The 9th International Conference on Multiscale Materials Modeling
181028~1102, OICC, Osaka, Japan

Symposium F-9
From Microstructure to Properties: Mechanisms, Microstructure, Manufacturing
Nov. 1. 2018 (Th.) 10:15~10:30

Equilibrium crystal shape of GaAs by ab-initio thermodynamics

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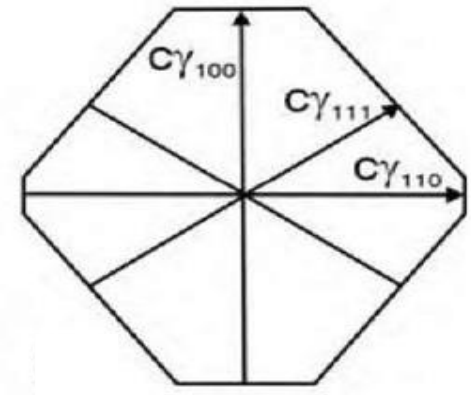
Equilibrium Crystal Shape (ECS)

Wulff construction:

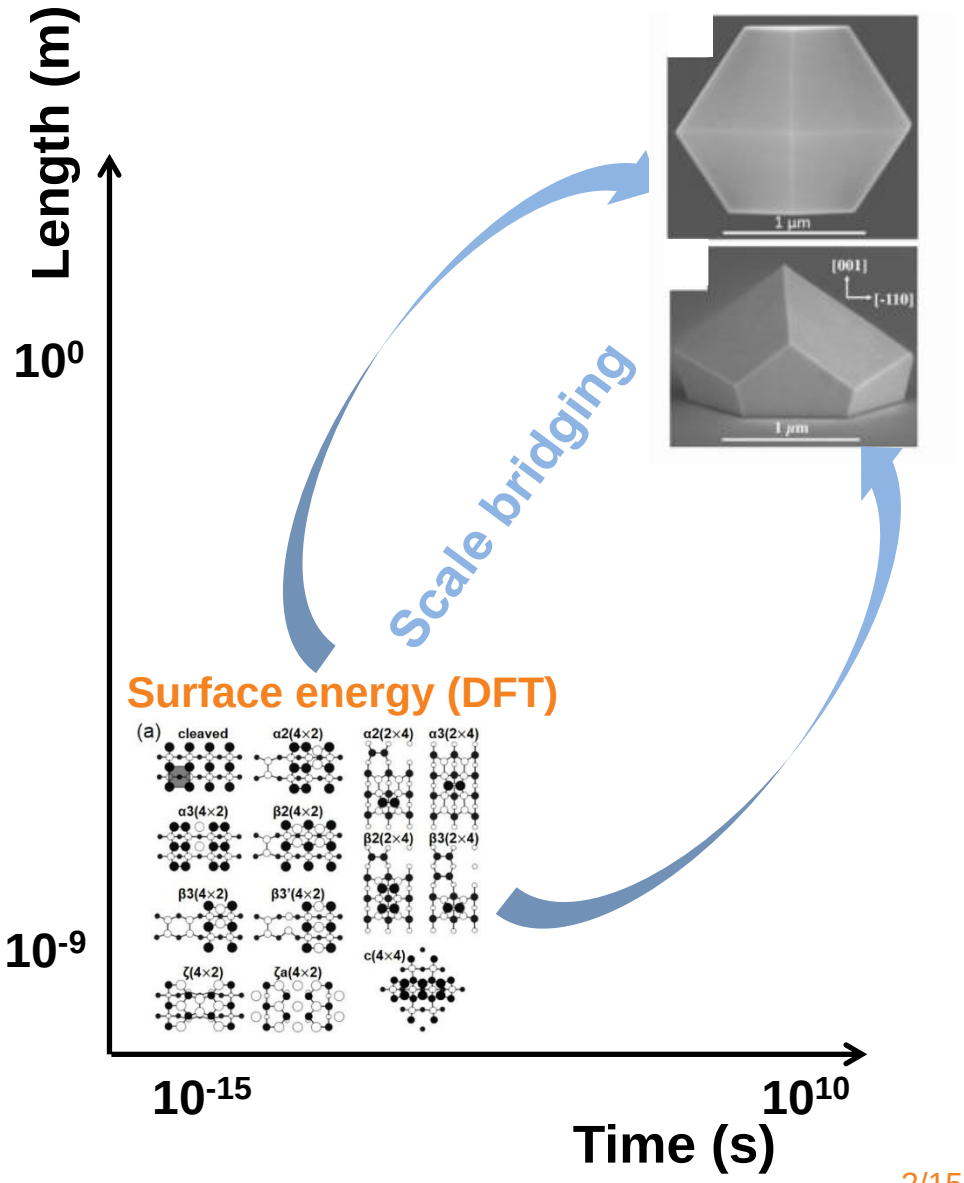
$$d^{(hkl)} \propto \gamma^{(hkl)}$$

; Minimum total surface energy



ECS(T, P)

Thermodynamics (ECS)



