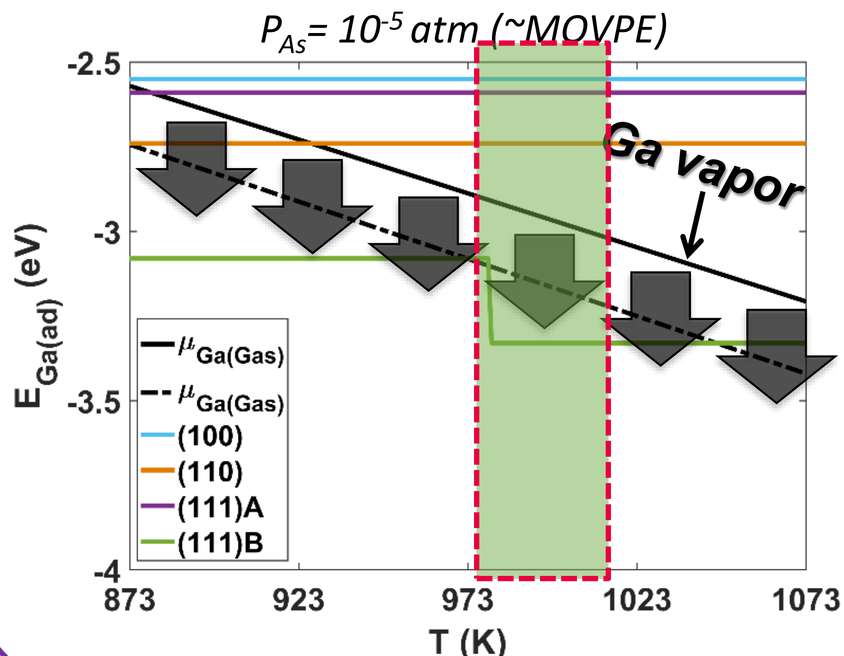


Possible adsorption sites

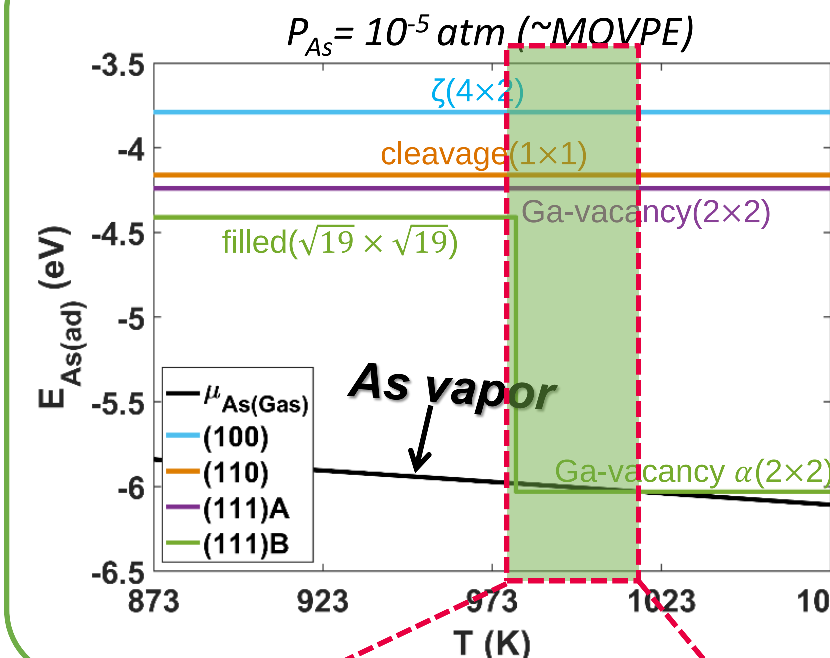


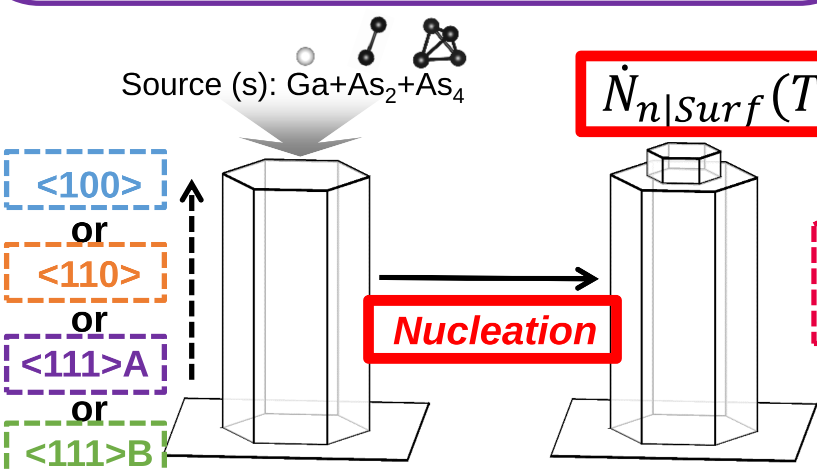
Adsorption vs. Desorption

Ga adsorption



As adsorption

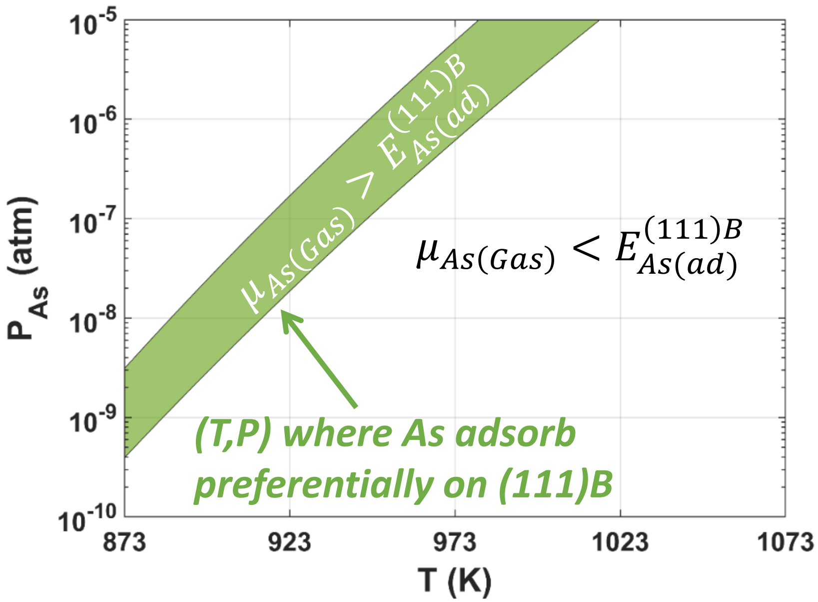


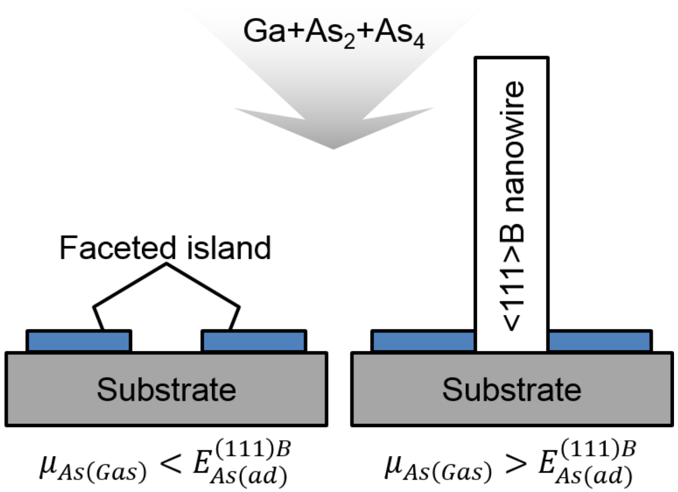


$$\dot{N}_{n|Surf}(T,P) = \dot{C}(Surf,T,P)\cdot\exp\left(-\frac{\Delta G^{*}_{sn}(Surf,T,P)}{kT}\right)$$

