PRiME 2020
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A joint international meeting

#G03-1758

G03-SiGe, Ge & Related Compounds: Materials, Processing and Devices
16:30, 08, Oct, 2020 (HST)

Atomistic Understanding on the Surface of GaAs by Ab Initio Thermodynamics; From Equilibrium Shape to Growth Shape

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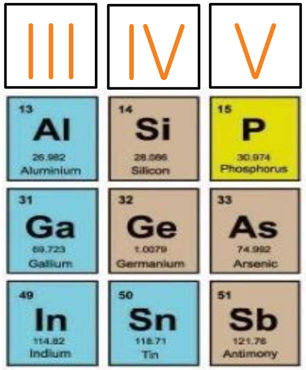
Integration of III–V on Si



	e^- mobility (cm^2/Vsec)	h^+ mobility (cm^2/Vsec)	Lattice constant (Å)
GaAs	8,000	400	5.65
Si	1,400	500	5.43

- Good electronic properties
- Compatibility with Si

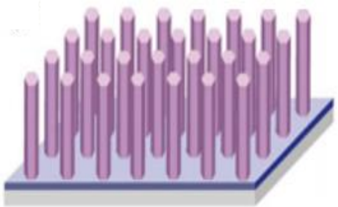
GaAs on Si

lattice mismatch → **Dislocation**

Difference in thermal expansion coefficients → **Crack**

Polar material on nonpolar surface → **Antiphase boundary**

Selective Area Growth



→ Confined to the bottom

→ Inhibition of propagation

→ Reduction due to small number of nuclei

Understanding the surface energy & growth kinetics

Contents

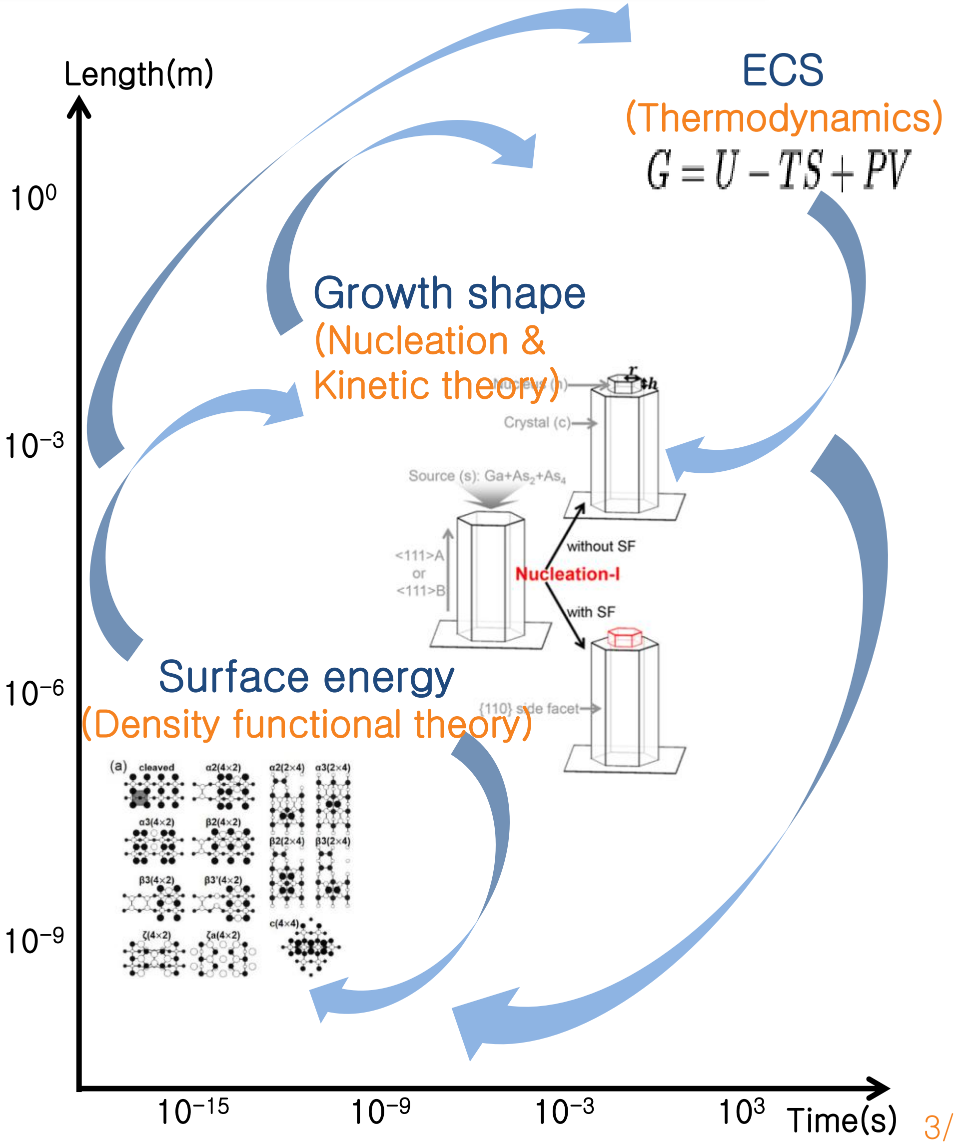
Morphology prediction by scale-bridging

I. Equilibrium crystal shape

- Surface reconstruction
- Surface energy
- Equilibrium crystal shape (ECS)

II. Growth shape

- Nanowire growth
- Asymmetric stacking



ECS

(Thermodynamics)

$G = U - TS + PV$

Growth shape

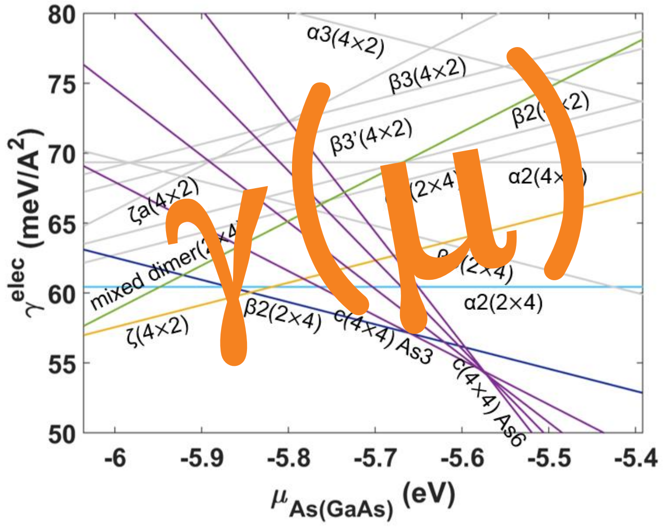
(Nucleation & Kinetic theory)

Surface energy

(Density functional theory)

I. Surface energy & Equilibrium crystal shape (ECS)

Surface energy

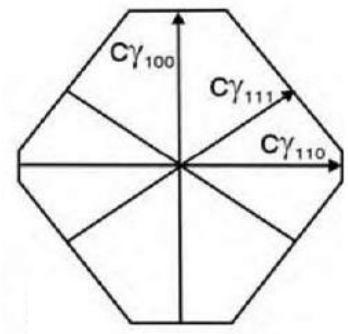


γ(T, P)

Wulff construction

$$d^{(hkl)} \propto \gamma^{(hkl)}$$

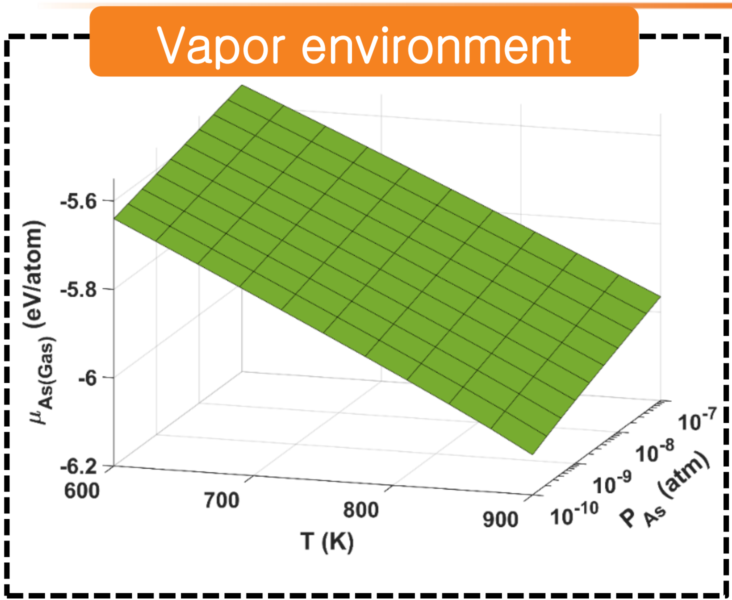
Minimum total surface energy

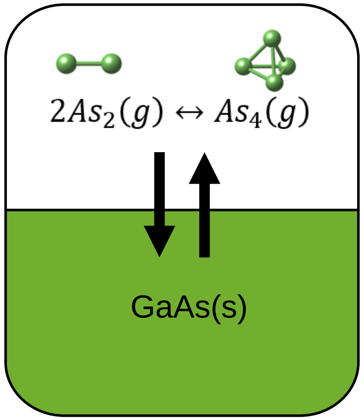


ECS(T, P)

I–1. Surface reconstruction & Surface energy of GaAs(100)

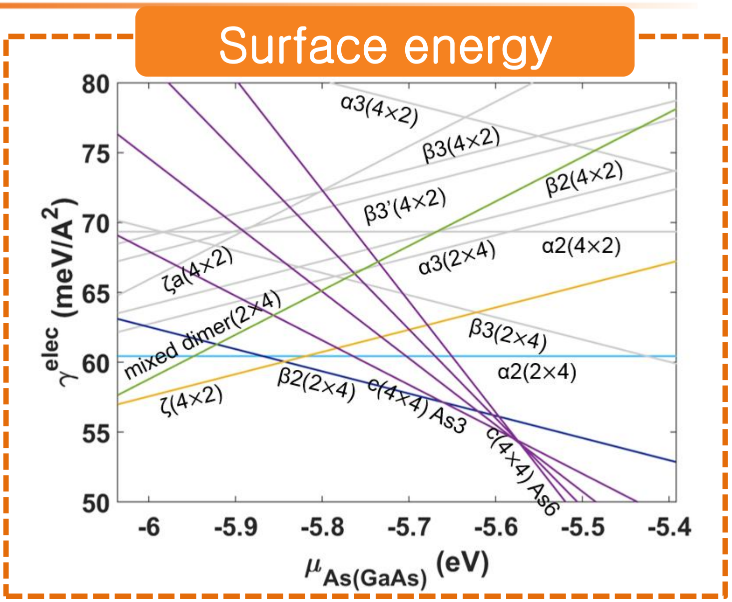
$\gamma(\mu)$ to $\gamma(T,P)$ by equil'm between surface & vapor

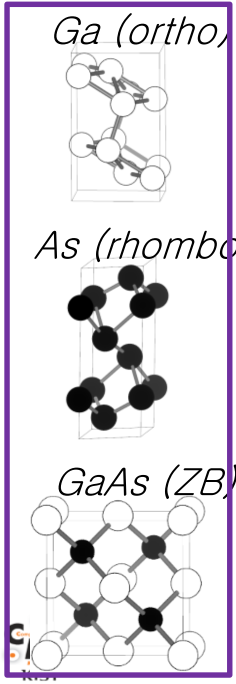


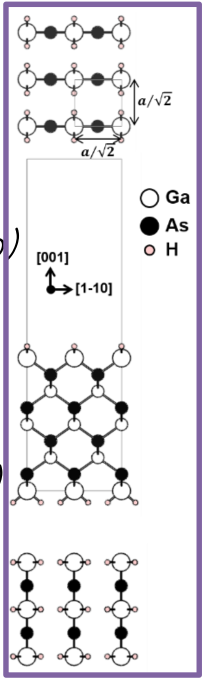


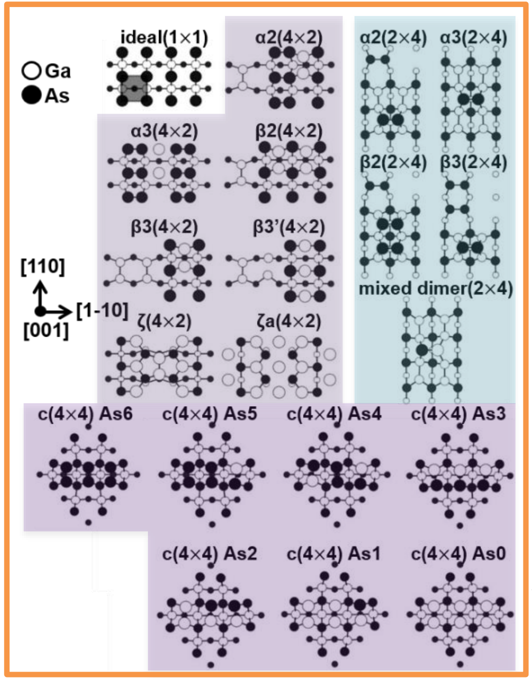
$$\mu_{As(Gas)} = \mu_{As(GaAs)}$$

"Equilibrium"









Equilibrium condition:

$$\mu^{elec}_{Ga(GaAs)} + \mu^{elec}_{As(GaAs)} = \boxed{\mu^{elec}_{GaAs(bulk)}}$$

Stable against decomposition:

$$\mu_{Ga(GaAs)} < \boxed{\mu_{Ga(bulk)}}; \quad \mu_{As(GaAs)} < \boxed{\mu_{As(bulk)}}$$

Constraints:

$$\mu_{GaAs(bulk)} - \mu_{Ga(bulk)} < \mu_{As(GaAs)} < \mu_{As(bulk)}$$

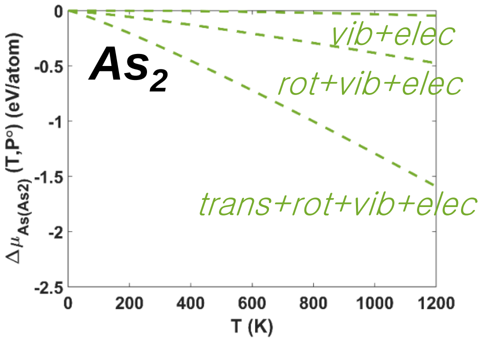
Electronic surface energy:

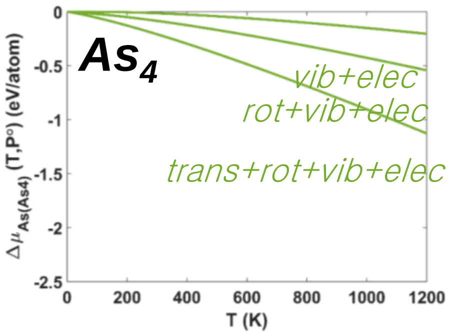
$$\gamma = \frac{\boxed{(E^{elec}_{surf})} - N_{Ga}(\mu^{elec}_{Ga(GaAs)}) - N_{As}(\mu^{elec}_{As(GaAs)})}{A} - \boxed{(\gamma_H + \alpha)}$$

Vapor environment of GaAs: As_2 & As_4

$$\mu_{i(Gas)}\left(T, P_{i(Gas)}\right) = E_{i(Gas)} + E^{ZPE}_{i(Gas)} + \Delta\mu_{i(Gas)}(T, P^o) + k_B T \ln \frac{P_{i(Gas)}}{P^o}$$

$$\Delta\mu_{i(Gas)}(T, P^o) = F^{trans} + F^{rot} + F^{vib} - k_B T \ln I^{spin}$$

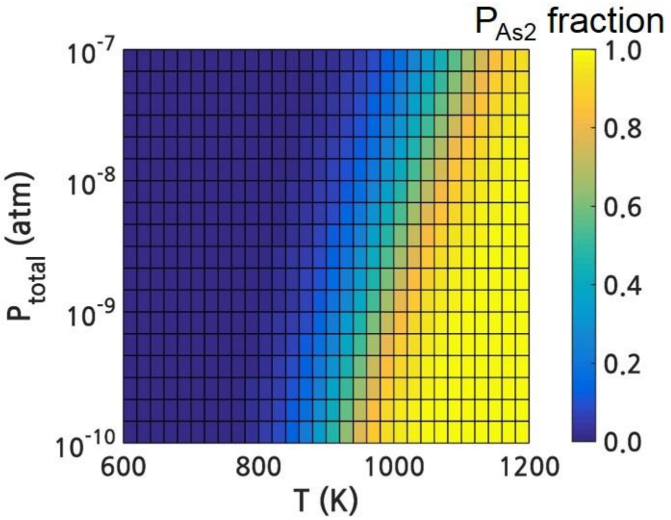


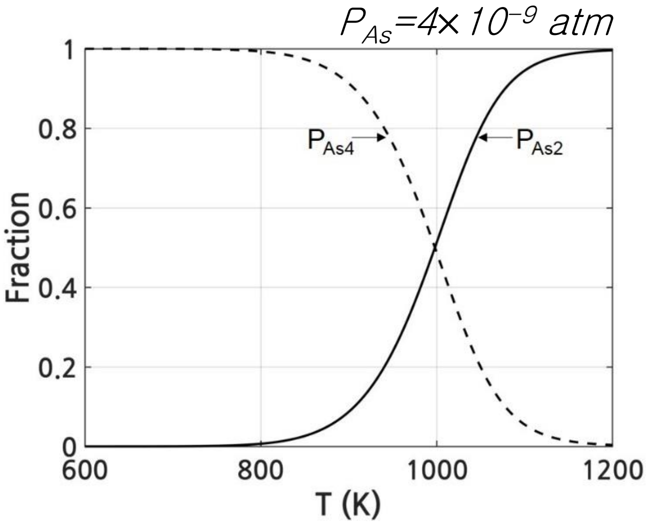


$$2As_2(g) \leftrightarrow As_4(g)$$

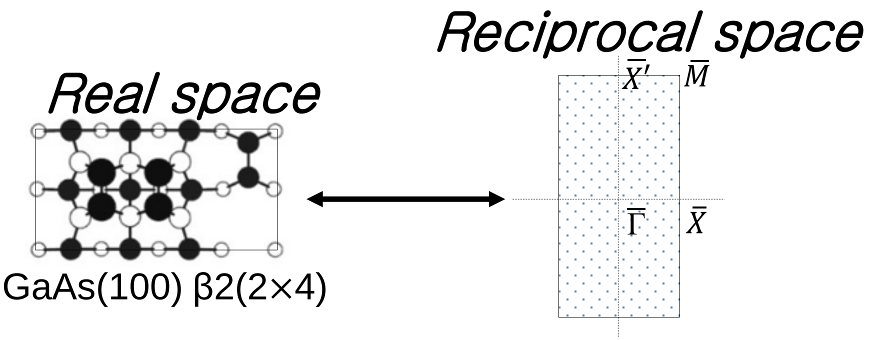
$$\mu_{As(Gas)} = \frac{1}{2}\mu_{As_2(Gas)} = \frac{1}{4}\mu_{As_4(Gas)}$$