$$\dot{N}_{n|Surf}: \mathbf{(111)}B \gg \mathbf{(111)}A \cong \mathbf{(110)} > \mathbf{(100)}$$

(T,P) window of the preferential adsorption

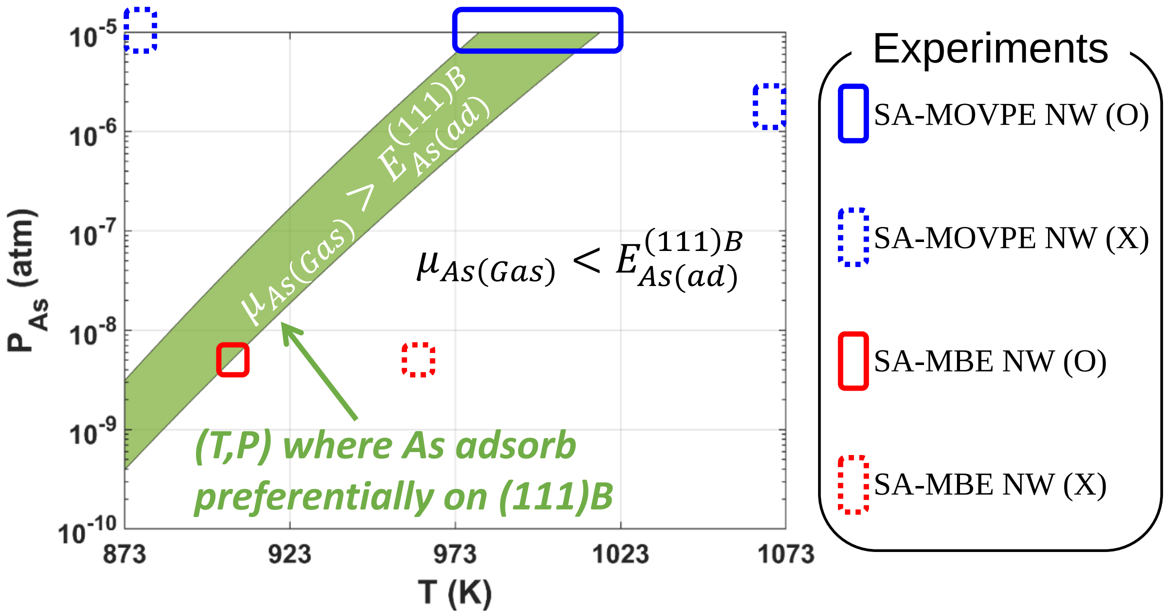


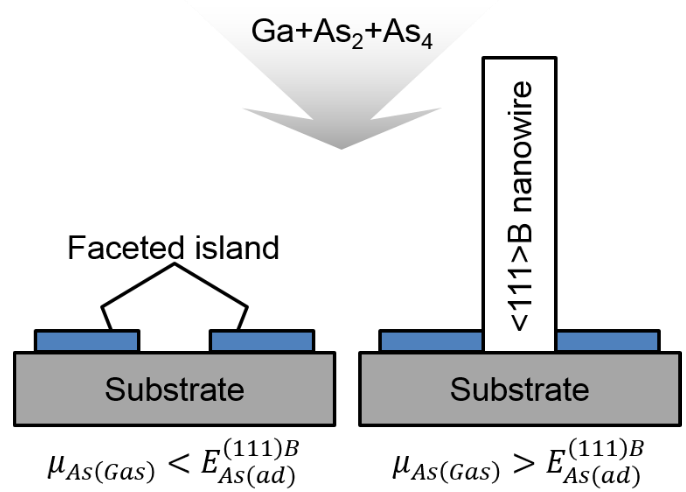


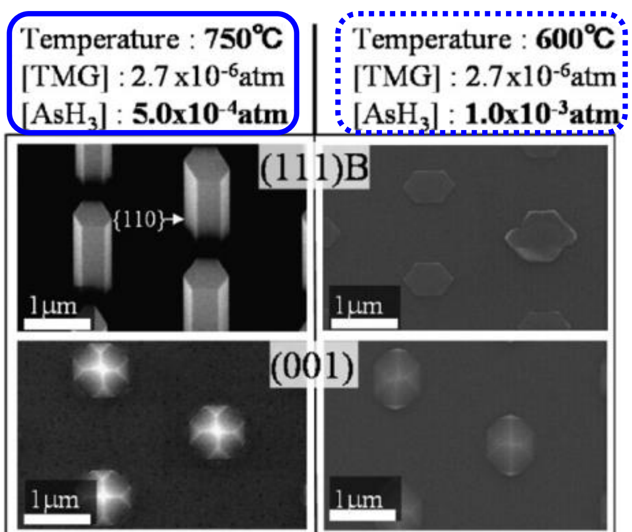
$$\dot{N}_{n|Surf}(T,P) = \boxed{\dot{C}(Surf,T,P)} \cdot \exp\left(-\frac{\Delta G^{*}_{sn}(Surf,T,P)}{kT}\right)$$

"Preferential adsorption → nucleation → BNW growth"

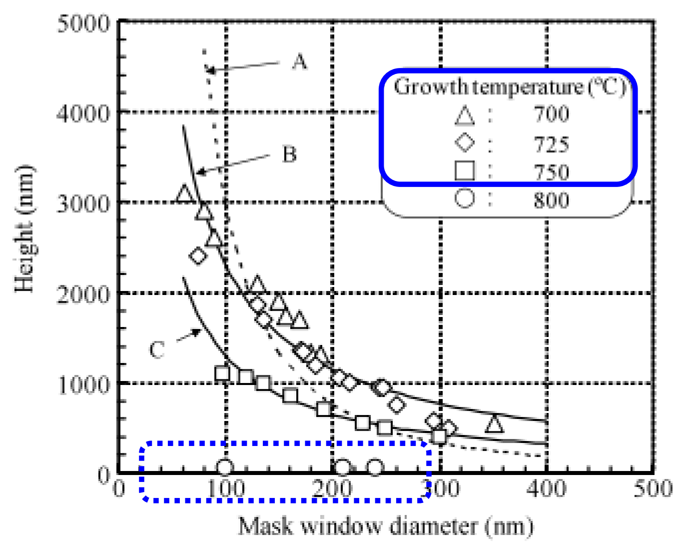
(T,P) window of the preferential adsorption







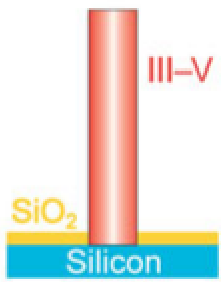
J. Cryst. Growth 298, 616 (2007)



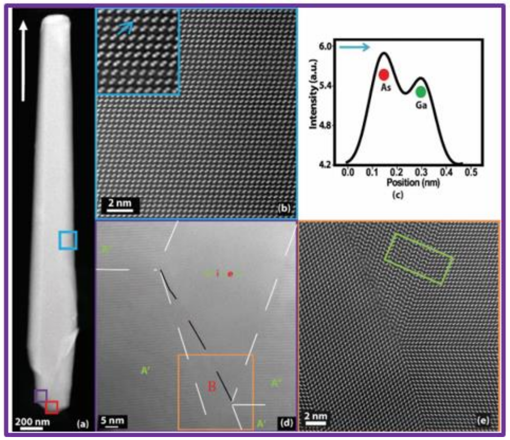
J. Mater. Res. 26, 2127 (2011)
Nanotechnology 19, 265604 (2008)

Asymmetric stacking: ANW vs. BNW

Vapor-Solid growth

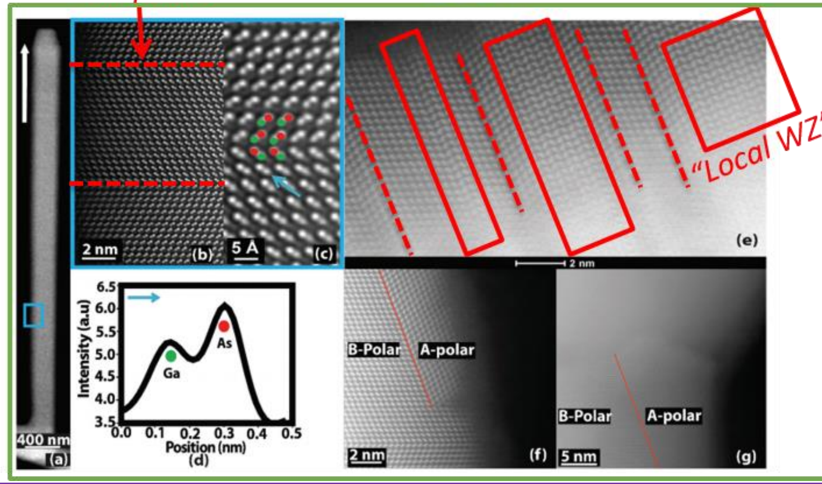


"ANW"

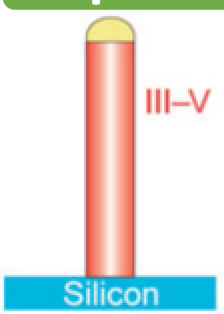


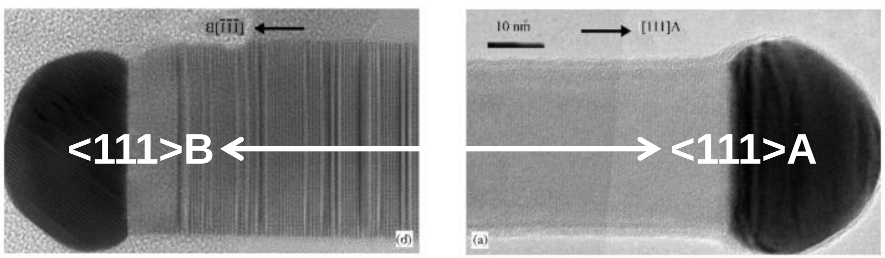
Nanoscale 10, 17080 (2018)

"BNW"