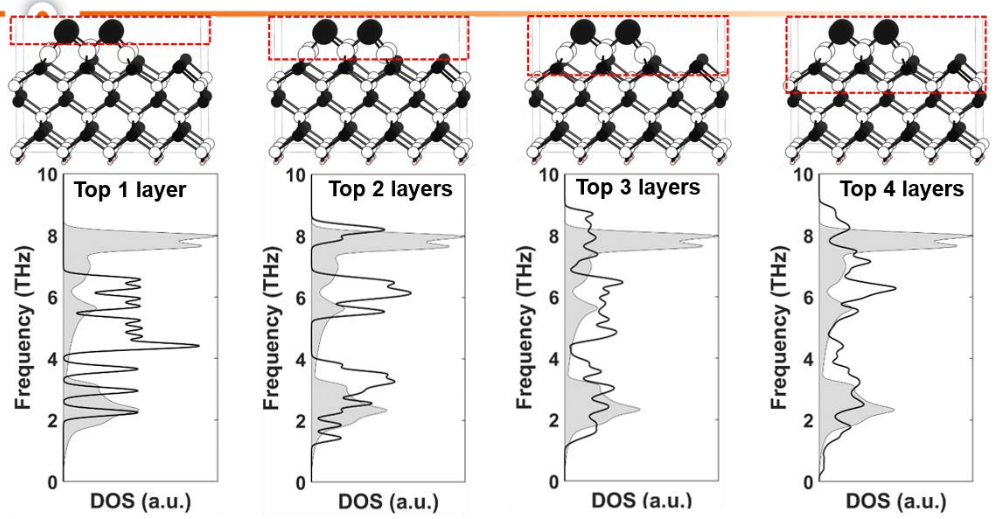
$$P_{As(Gas)} = P_{As_2} + P_{As_4}$$





Vibrational effects on $\gamma(T,\mathrm{P})$





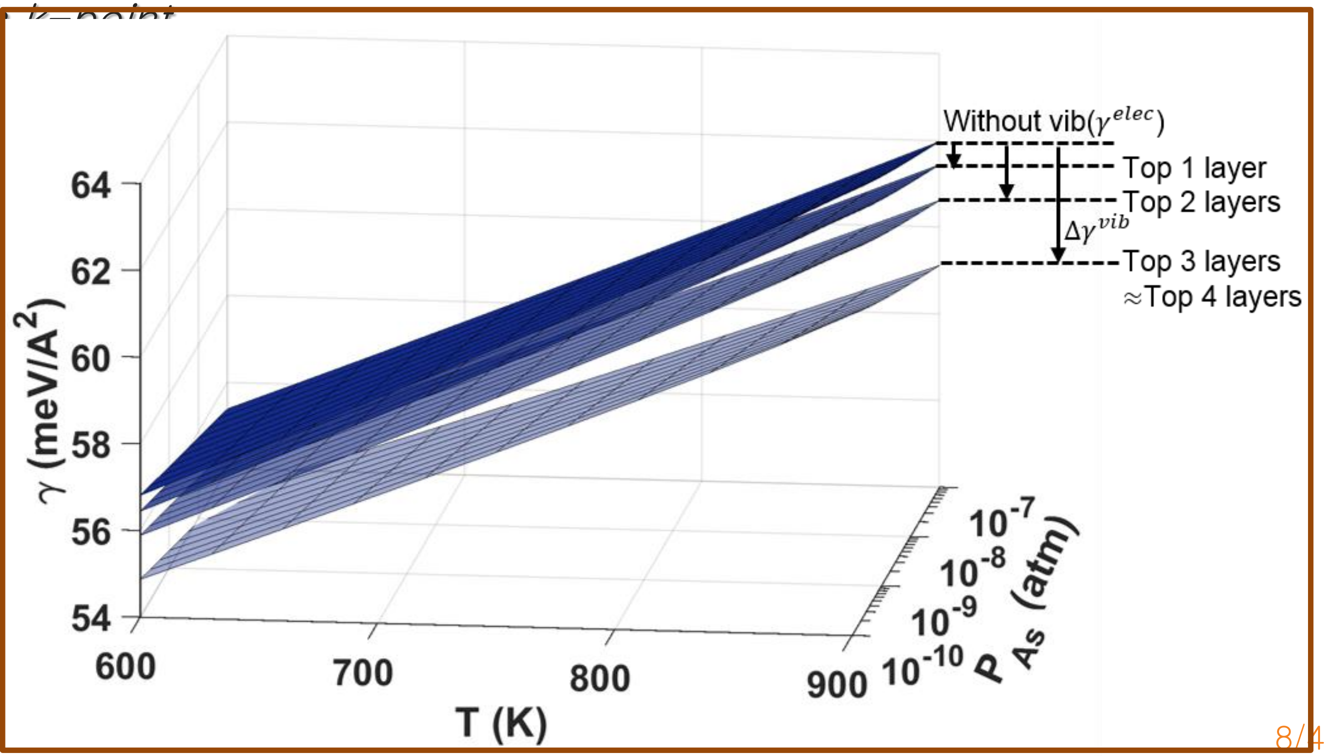
1. *Sampling 21×21 k-points*
2. *Calculate D(k) at each k-point*
3. *Obtain w(k) at each*

$$F^{vib}(T) = \frac{1}{N_k}\sum_{k\in BZ}\sum_{i=1}^{M}\{\frac{\hbar w_i(k)}{2} +$$

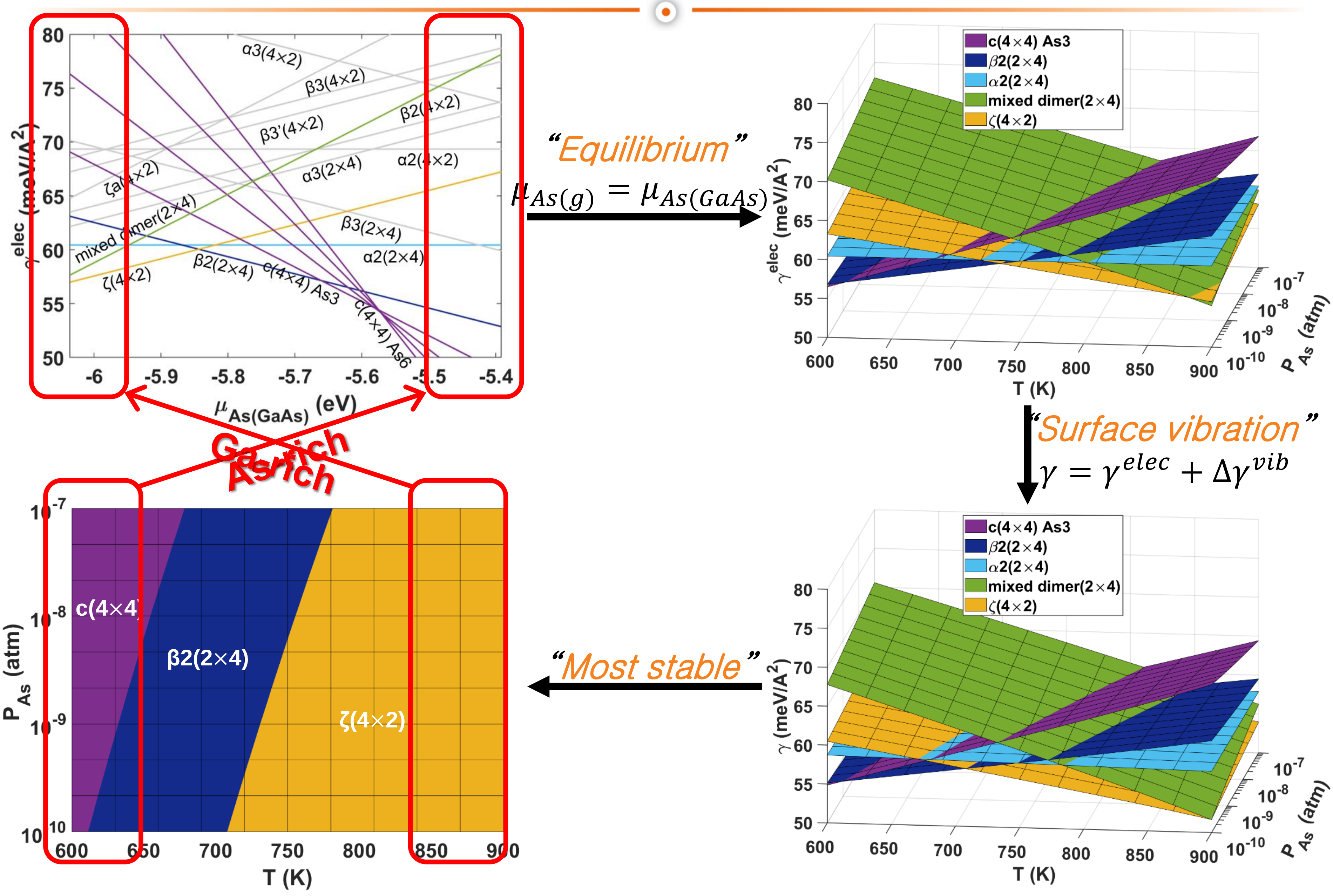
$$\gamma^{elec}(T,P) = \frac{(E^{elec}_{surf}) - N_{Ga}(E^{elec}_{Ga(}}{}$$

$$\Delta\gamma^{vib}(T) = \frac{(F^{vib}_{surf}) - N_{Ga}(F^{vib}_{Ga(Ga}}{}$$

$$\boxed{\gamma(T,\mathrm{P}) = \gamma^{elec}(T,\mathrm{P}) + \Delta\gamma^{vib}(T)}$$



GaAs(001) phase diagram (T, P_{As})



"Equilibrium"

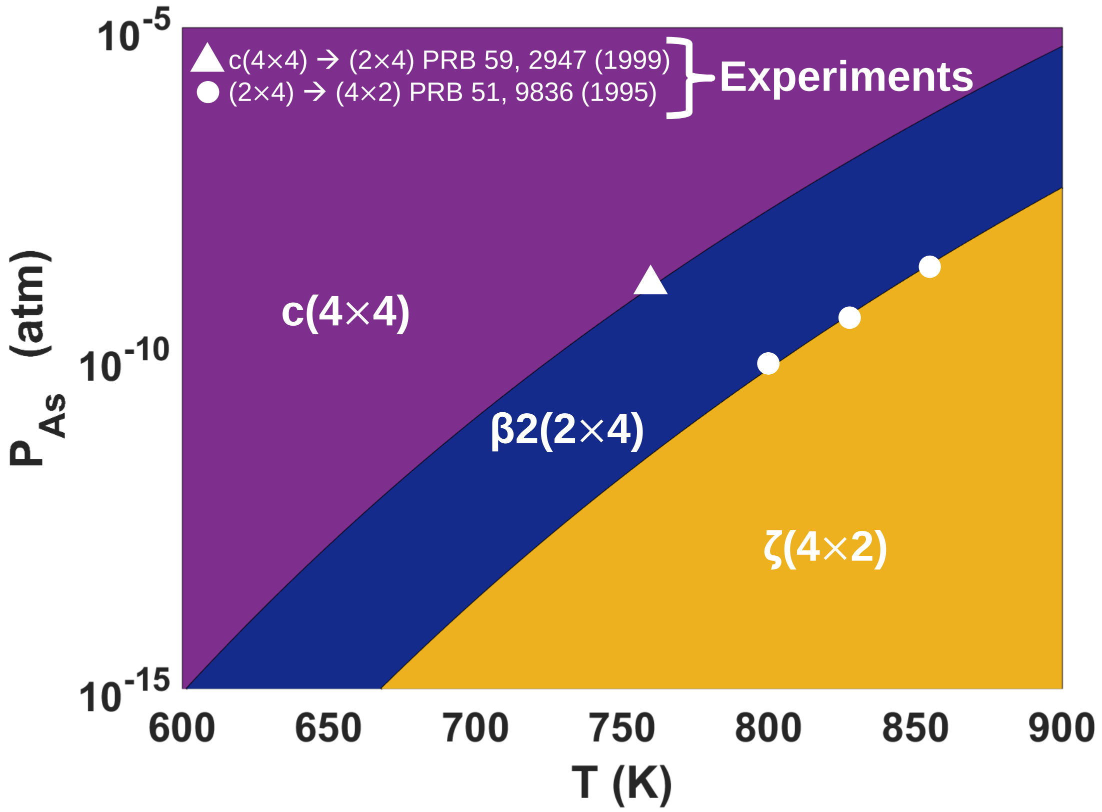
$\mu_{As(g)} = \mu_{As(GaAs)}$

"Surface vibration"

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

"Most stable"

GaAs(100) surface transition (T, P_{As})



- Calculated transition lines show good agreements with experimental transition (T,P) points.

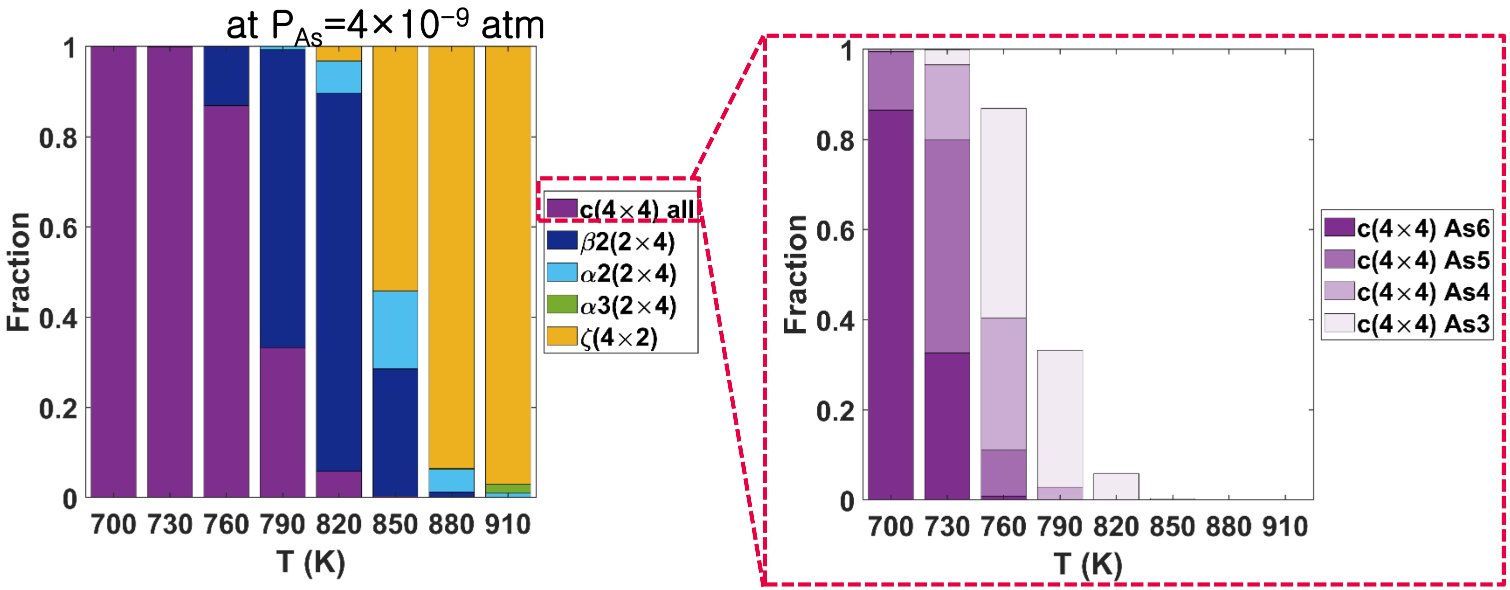
- At the transition lines, coexistence of reconstructions occurs in experiments.