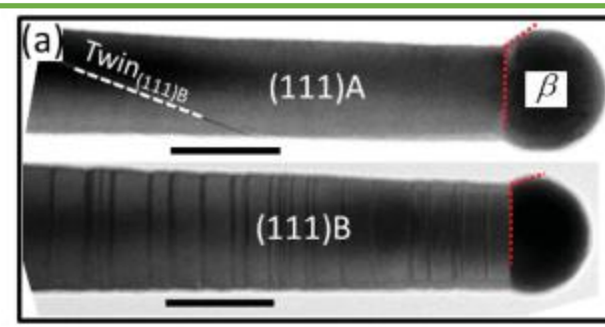


Vapor-Liquid-Solid growth

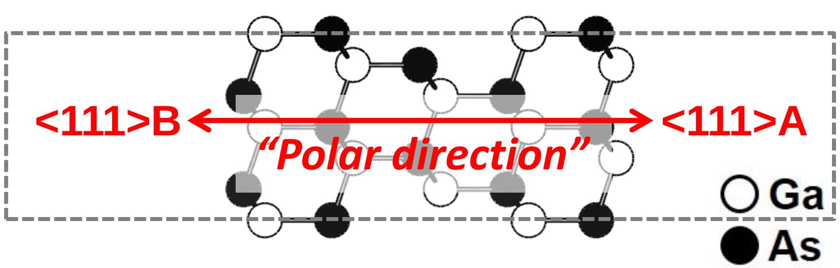




J. Cryst. Growth 287, 5004 (2006)



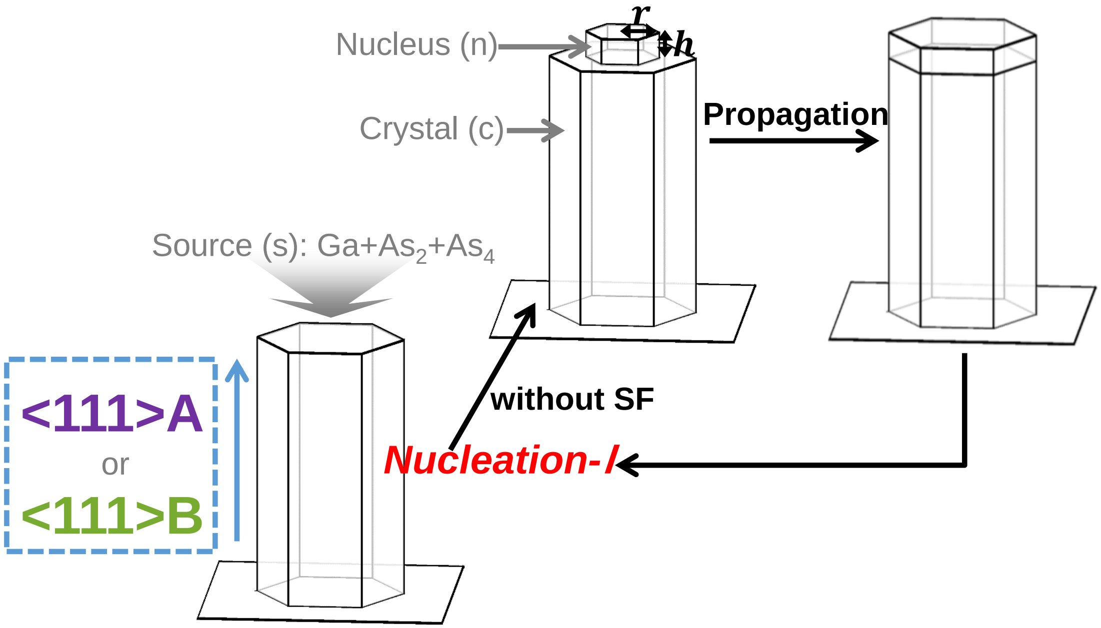
Adv. Mater. 27, 6096 (2015)



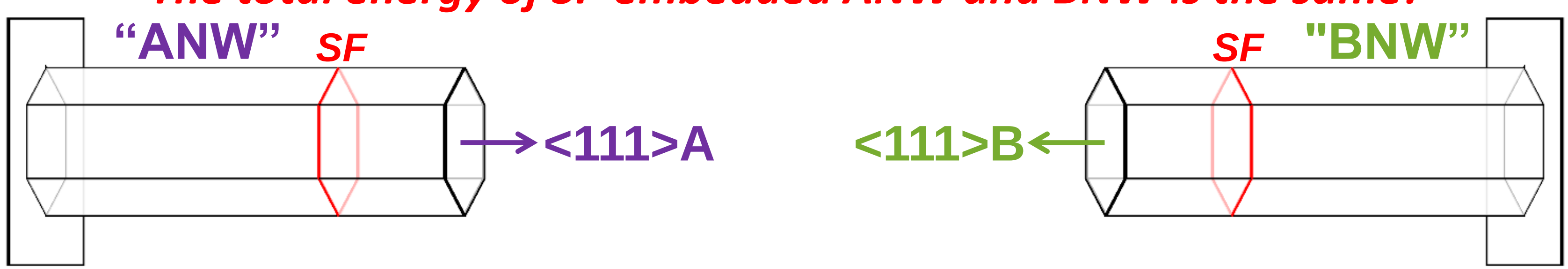
"Polarity dependent stacking"

*Between the **two opposite directions of <111>**, density of **planar defects is much higher in <111>B than <111>A***

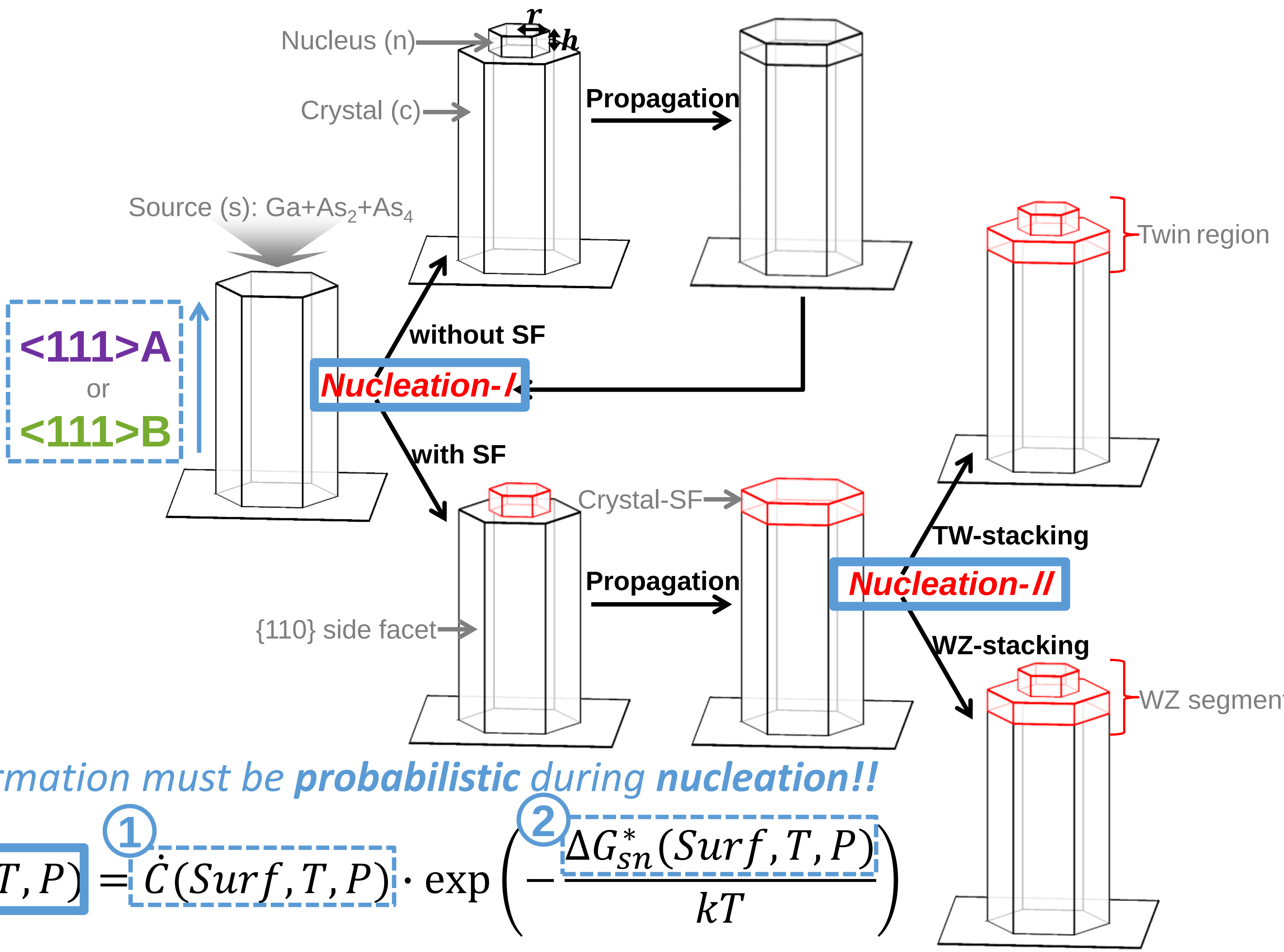
Energetics of fully formed NW?



The total energy of SF-embedded ANW and BNW is the same!



Energetics of fully formed NW?



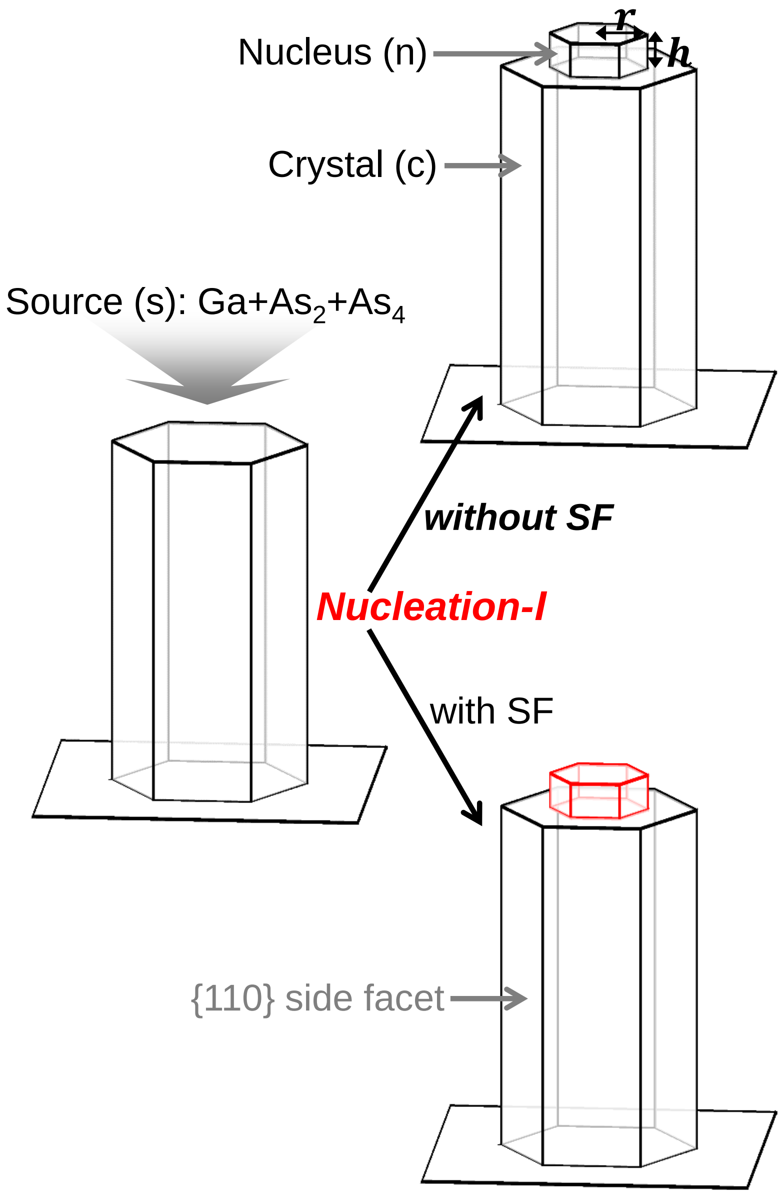
*The SF formation must be **probabilistic** during **nucleation!!***

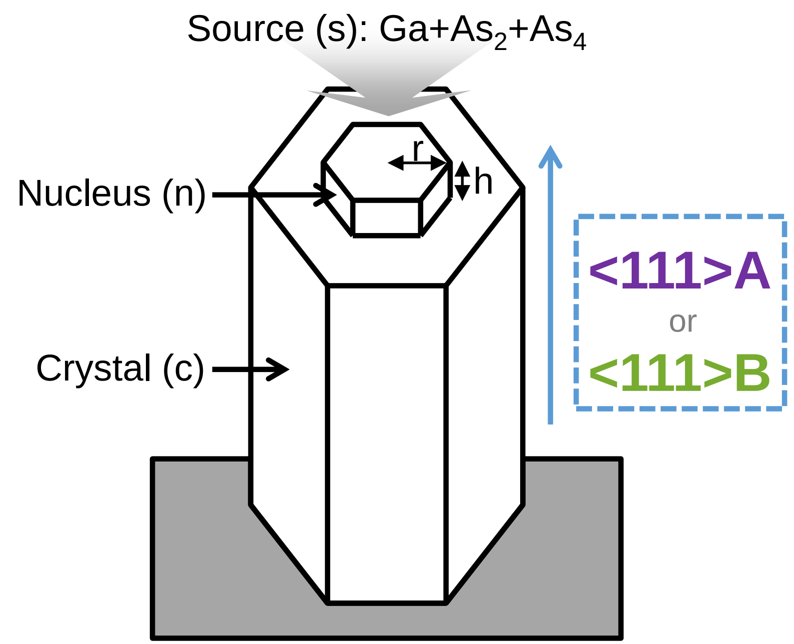
$$\dot{N}_{n|Surf}(T,P) = \dot{C}(Surf,T,P) \cdot \exp\left(-\frac{\Delta G^{*}_{sn}(Surf,T,P)}{kT}\right)$$