Configurational entropy; Coexistence of reconstructions

A real situation is not the ground state,
rather an ensemble of possible configurations with statistical probability

Population of reconstruction i: $c_i = \frac{Z_i}{Z}$ $where\ i \in \{reconstructions\}$

$$Z = \sum_i Z_i = \sum_i g_i \exp(-\frac{\gamma_i(T,P)A}{k_B T})$$

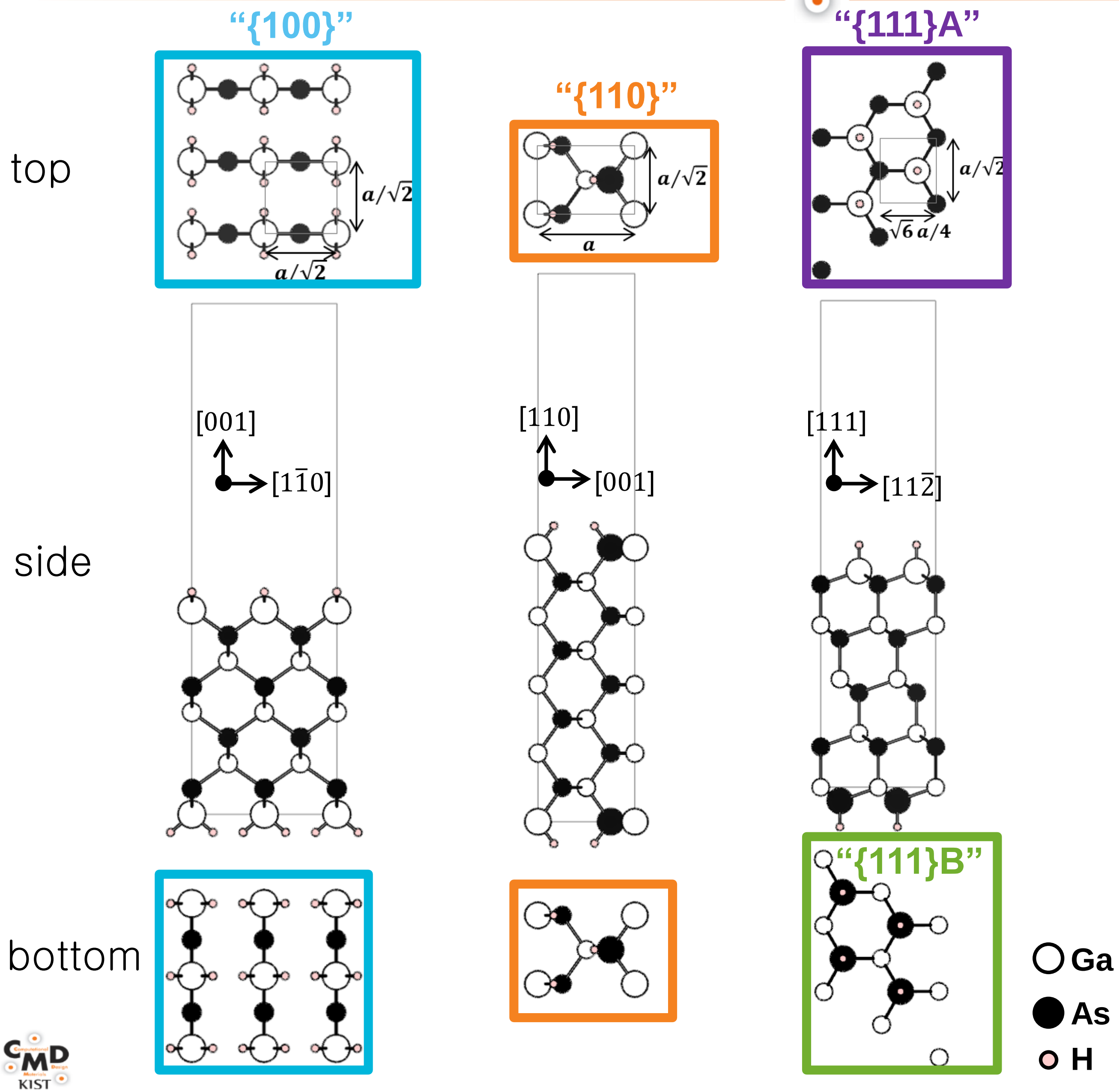


~760 K **~850 K**

c(4×4) ⇆ mixture ⇆ (2×4) ⇆ mixture ⇆ (4×2)

I-2. Equilibrium crystal shape (ECS)

Surface in zinc blende symmetry



"{100}"

"{110}"

"{111}A"

"{111}B"

top

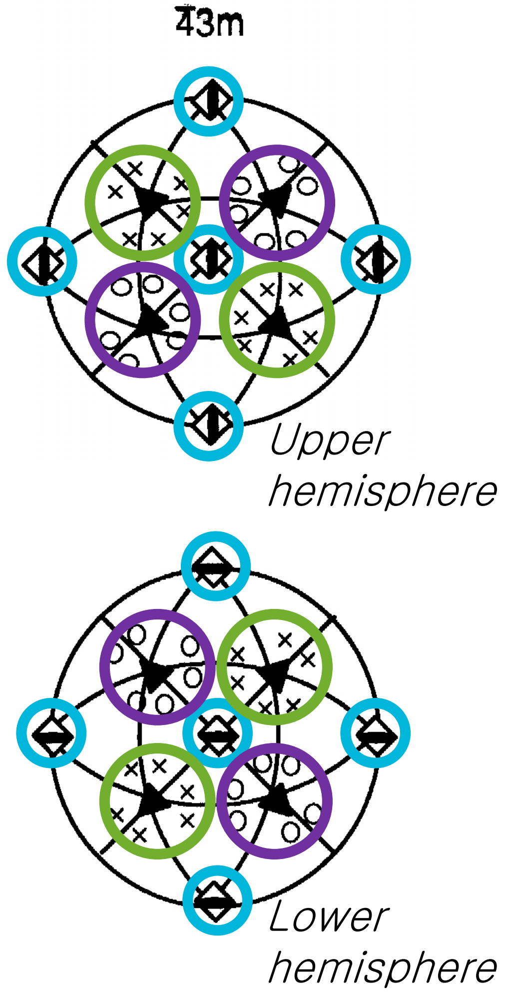
side

bottom

○ Ga

● As

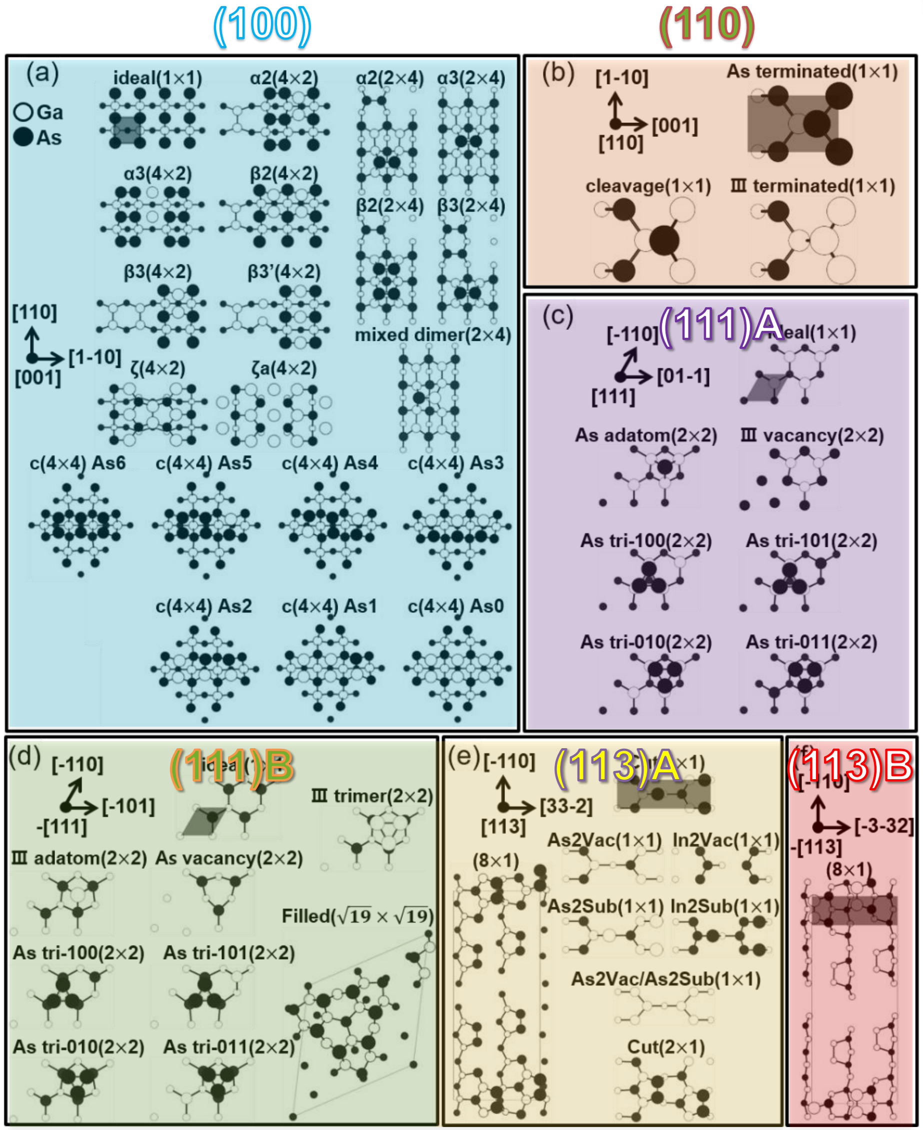
○ H

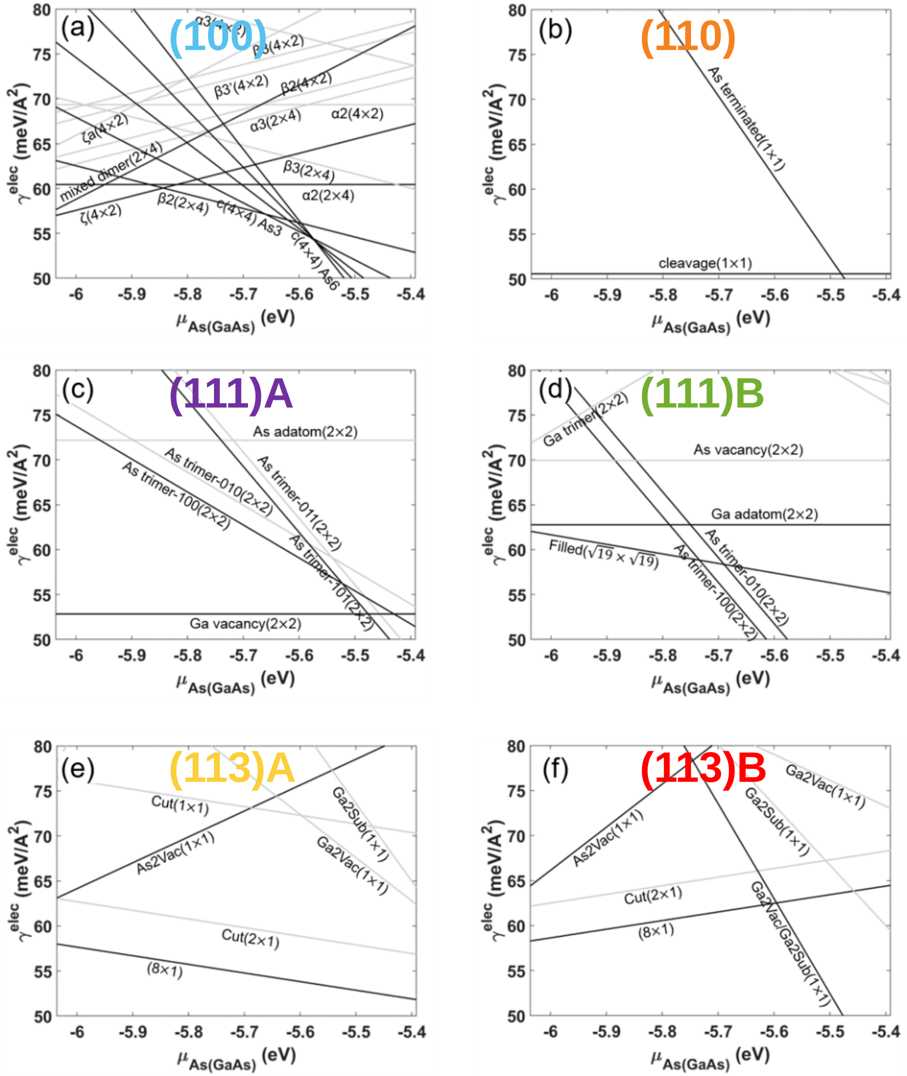


Upper hemisphere

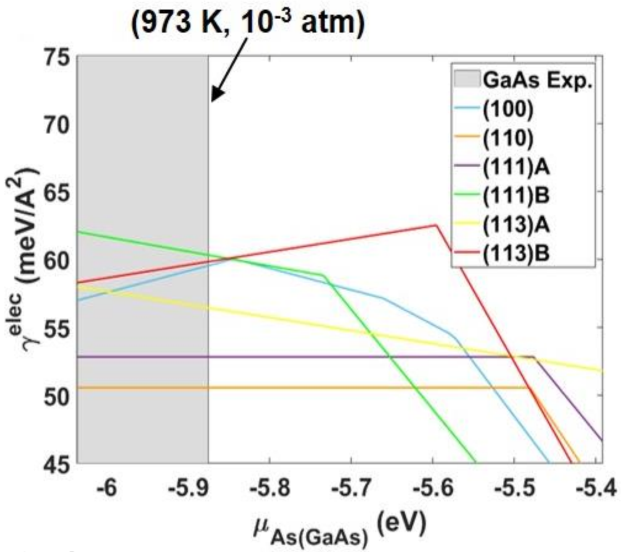
Lower hemisphere

Reconstructions of various surfaces of GaAs





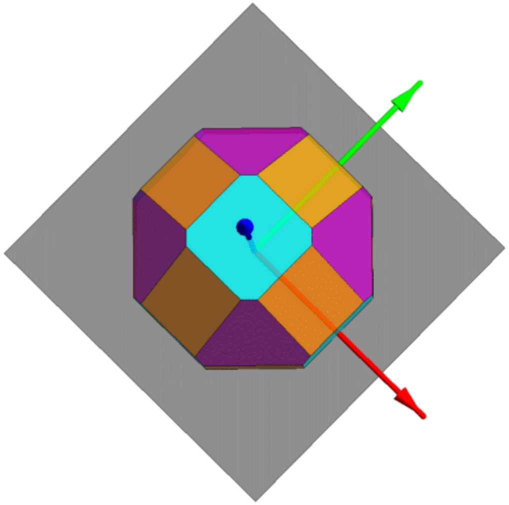
Wulff shape (T, P_{As}) of GaAs

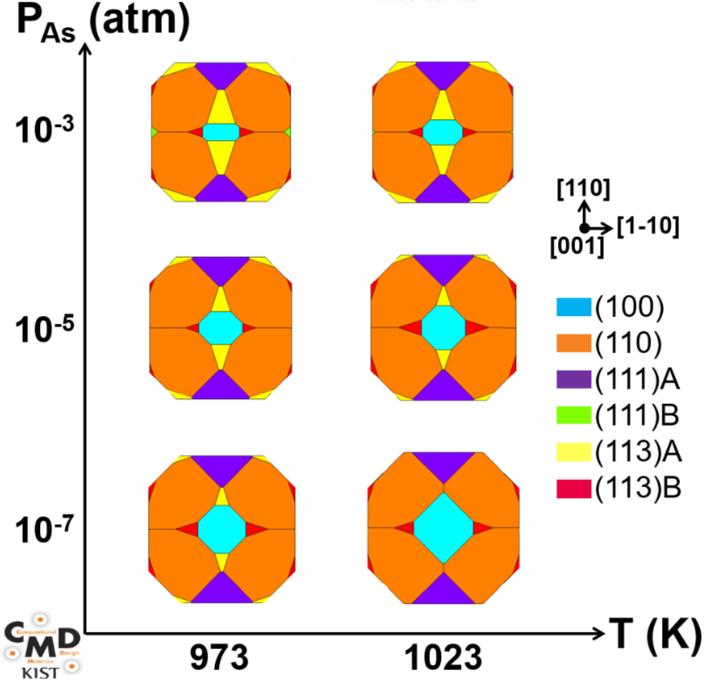


Wulff construction:

$$d^{(hkl)} \propto \gamma^{(hkl)}$$

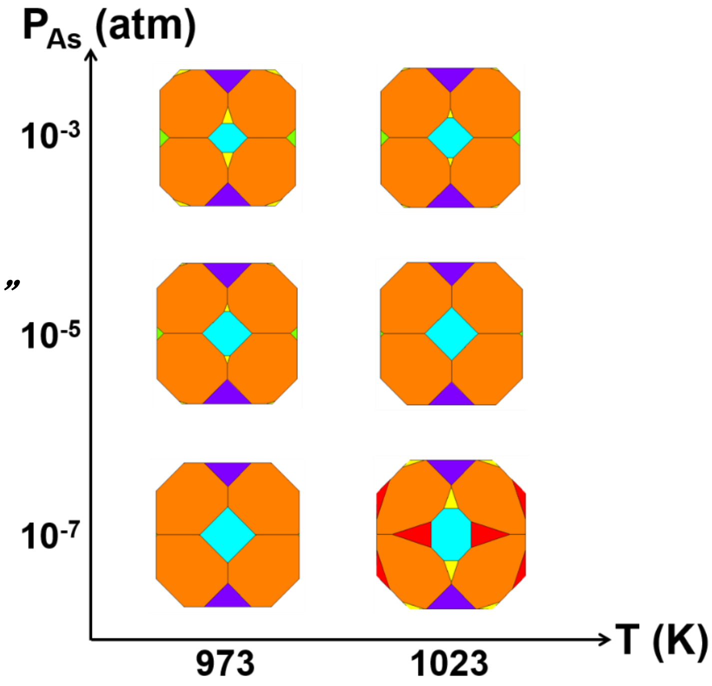
Minimum total surface energy





"Surface vibration"

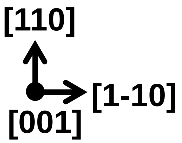
$$\gamma = \gamma^{elec} + \Delta\gamma^{vib}$$



Wulff shape vs. Growth shape ??

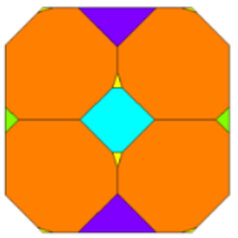
Calculated Wulff shape

T: 1023 K

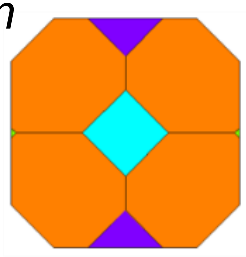


- 🟦 (100)
- 🟧 (110)
- 🟪 (111)A
- 🟩 (111)B
- 🟨 (113)A
- 🟥 (113)B

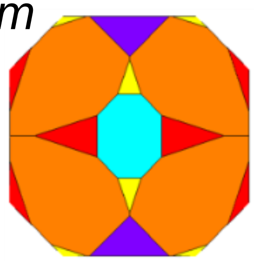
P_{As}: 10^{-3} atm



10^{-5} atm



10^{-7} atm



(111)B does NOT appear.

Experimental growth shape

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

SA-MOVPE

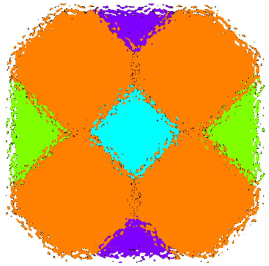
T: 1023 K	T: 873 K
[TMGa]: 2.7×10^{-6} atm	[TMGa]: 2.7×10^{-6} atm
[AsH_3]: 5.0×10^{-4} atm	[AsH_3]: 1.0×10^{-3} atm

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

SA-MOVPE

TMGa & TBAs or AsH_3

T: 973~1023 K

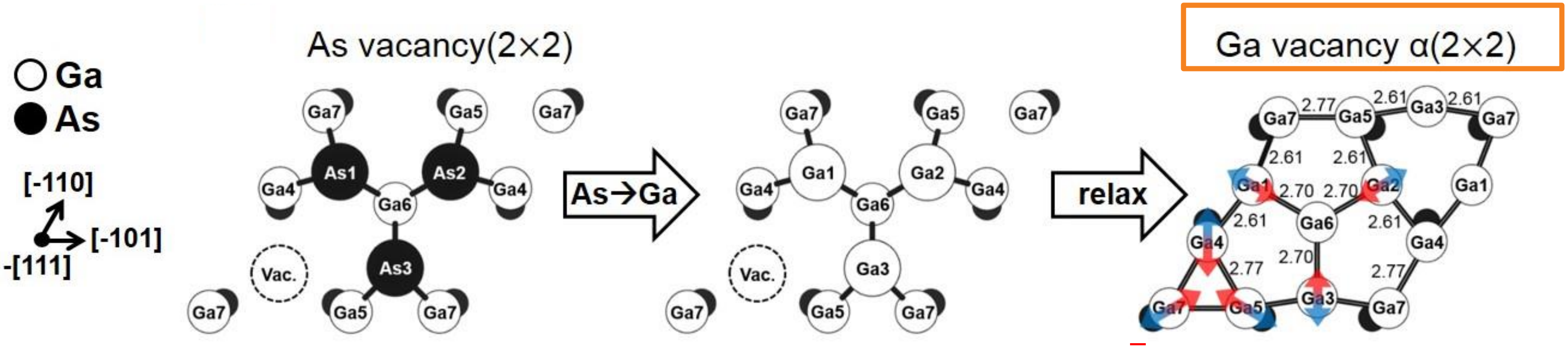


(111)B does appear!!!