① ***"Rate of source supply"***

② ***"Nucleation barrier"***

Nucleation-I: with ZB or SF stacking





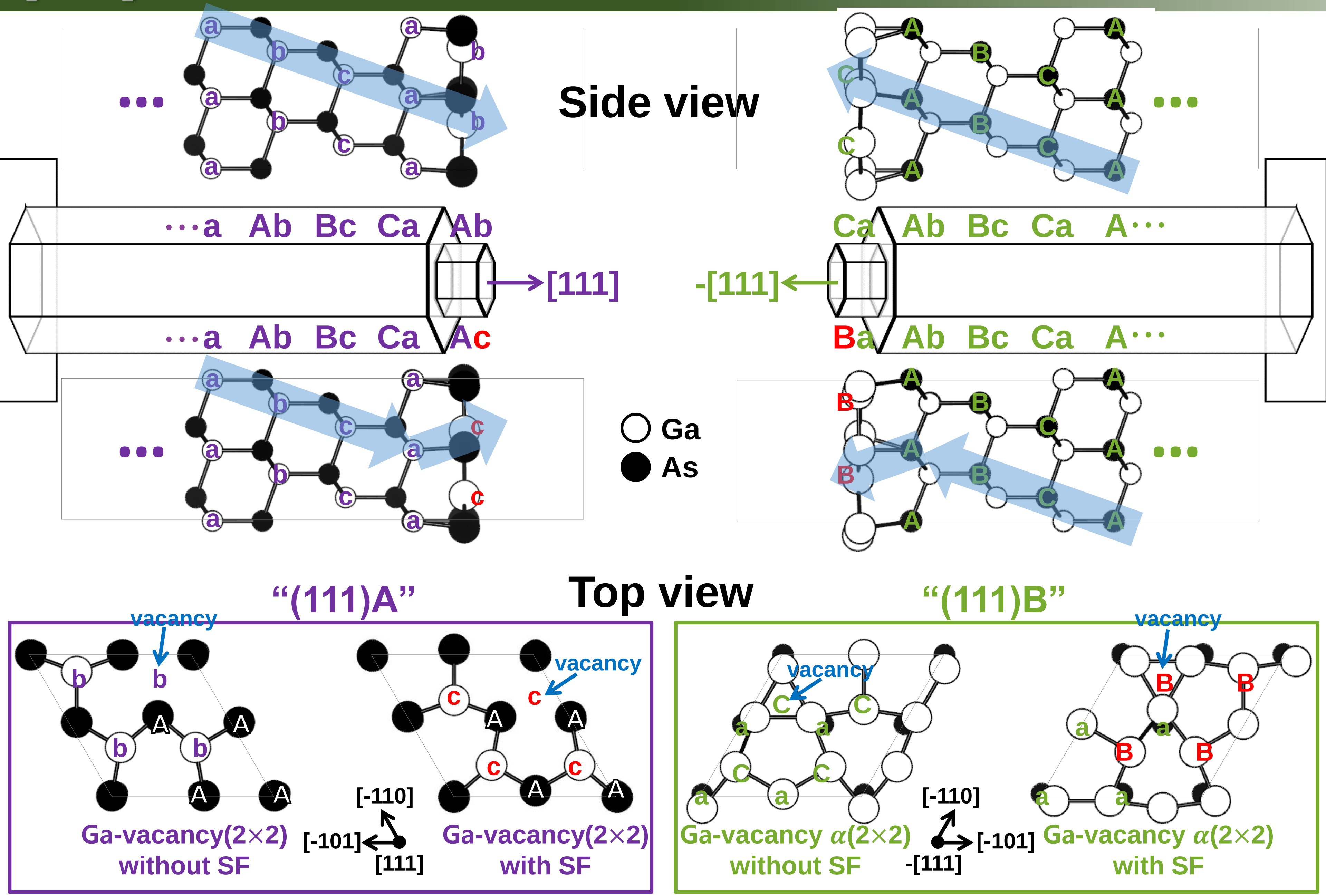
$\Delta G_{sn} =$

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

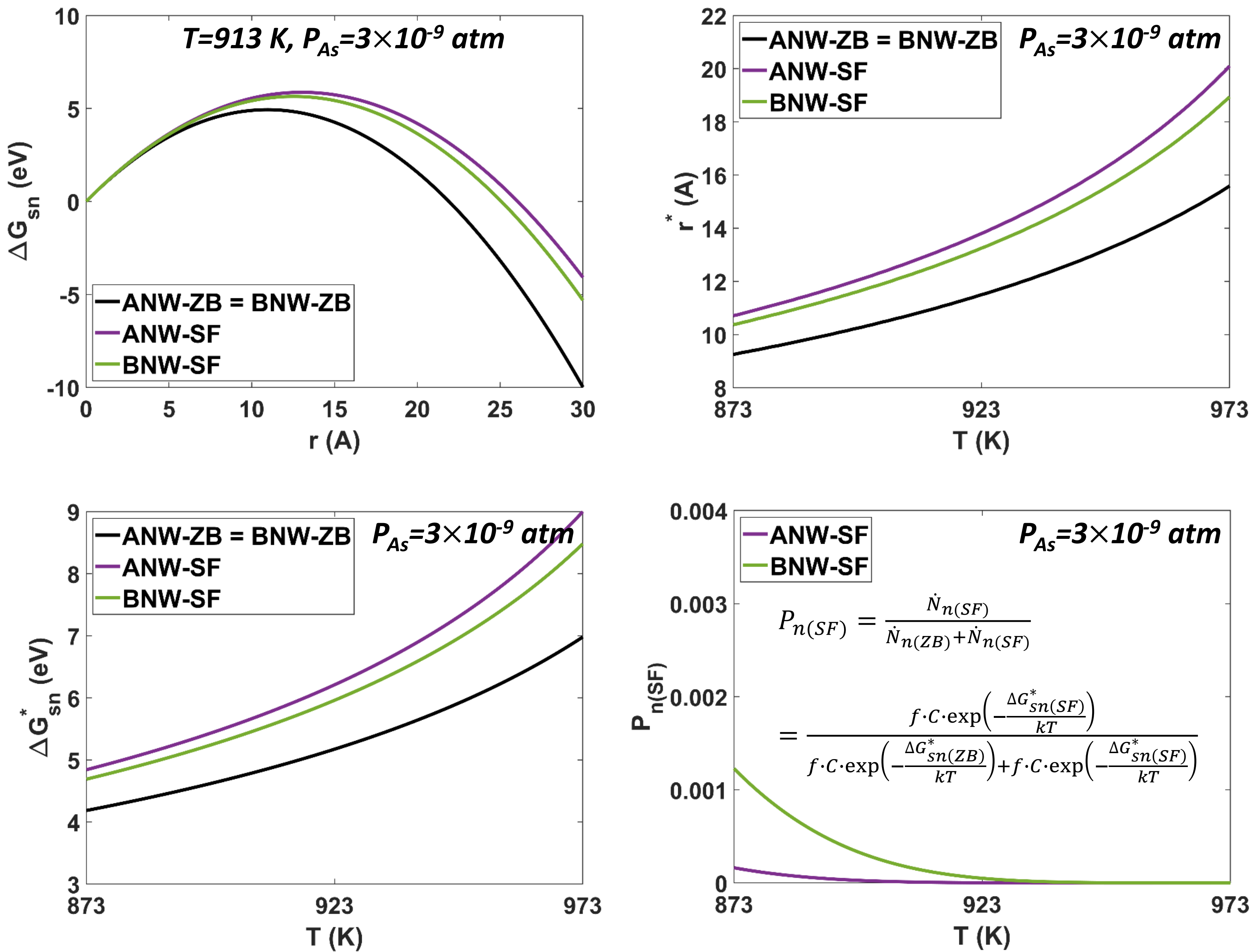
"Side surface energy" $+A_{side}\gamma_{sn(110)}$

"Top surface energy" $+A_{top}\left(\gamma_{cn(111)} - \gamma_{sc(111)}\right)$

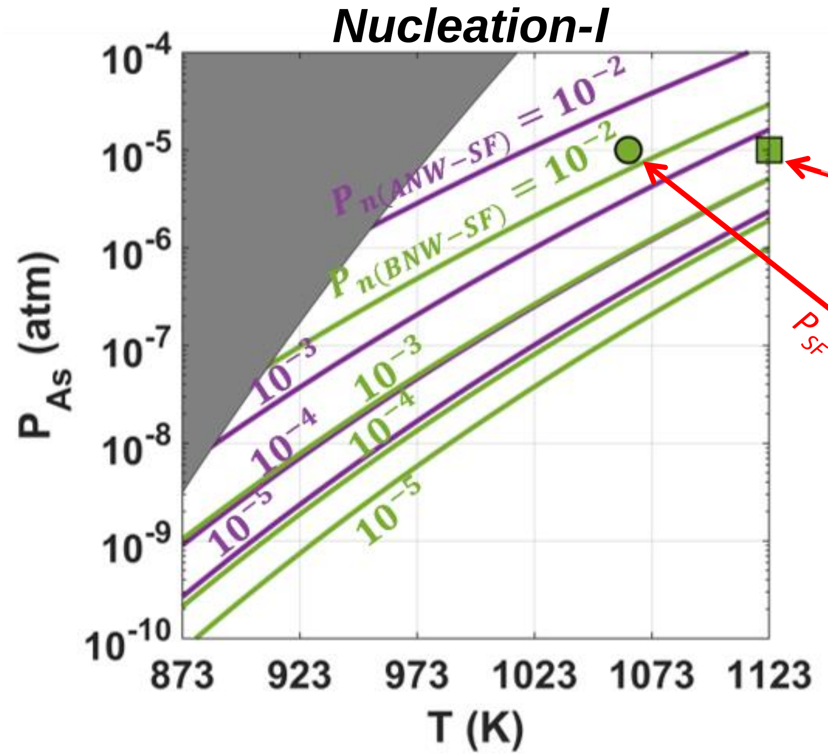
(111)A & B reconstruction with SF



Nucleation-I: ZB vs. SF



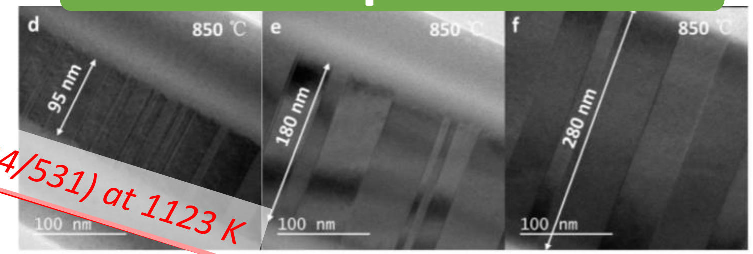
Asymmetric stacking in nucleation-I

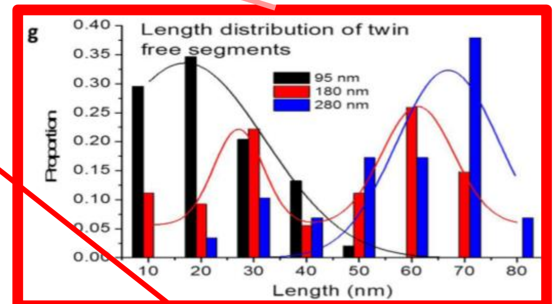


P_{SF} ~ 0.006 (=3.24/531) at 1123 K

P_{SF} = 0.03 at 1063 K

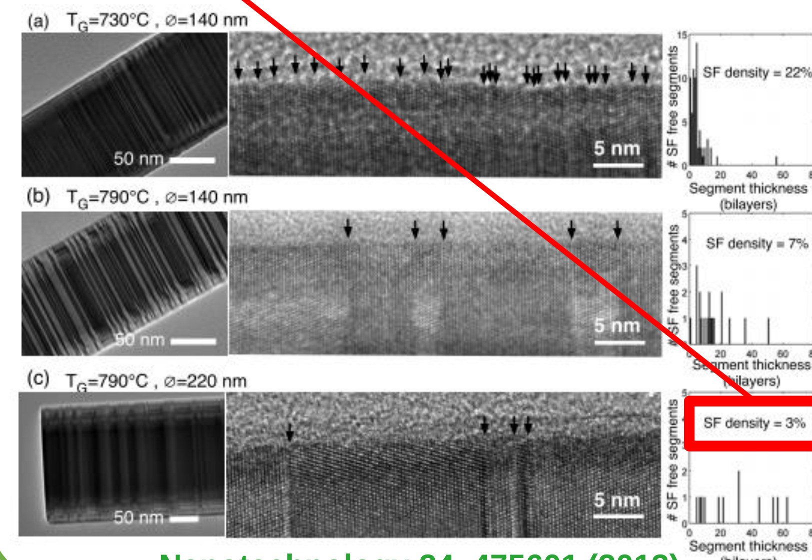
BNW experiments





The average twin-free length = 531 Å

ACS Nano 10, 2424 (2016)



Nanotechnology 24, 475601 (2013)

"SF density"

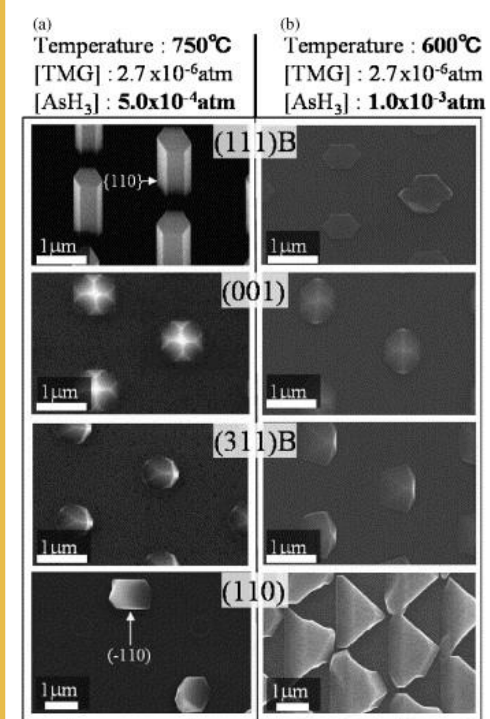
Polarity** dependence: **ANW < BNW