→ *Questions?*

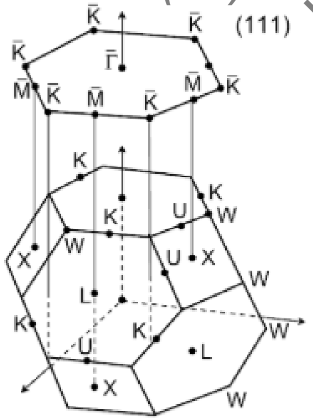
- Kinetics dominant?
- Unknown (111)B reconstruction?

Newly proposed reconstruction of (111)B

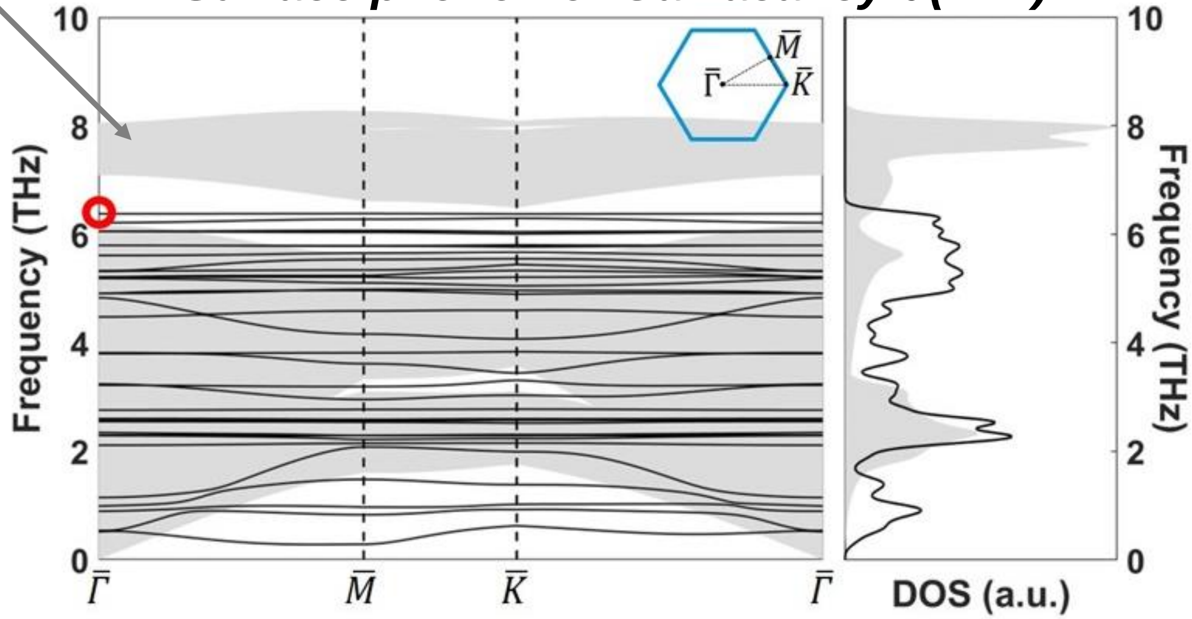


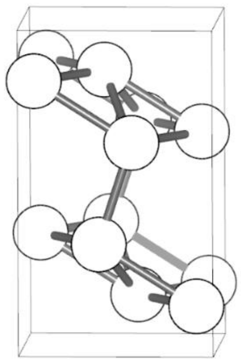
Γ̄ mode (6.38 THz)

"projection of bulk phonon onto (111) BZ"



Surface phonon of Ga vacancy α(2×2)





Ga (orthorhombic)

Bond length (Å):

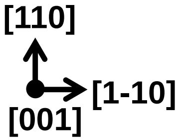
2.45, 2.63, 2.65, 2.73

Wulff shape in accordance with experiments

Calculated Wulff shape

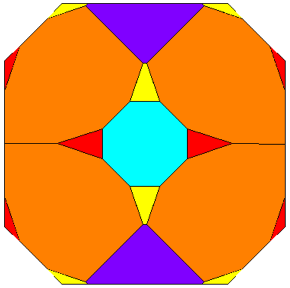
T: 1023 K,

P_{As}: 10^{-5} atm

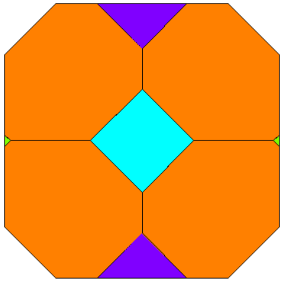


- 🟦 (100)
- 🟧 (110)
- 🟪 (111)A
- 🟩 (111)B
- 🟨 (113)A
- 🟥 (113)B

γ^{elec}

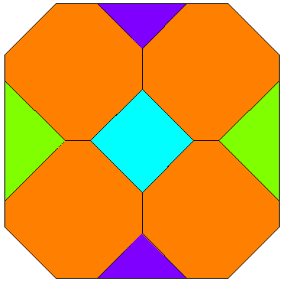


$\gamma^{\text{elec}} + \Delta\gamma^{vib}$



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

with a new (111)B reconstruction



Experimental growth shape

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

SA-MOVPE

T: 1023 K	T: 873 K
[TMGa]: 2.7×10^{-6} atm	[TMGa]: 2.7×10^{-6} atm
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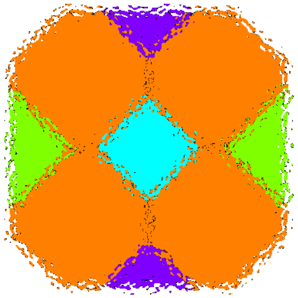
SA-MOVPE

TMGa & TBAs or AsH_3

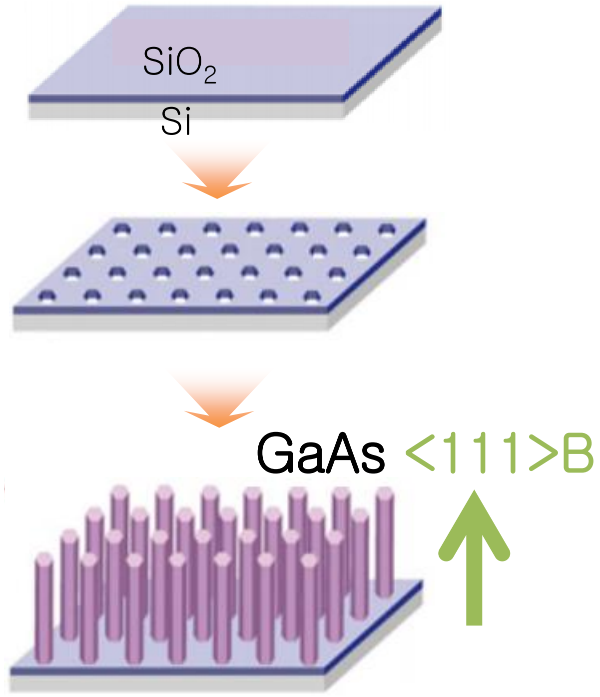
T: 973~1023 K



(111)B appear in calculated ECS & experiments.

II. GaAs (111)B nanowire

Selective Area Growth

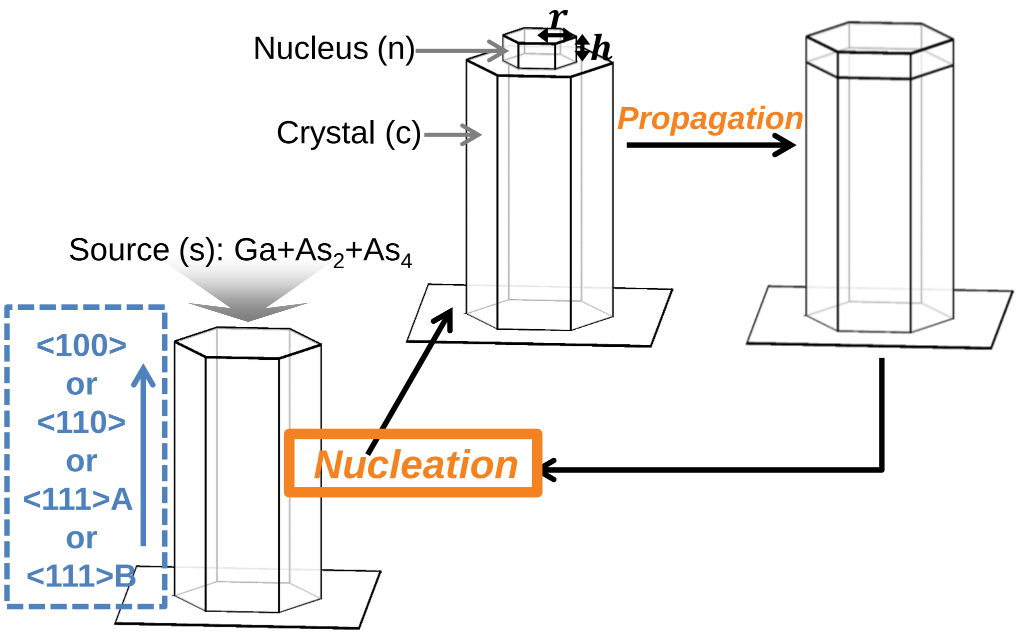


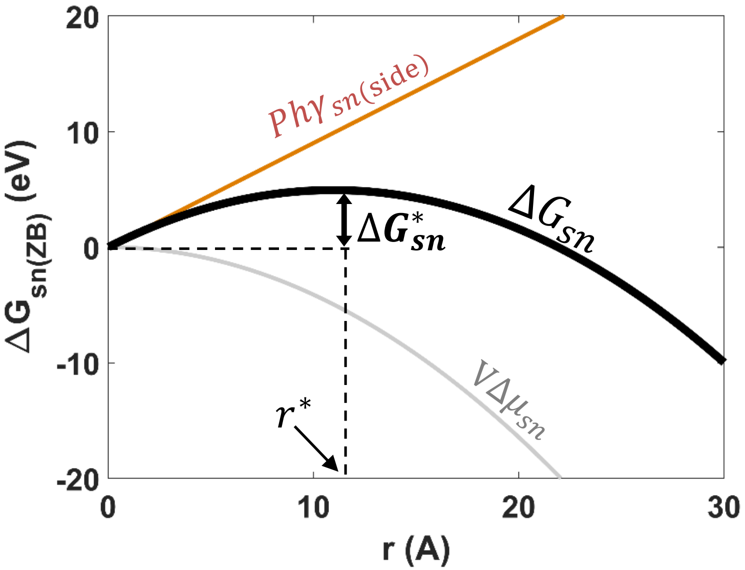
Two basics of NW growth

- Preferential nucleation
- Layer-by-Layer growth

II-1. Nanowire (NW) growth

Anisotropic growth model





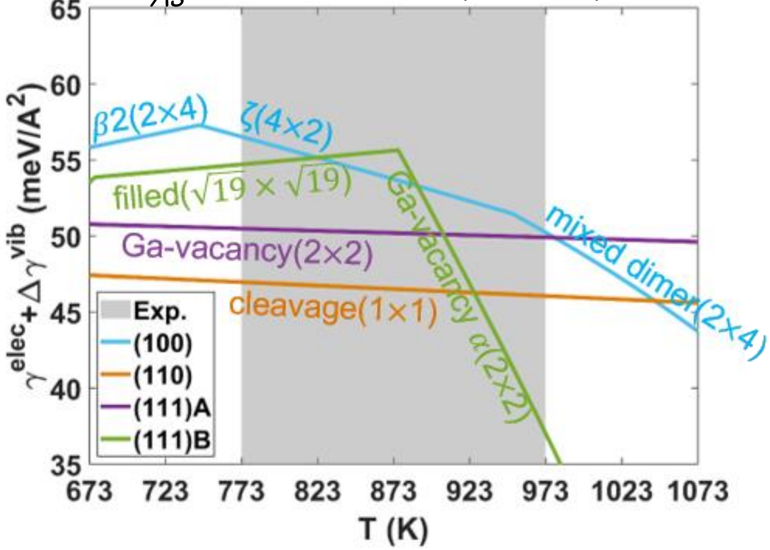
$$\dot{N}_{n|Surf}(T,P) = \dot{C}(Surf,T,P)\cdot\exp\left(-\frac{\boxed{\Delta G^*_{sn}(Surf,T,P)}}{kT}\right)$$

$$\Delta G_{sn} = V\Delta\mu_{sn} + Ph\gamma_{sn(side)} + A(\gamma_{sn(top)} - \gamma_{sc(top)})$$

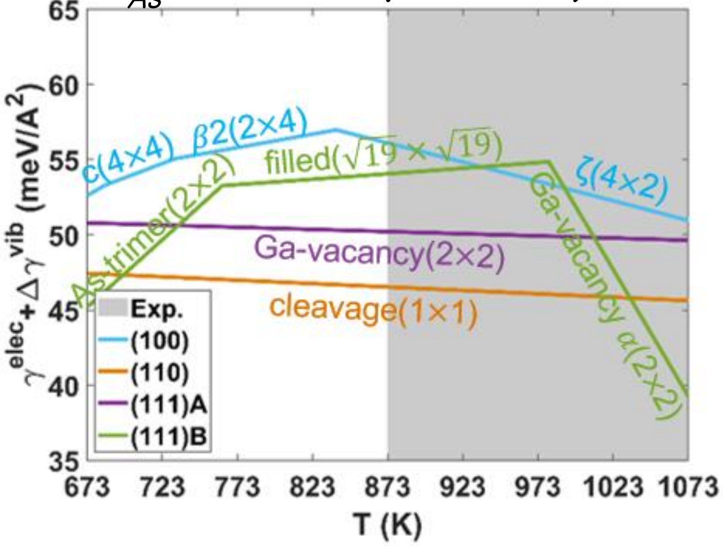
What is the key factor that determines the direction of preferential nucleation?

Variation of surface reconstructions wrt (T,P)

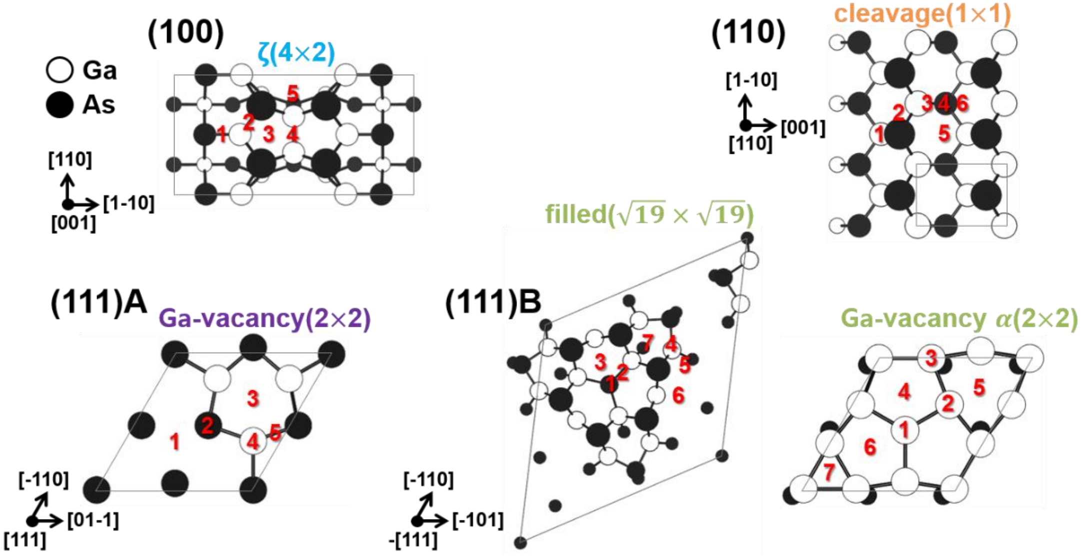
P_{As}= 4× 10^{-9} atm (~MBE)



P_{As}= 10^{-5} atm (~MOVPE)

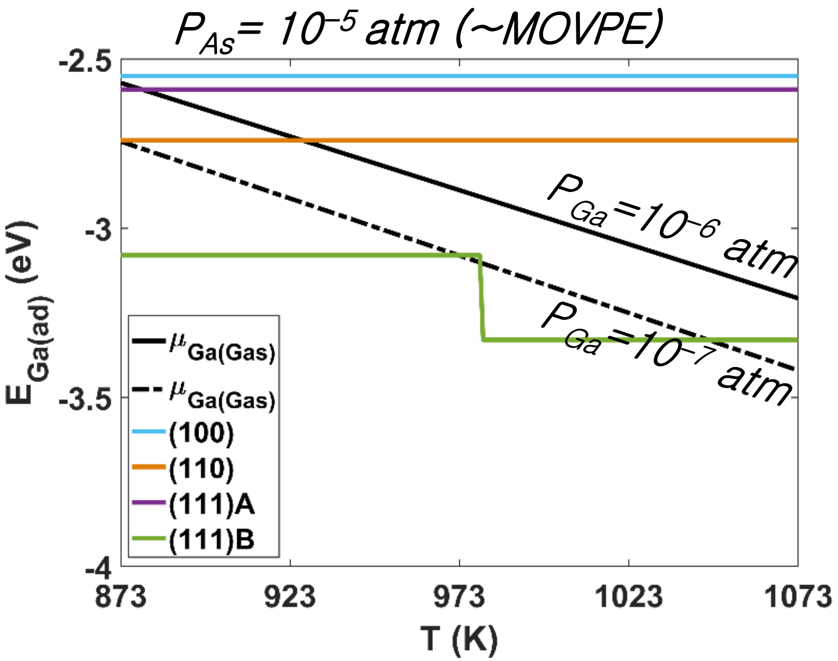


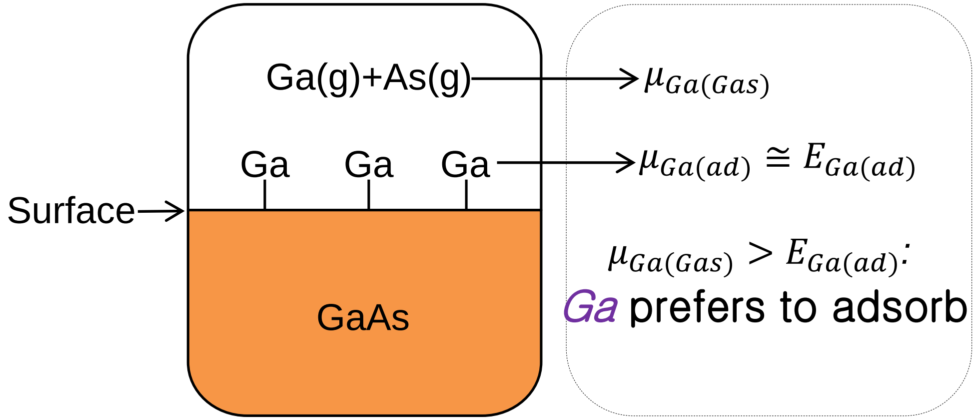
Where would sources(Ga or As) be adsorbed at given (T,P) conditions?