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

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

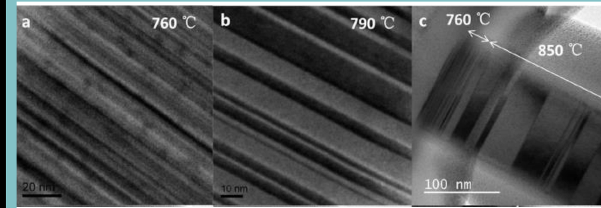
Thank you

Anisotropic growth

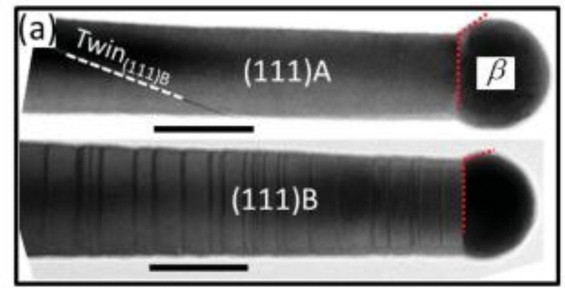


J. Cryst. Growth, 298, 616 (2007)

Asymmetric stacking

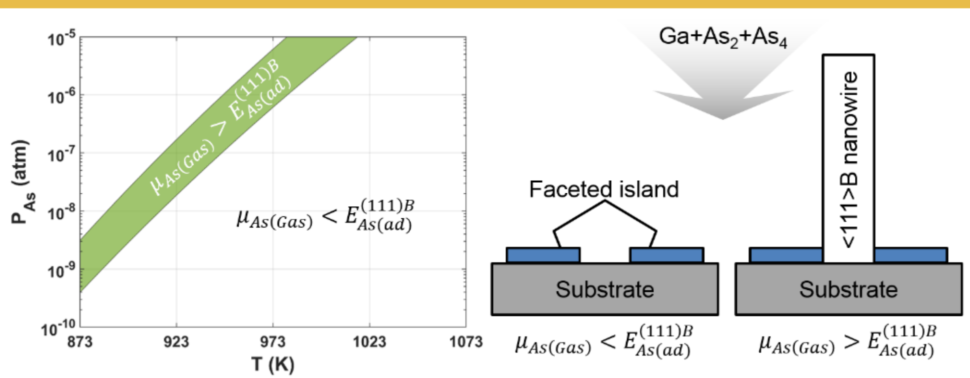


ACS Nano 10, 2424 (2016)

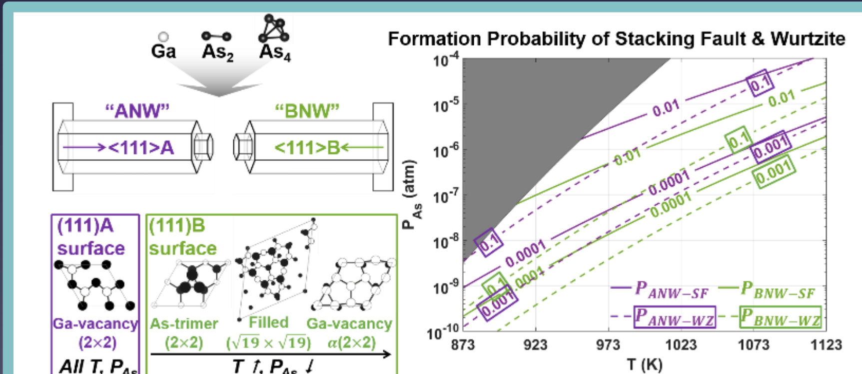


Adv. Mater. 27, 6096 (2015)

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



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



Yeu *et al.*, *Nanoscale*, DOI: 10.1039/D0NR02010A (2020)