Adsorption condition

Ga adsorption


$P_{As}= 10^{-5}$ *atm (~MOVPE)*

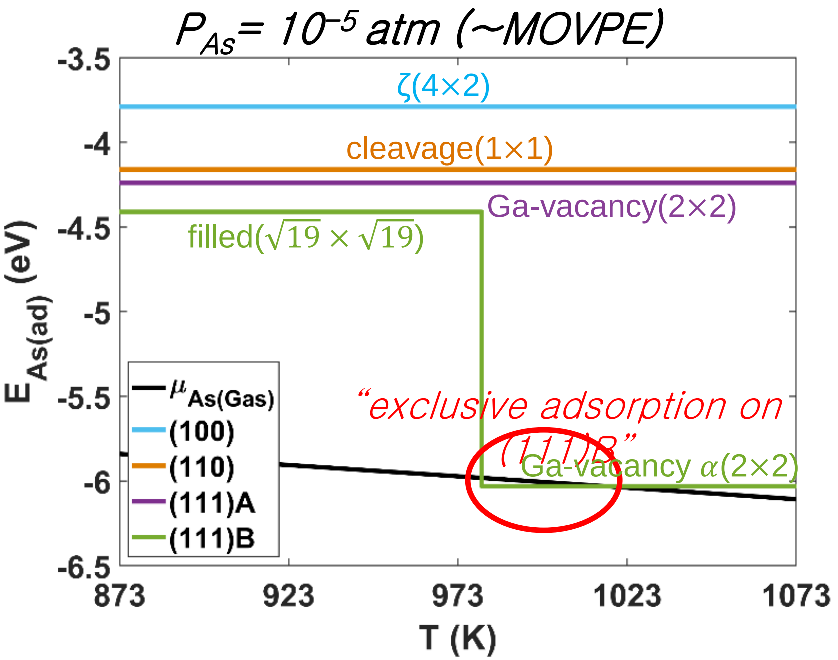


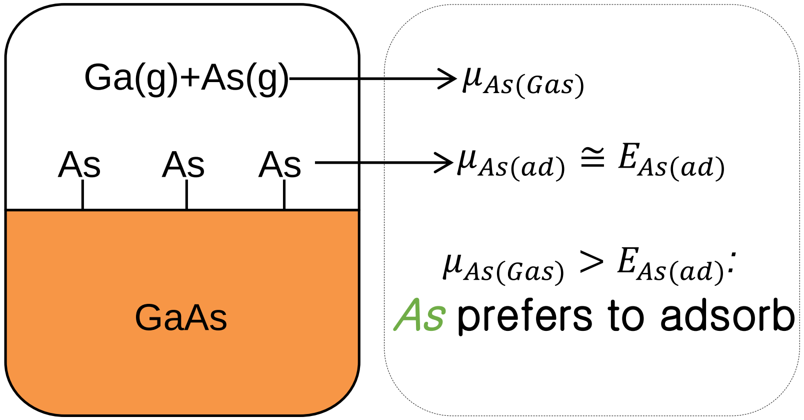
$\rightarrow \mu_{Ga(Gas)}$

$\rightarrow \mu_{Ga(ad)} \cong E_{Ga(ad)}$

$\mu_{Ga(Gas)} > E_{Ga(ad)}$:
Ga prefers to adsorb

As adsorption


$P_{As}= 10^{-5}$ *atm (~MOVPE)*

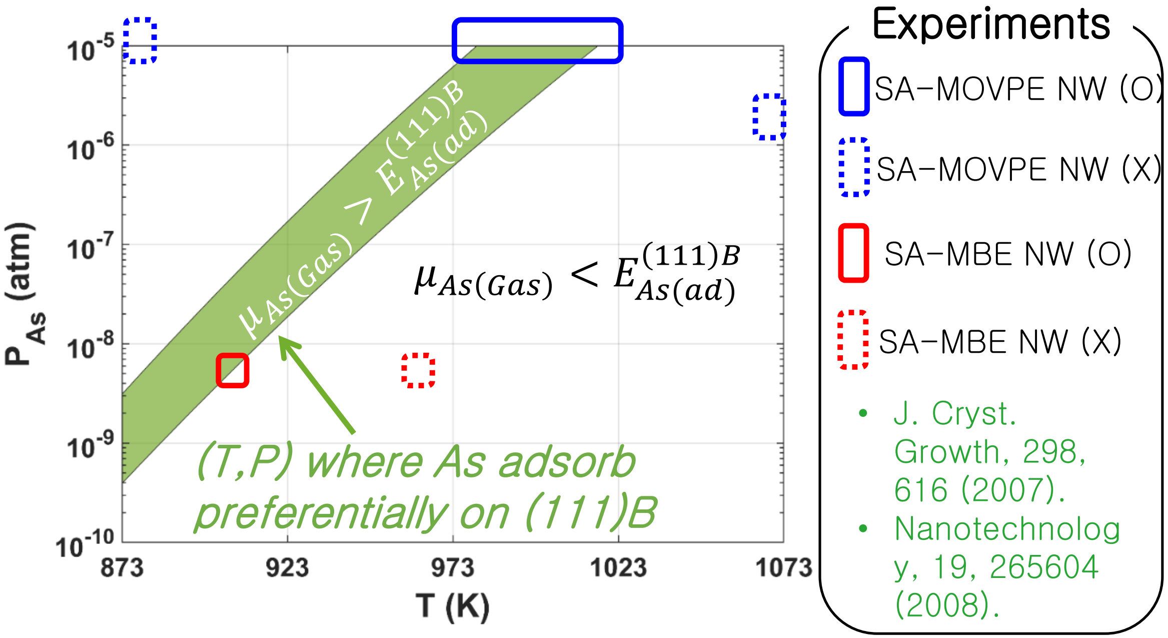


$\rightarrow \mu_{As(Gas)}$

$\rightarrow \mu_{As(ad)} \cong E_{As(ad)}$

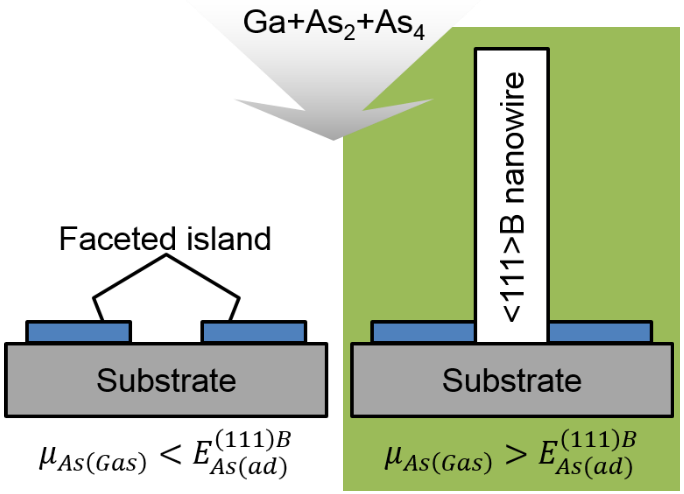
$\mu_{As(Gas)} > E_{As(ad)}$:
As prefers to adsorb

(T,P) window of the preferential adsorption of As on (111)B: <111>B NW



(T,P) where As adsorb preferentially on (111)B

- J. Cryst. Growth, 298, 616 (2007).
- Nanotechnology, 19, 265604 (2008).



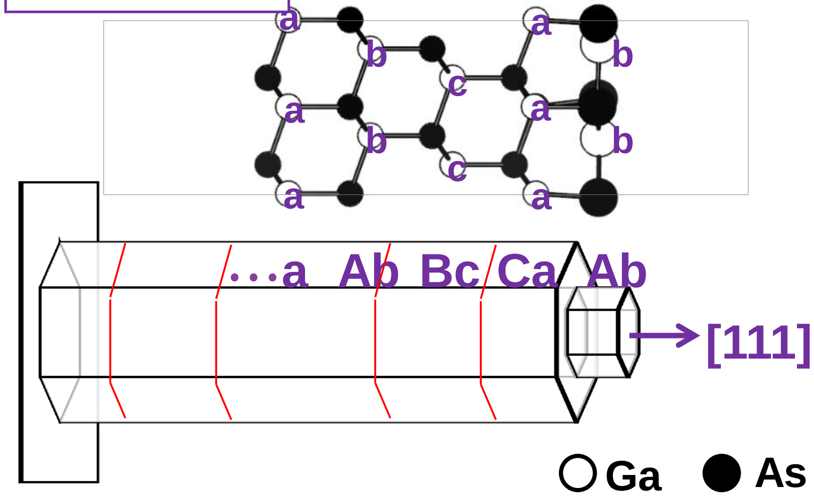
$$\dot{N}_{n|Surf}(T,P) = \boxed{\dot{C}(Surf,T,P)} \cdot \exp\left(-\frac{\Delta G^{*}_{sn}(Surf,T,P)}{kT}\right)$$

“Preferential adsorption → nucleation → (111)B NW growth”

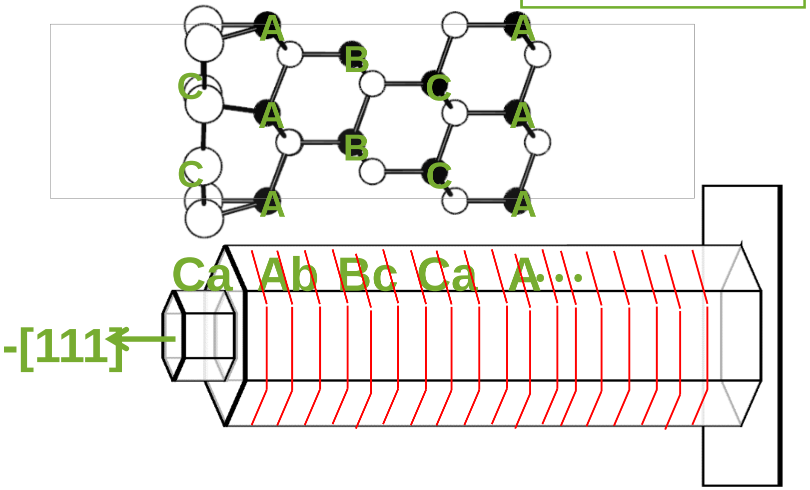
II–2. Asymmetric stacking

Asymmetric stacking: ANW vs. BNW

ANW
(111)A NW



BNW
(111)B NW



ANW growth

- VLS growth

  Adv. Mater. 27, 6096 (2015).

  J. Cryst. Growth 287, 5004 (2006).

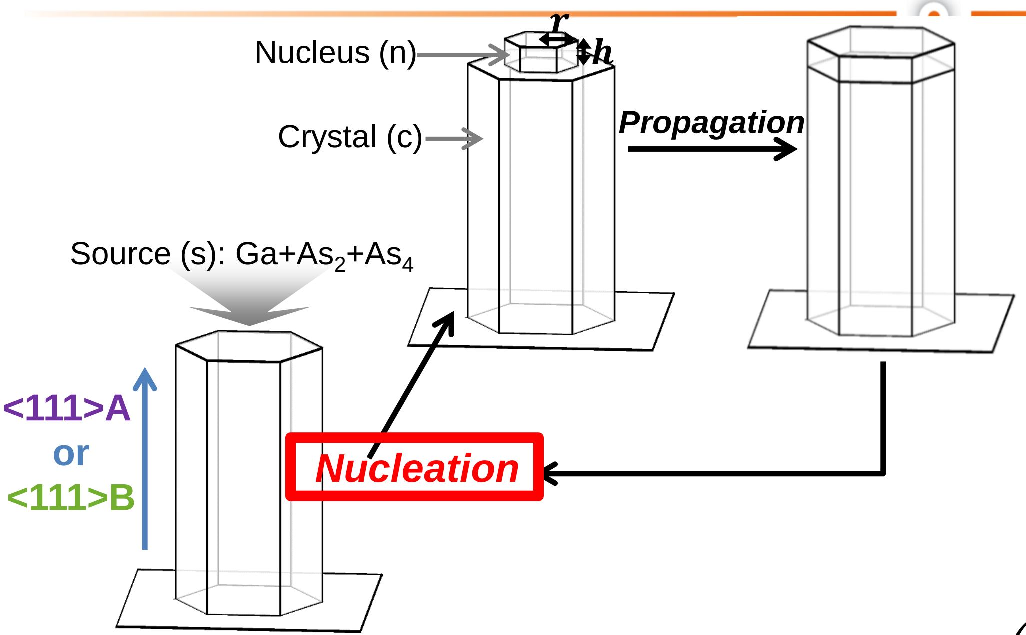
- VS growth

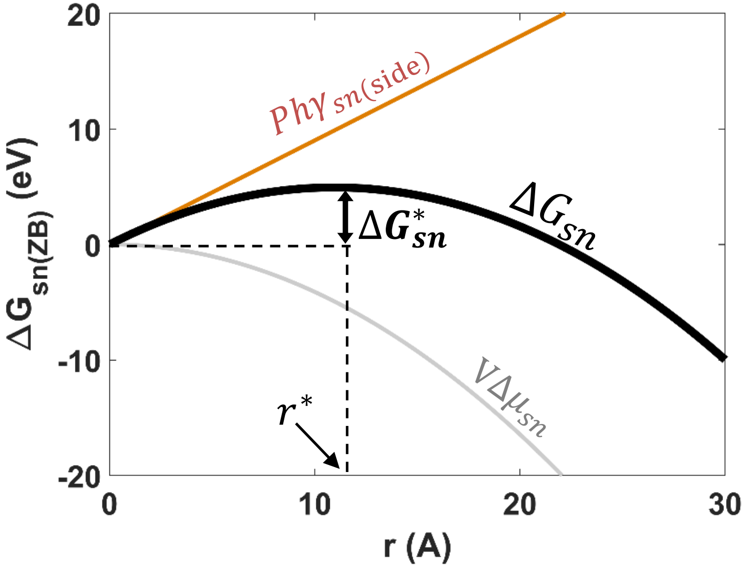
  Nanoscale 10, 17080 (2018).

Density of planar defects;

ANW << BNW

Anisotropic growth model

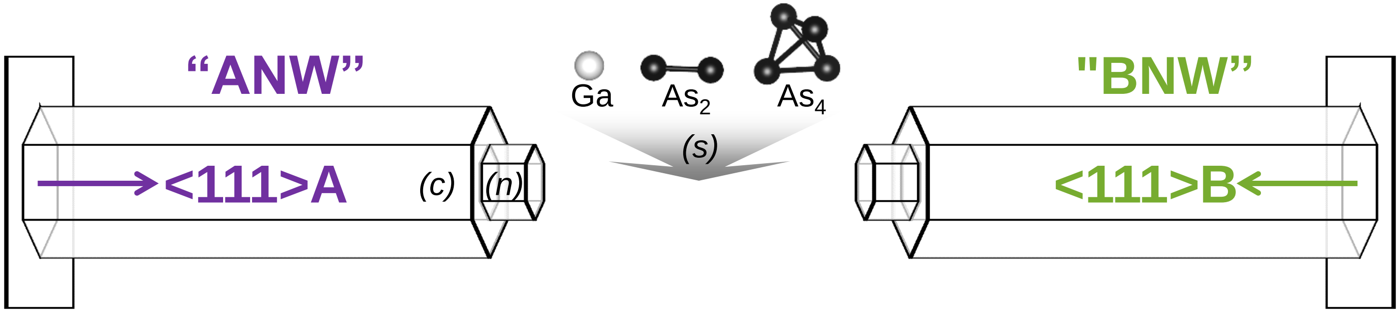




$$\dot{N}_{n|Surf}(T,P) = \boxed{\dot{C}(Surf,T,P)} \cdot \exp\left(-\frac{\boxed{\Delta G^*_{sn}(Surf,T,P)}}{kT}\right)$$

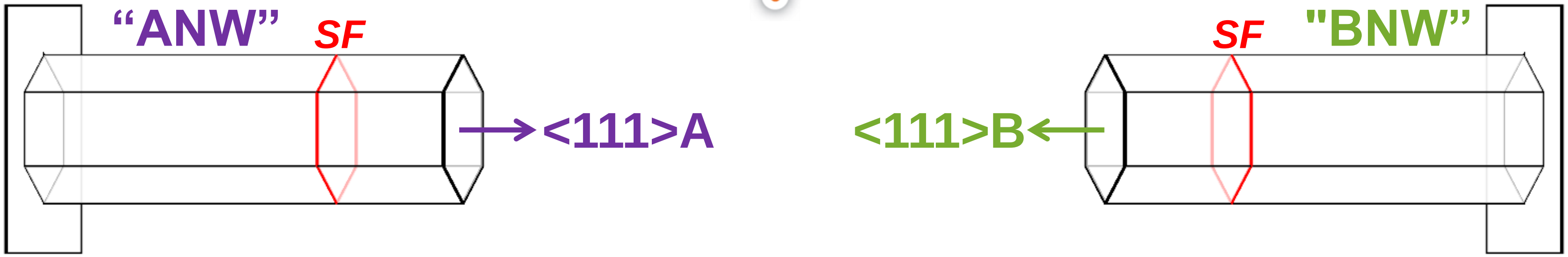
This term is the same between ANW and BNW!

$$\Delta G_{sn} = V\Delta\mu_{sn} + Ph\gamma_{sn(side)} + A\left(\gamma_{sn(top)} - \gamma_{sc(top)}\right)$$



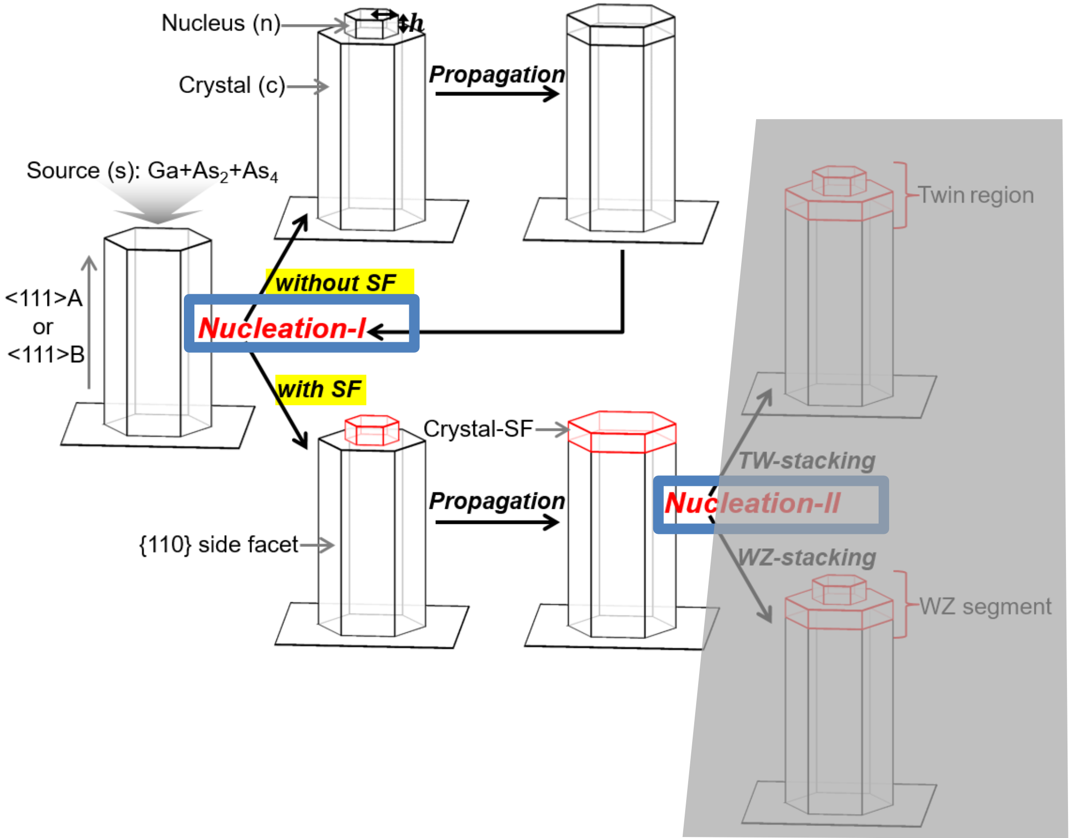
What is the key factor that determines the difference?

Energetics of fully formed NW

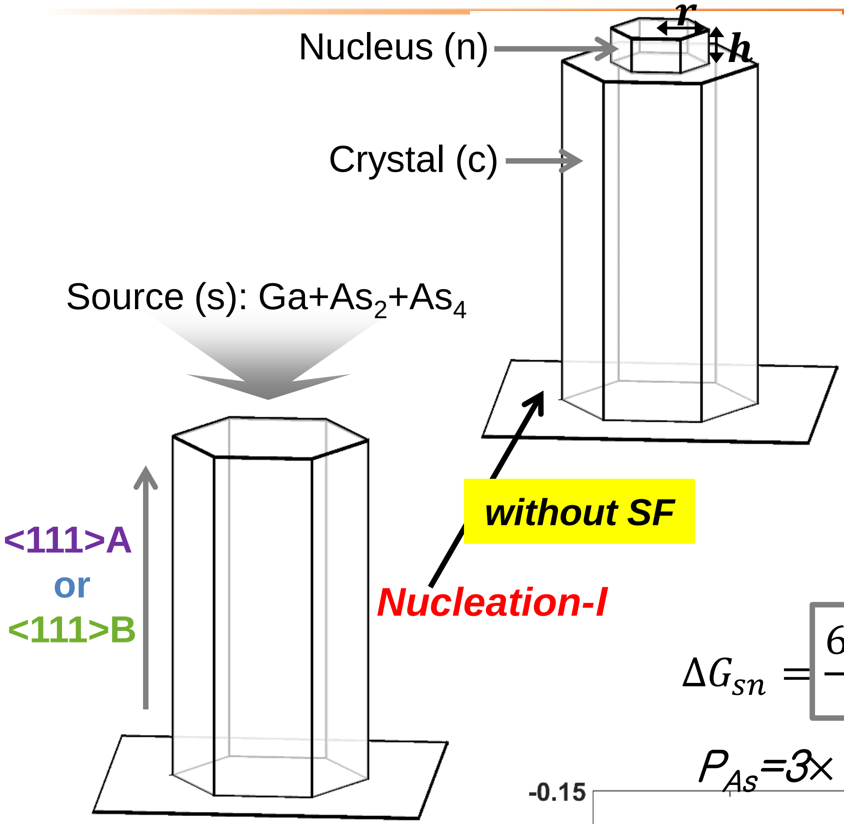


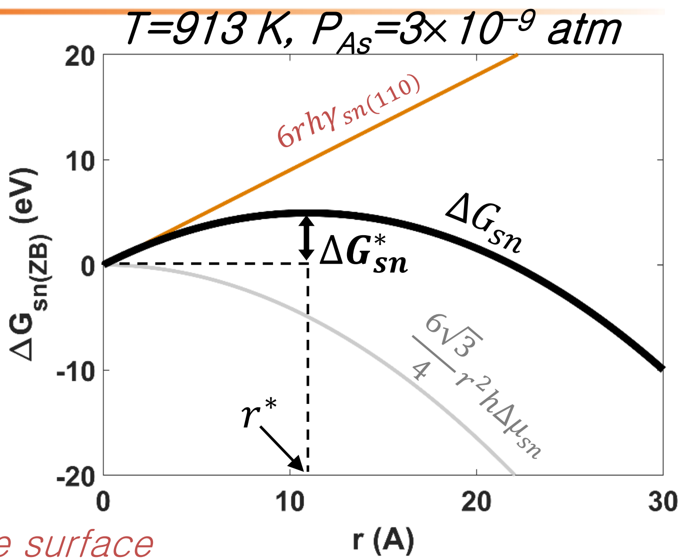
The total energy of stacking faults-embedded in ANW and BNW is the same!

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



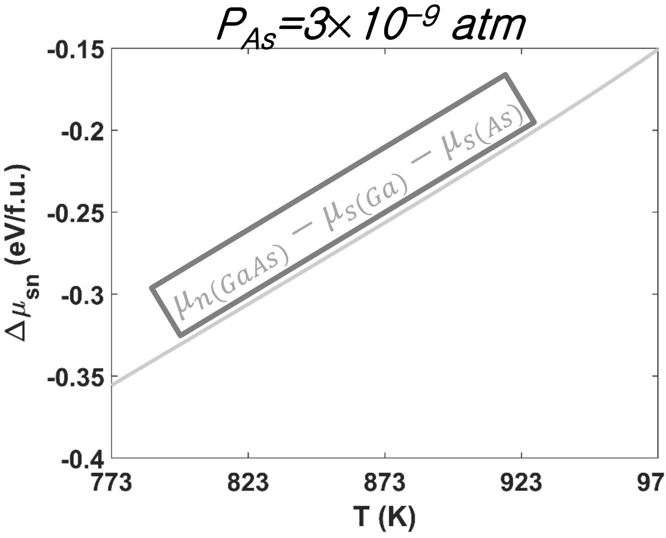
Nucleation–I without SF (ZB stacking)

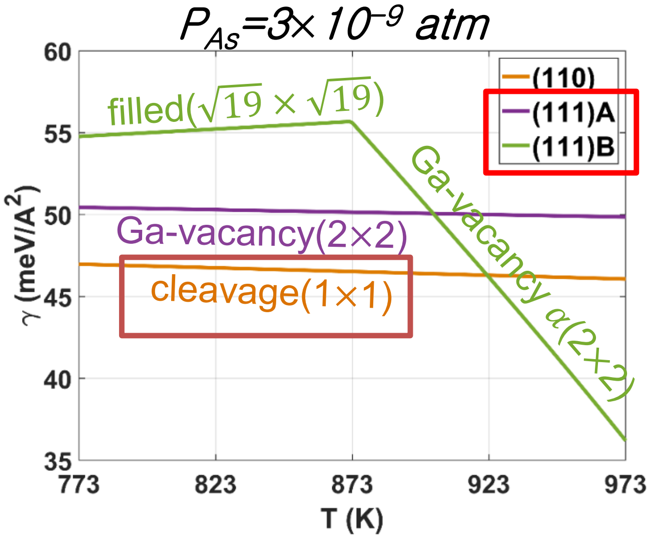




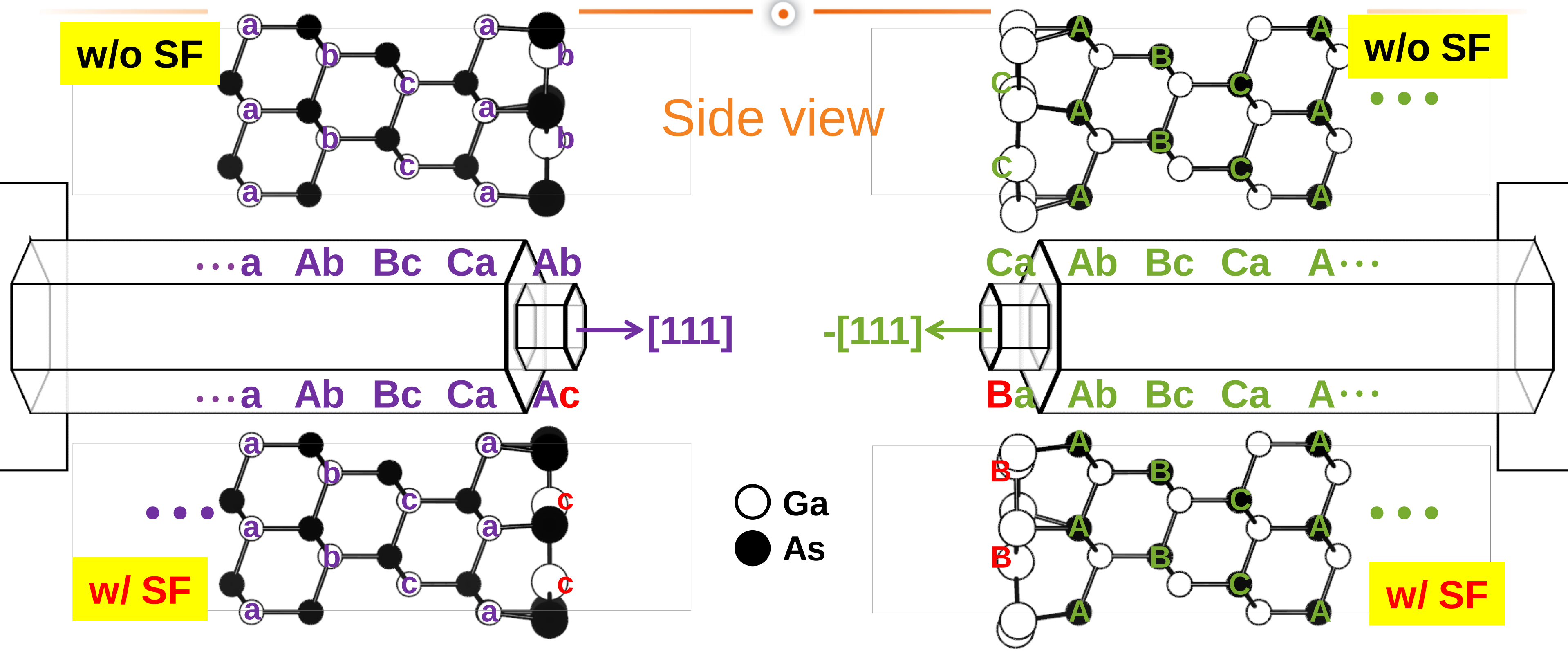
"incorporation energy" "side surface energy" "top surface energy"

$$\Delta G_{sn} = \boxed{\frac{6\sqrt{3}}{4}r^2h\Delta\mu_{sn}} + \boxed{6rh\gamma_{sn(110)}} + \boxed{\frac{6\sqrt{3}}{4}r^2(\gamma_{sn(111)} - \gamma_{sc(111)})}$$

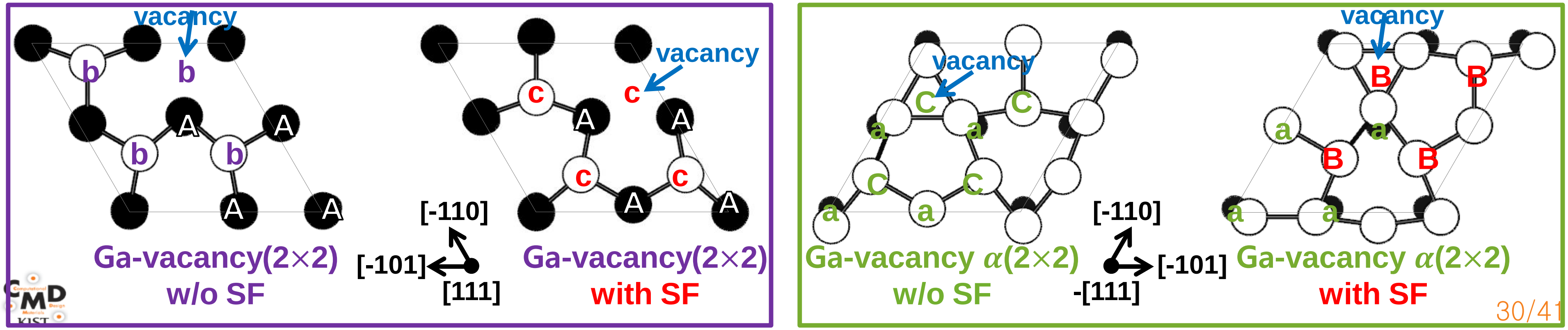




ANW & BNW with SF



Top view



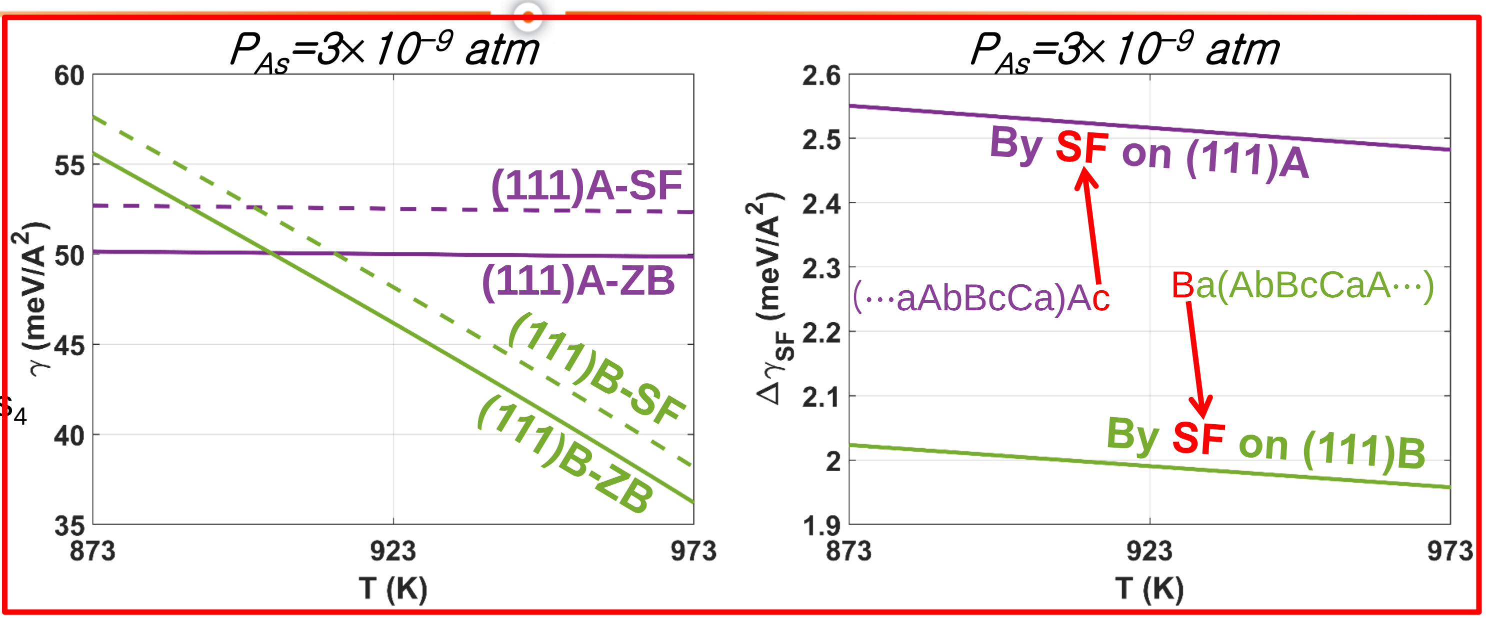
Ga-vacancy(2×2)
w/o SF

Ga-vacancy(2×2)
with SF

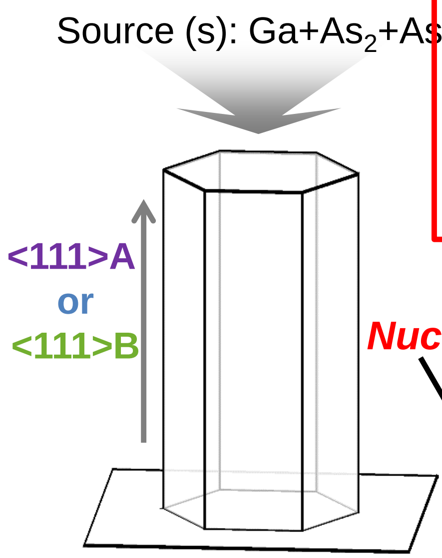
Ga-vacancy α(2×2)
w/o SF

Ga-vacancy α(2×2)
with SF

Nucleation–I with SF



$$\Delta G_{sn} = \frac{6\sqrt{3}}{4} r^2 h \Delta\mu_{sn} + 6rh\gamma_{sn(110)} + \boxed{\frac{6\sqrt{3}}{4} r^2 \left(\gamma_{sn(111)} - \gamma_{sc(111)}\right)}$$



Source (s): Ga+As$_2$+As$_4$

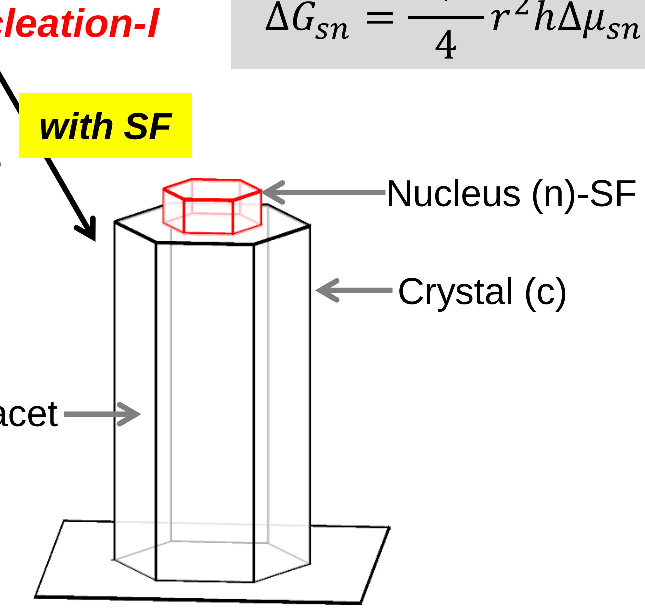
<111>A

or

<111>B

Nucleation-I

with SF



Nucleus (n)-SF

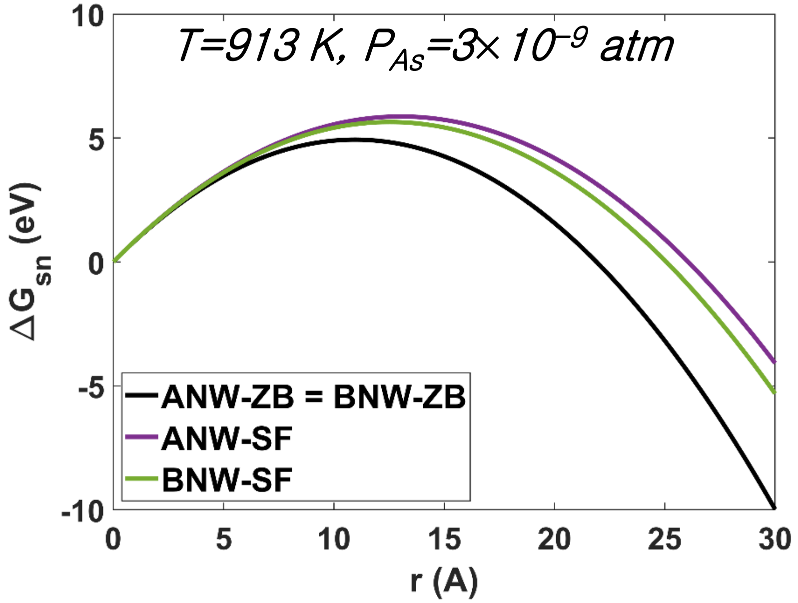
Crystal (c)

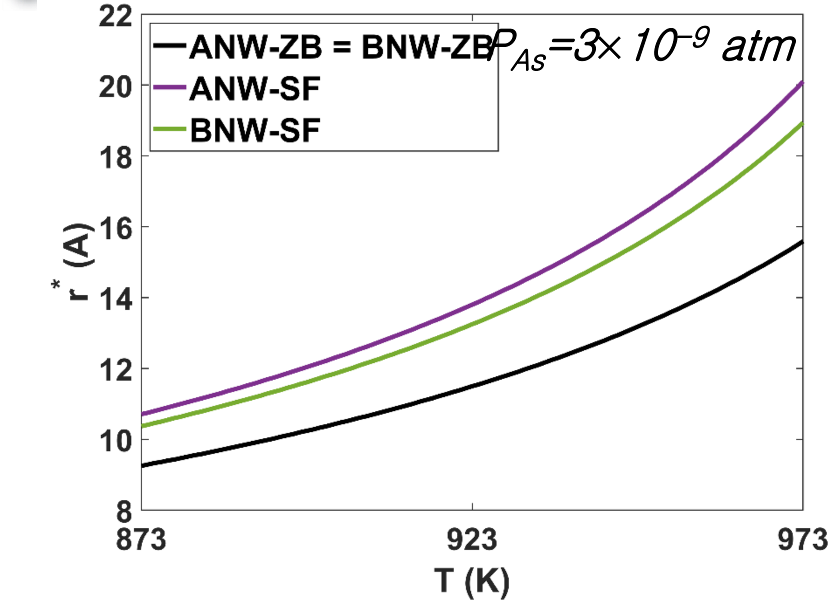
{110} side facet

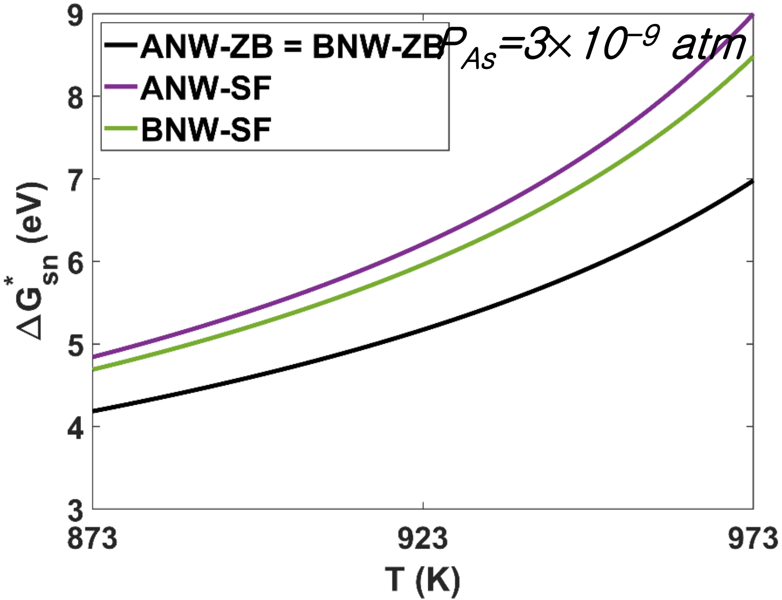
Stacking fault energy of GaAs
45±7 mJ/m^2 (=2.8 meV/Å)

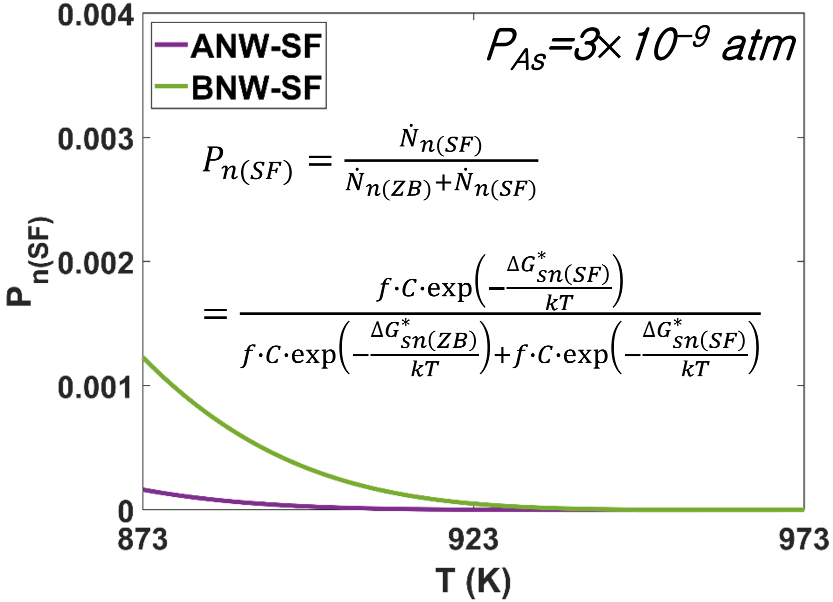
Phys. Stat. Sol. (a) 171, 99, (1999).

Nucleation–I: ZB vs. SF







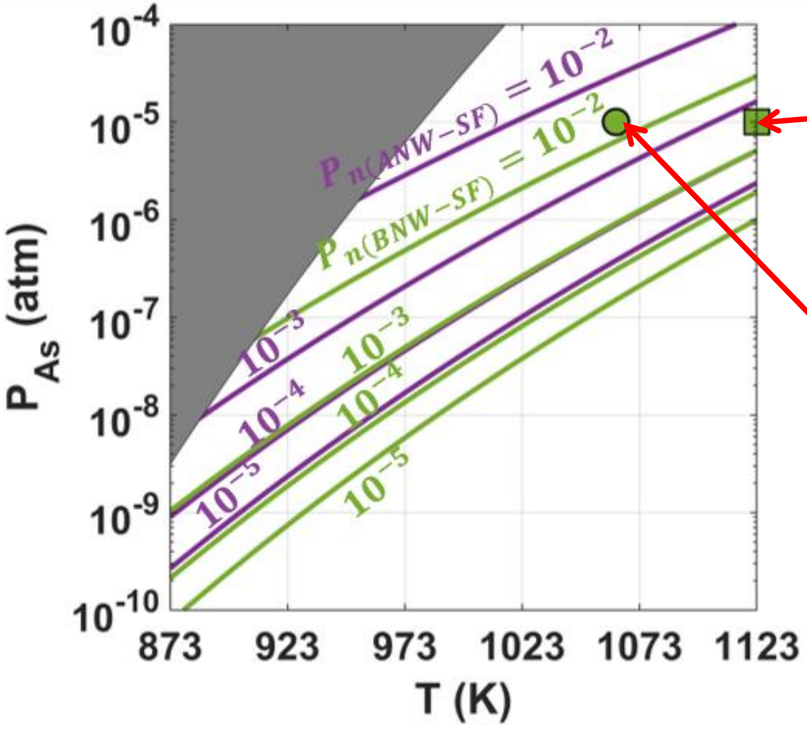


$$P_{n(SF)} = \frac{\dot{N}_{n(SF)}}{\dot{N}_{n(ZB)}+\dot{N}_{n(SF)}}$$

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

Asymmetric stacking in nucleation–I

NW calculations



BNW experiments

ACS Nano 10, 2424 (2016).

SA-MOCVD conditions (~10^{-5} atm)

"The average twin-free length = 531 Å"

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

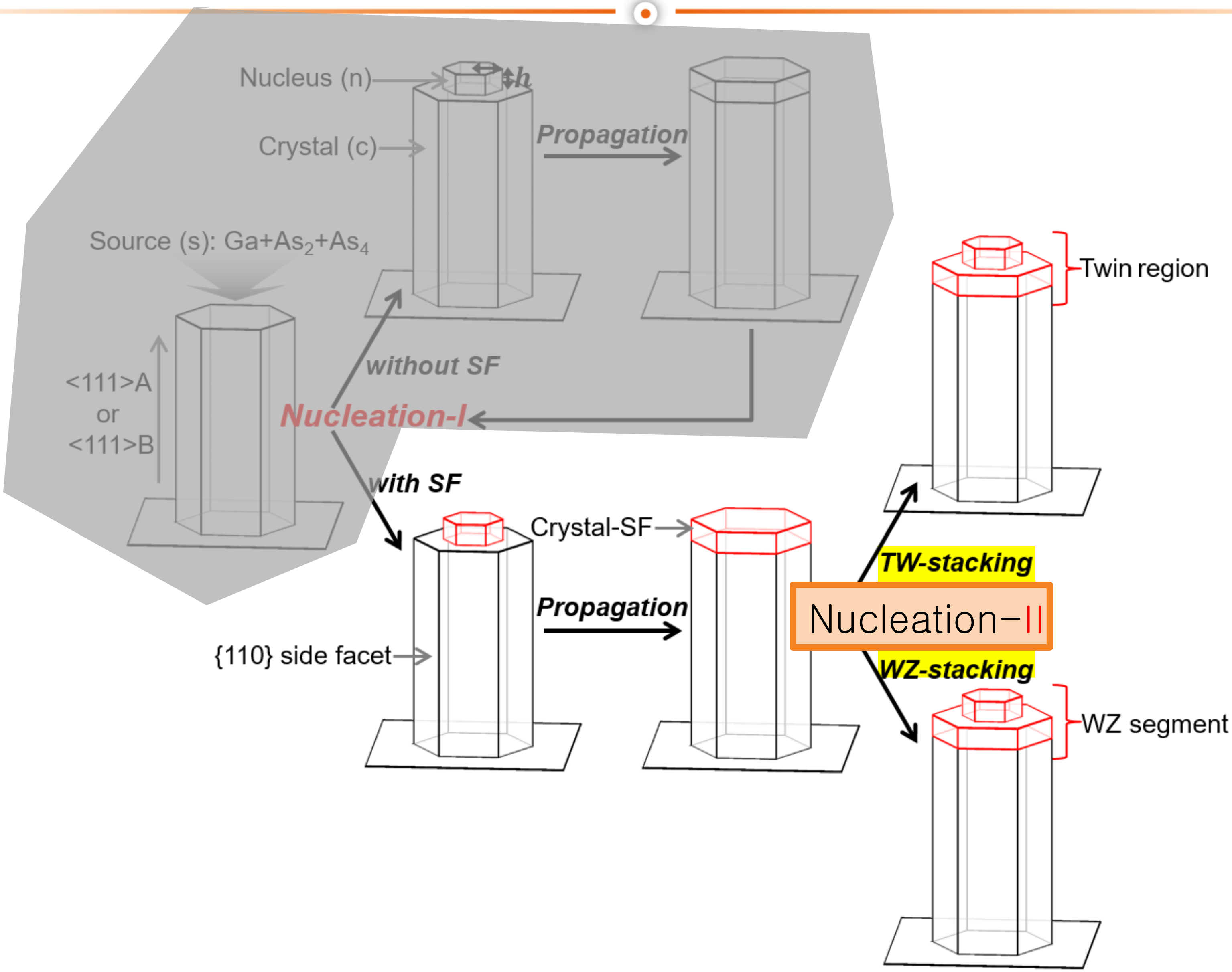
Nanotechnology 24, 475601 (2013).

SA-MOCVD conditions (~10^{-5} atm)

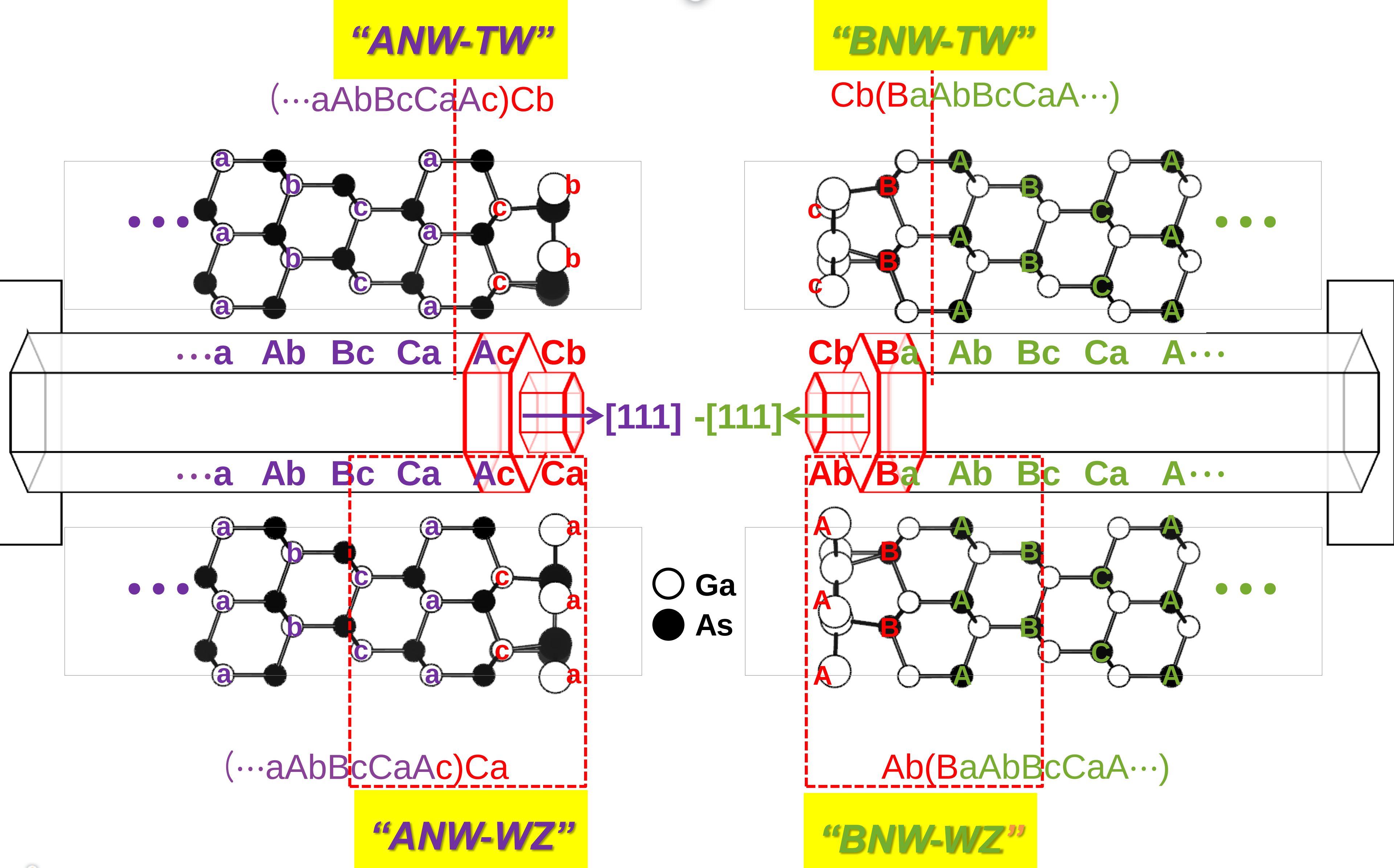
"Stacking fault density = 3%"

P_{SF} =0.03 at 1063 K

Nucleation-II: on the SF-crystal



Nucleation-II: on the SF-crystal



"ANW-TW"

(…aAbBcCaAc)Cb

"BNW-TW"

Cb(BaAbBcCaA…)

…a Ab Bc Ca Ac Cb

Cb Ba Ab Bc Ca A…

[111] **-[111]**

…a Ab Bc Ca Ac Ca

Ab Ba Ab Bc Ca A…

○ **Ga**
● **As**

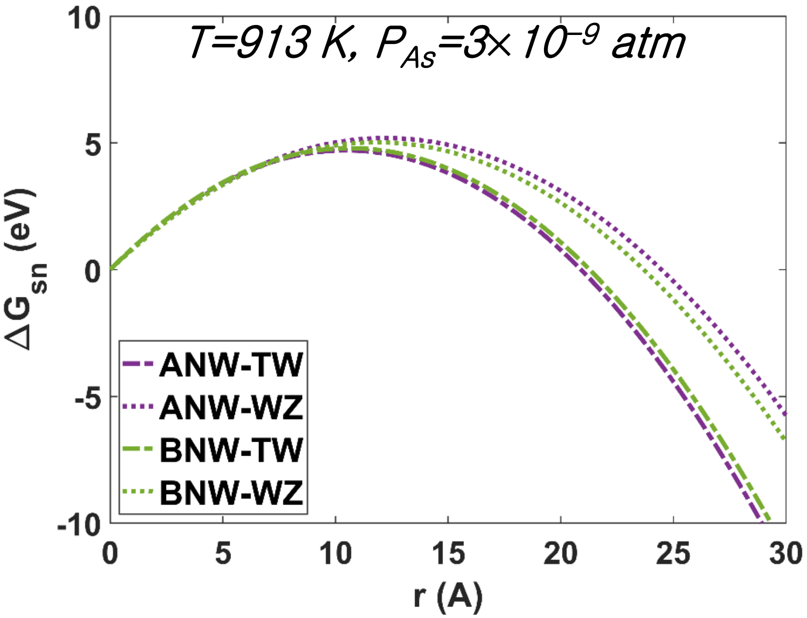
(…aAbBcCaAc)Ca

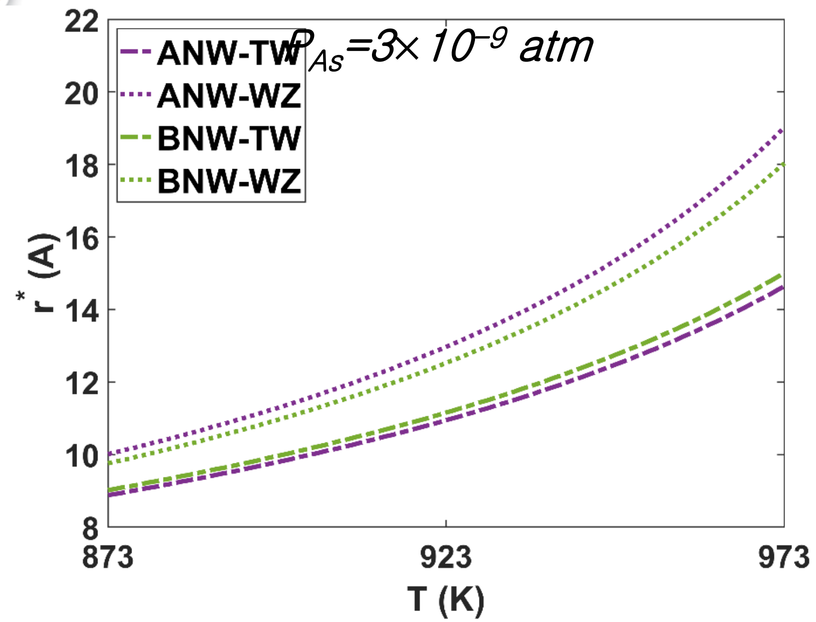
Ab(BaAbBcCaA…)

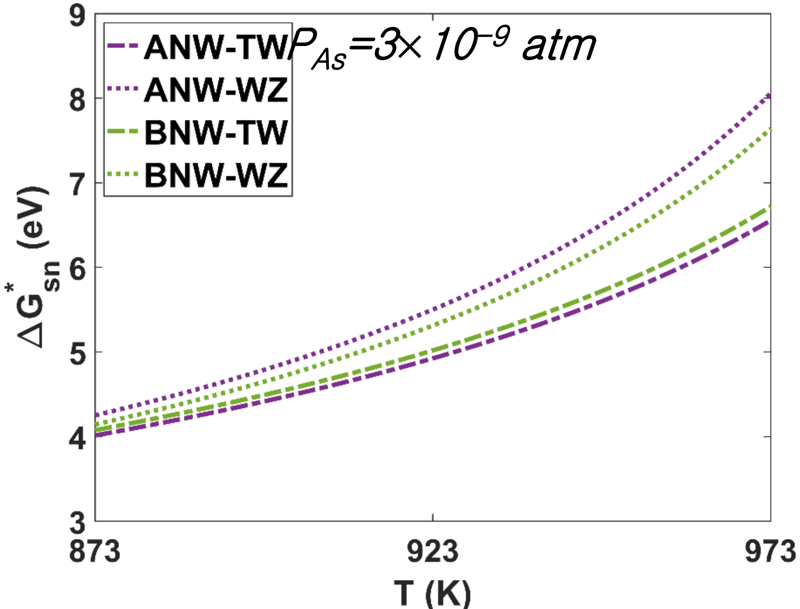
"ANW-WZ"

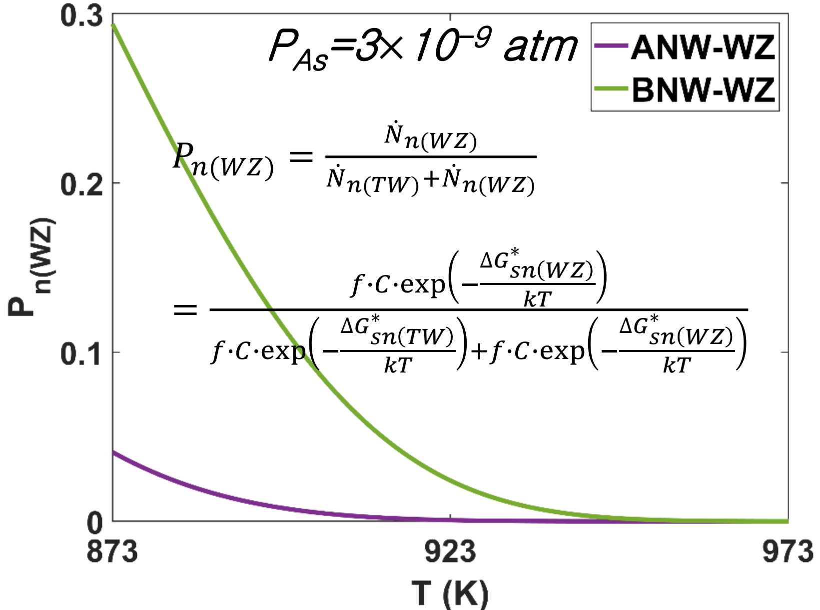
"BNW-WZ"

Nucleation–II: TW vs. WZ







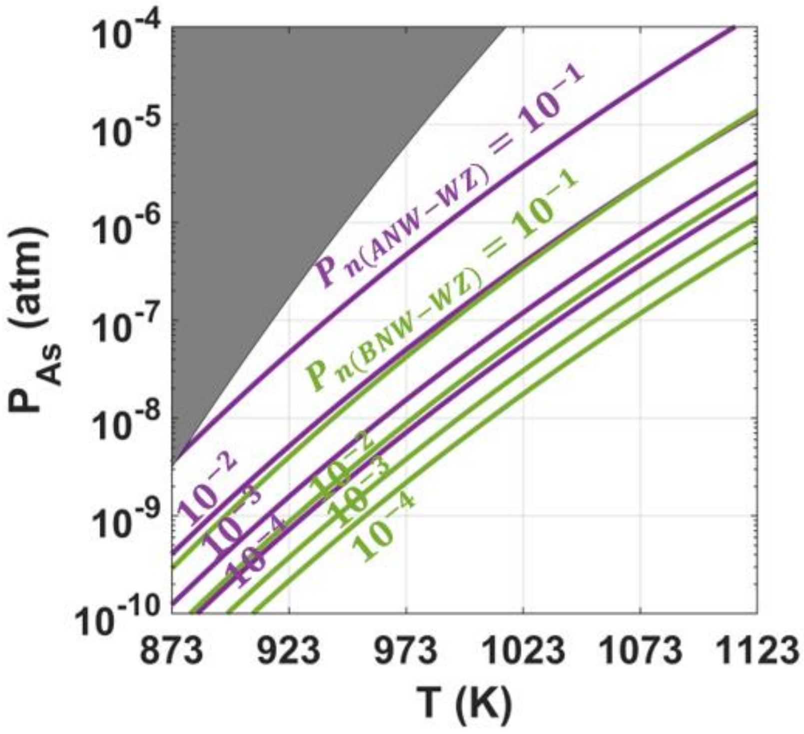


$$P_{n(WZ)} = \frac{\dot{N}_{n(WZ)}}{\dot{N}_{n(TW)}+\dot{N}_{n(WZ)}}$$

$$= \frac{f\cdot C\cdot \exp\left(-\frac{\Delta G^*_{sn(WZ)}}{kT}\right)}{f\cdot C\cdot \exp\left(-\frac{\Delta G^*_{sn(TW)}}{kT}\right)+f\cdot C\cdot \exp\left(-\frac{\Delta G^*_{sn(WZ)}}{kT}\right)}$$

Asymmetric stacking in nucleation–II

NW calculations



NW experiments

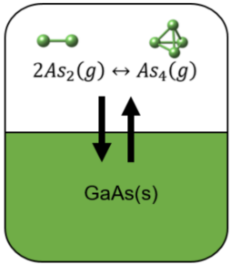
Nanoscale 10, 17080 (2018)

"Unlike in A–polar case, B–polar NWs show high density of TW and alternating sections of ZB/WZ phases."

"The exceptional crystal quality of A–polar NWs calls for discussion."

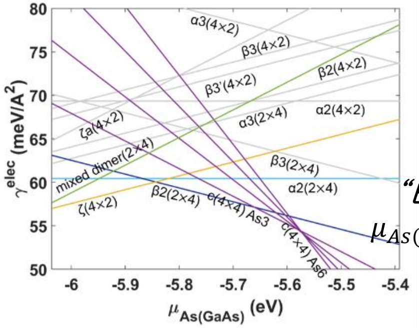
Summary

Surface reconstructions of GaAs (100)



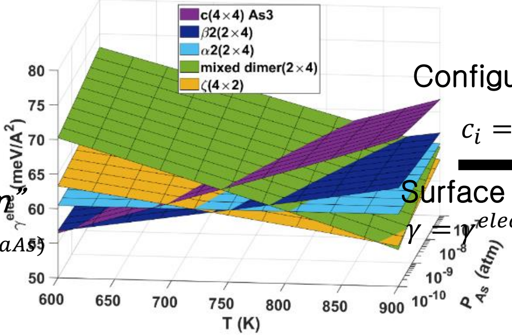
$\mu_{As(Gas)} = \mu_{As(GaAs)}$

"Equilibrium"



"Equilibrium"

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



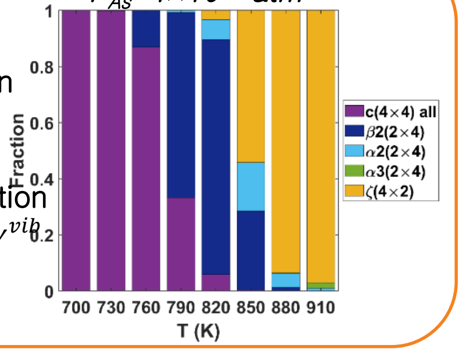
Configuration

$c_i = \frac{Z_i}{Z}$

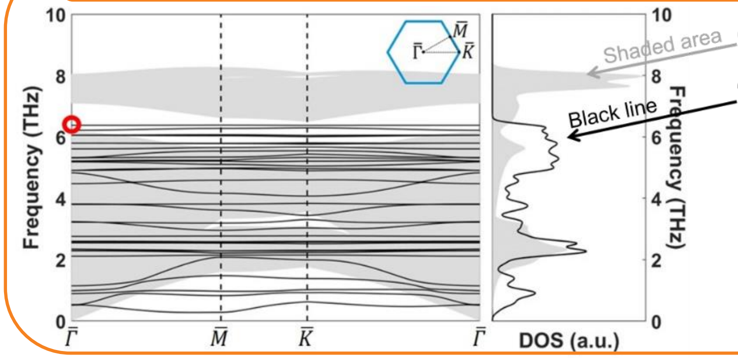
Surface vibration

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

P_{As}=4× 10^{-9} atm

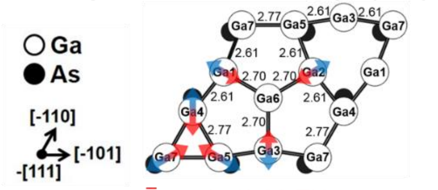


Equilibrium crystal shapes of GaAs



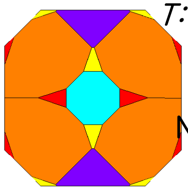
"bulk phonon of GaAs(ZB)"

"surface phonon of Ga vacancy α(2×2)"



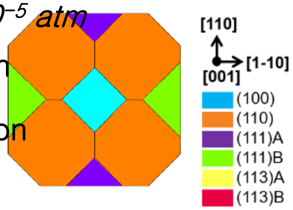
$\bar{\Gamma}$ mode (6.38 THz)

T: 1023 K, P_{As}: 10^{-5} atm



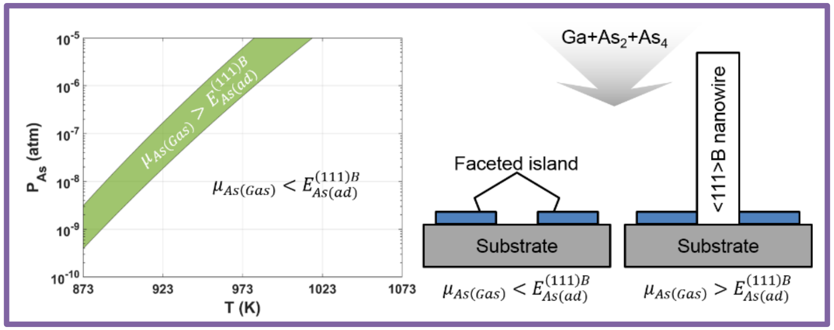
Surface vibration

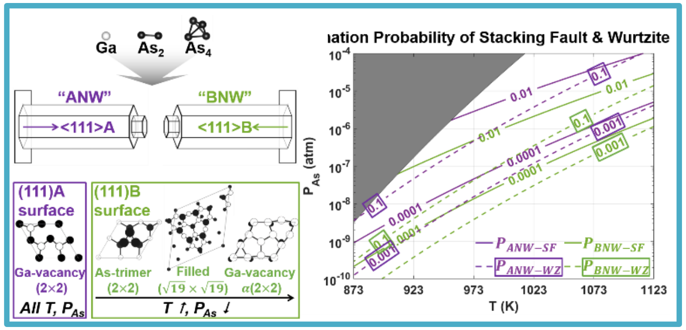
New reconstruction



Nanowire growth of GaAs

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





Journal Papers on this Talk

Papers by Dr. In Won Yeu *et al.*

Sci. Rep. 7, 10691 (2017).

-Surface energy

Sci. Rep. 9, 1127 (2019).

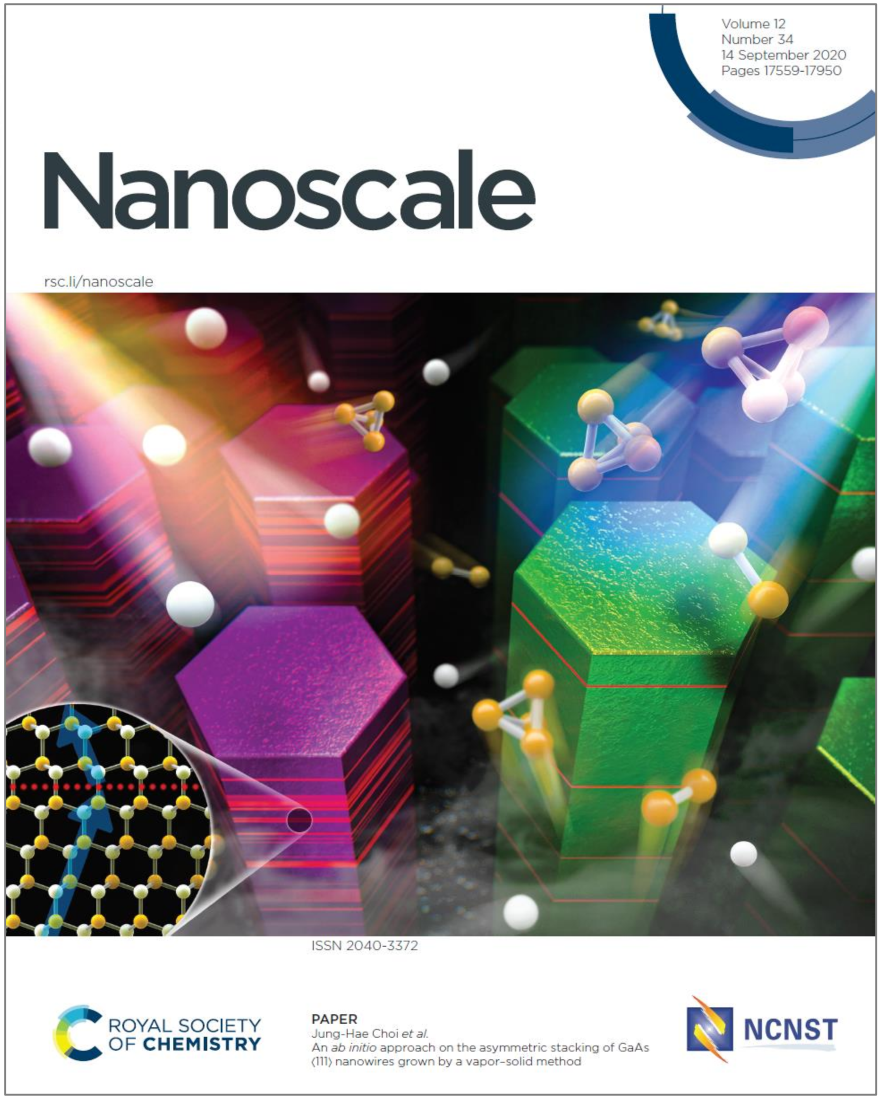
-Equilibrium crystal shape

Appl. Surf. Sci. 497, 143740 (2019).

-Nanowire growth

Nanoscale 12, 17703 (2020).

-Asymmetric stacking of nanowires



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PAPER
Jung-Hae Choi *et al.*
An *ab initio* approach on the asymmetric stacking of GaAs (111) nanowires grown by a vapor–solid method

NCNST

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- Future Semiconductor Device Technology Development Program [10048490]

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  by KIST

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- This work was partly done by

  NURION (5th Supercomputer)

  of KISTI National Supercomputing Center

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Atomistic Understanding on the Surface of GaAs by Ab Initio Thermodynamics; From Equilibrium Shape to Growth Shape

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Thank you !