GaAs as a model system

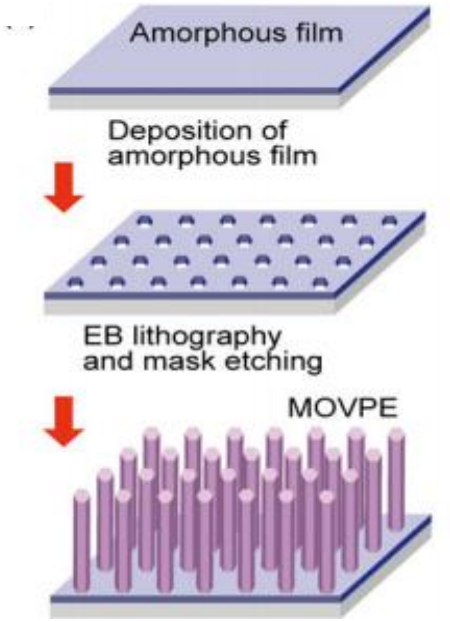
	e^- mobility (cm^2/Vsec)	h^+ mobility (cm^2/Vsec)	Lattice constant (Å)
GaAs	8,000	400	5.65
Si	1,400	500	5.43

- Good electronic properties
- Compatibility with Si

GaAs on Si

- lattice mismatch → **Dislocation**
- Difference in thermal expansion coefficients → **Crack**
- Polar material on nonpolar → **Antiphase domain**

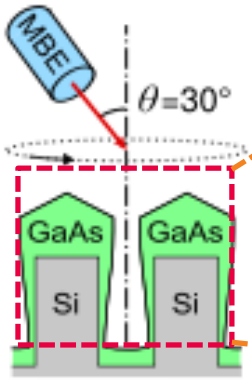
Selective Area Growth



Surface engineering of GaAs

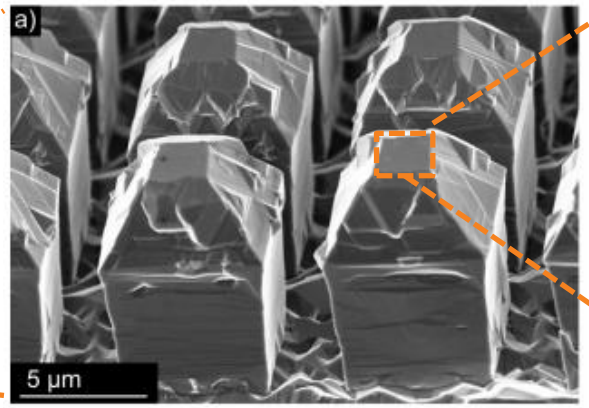
Continuum Property → **Experimental measurements** → **Atomic Structure**

Growth Variables: T & P



SEM

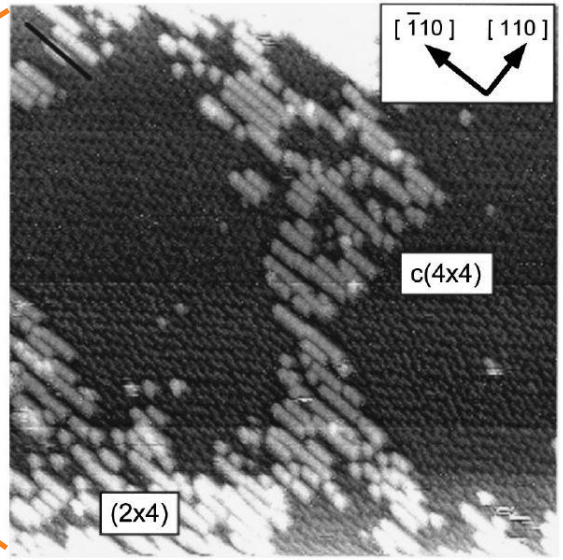
Morphology



Appl. Phys. Lett. 103, 262106 (2013)

STM

Surface reconstruction



Temperature: 768 K
Pressure: ~10^{-9} atm

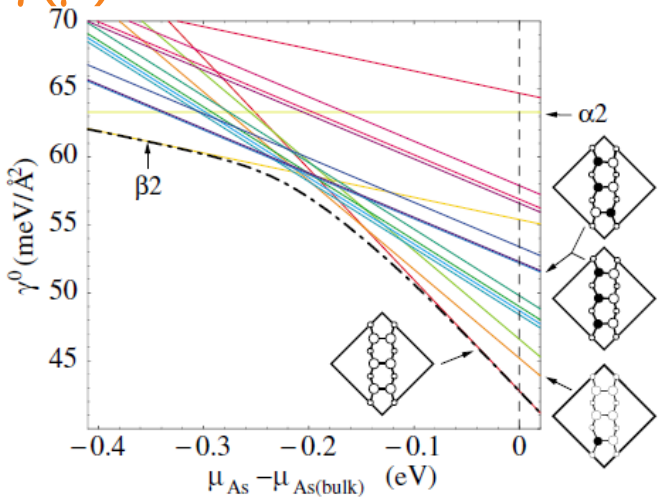
Phys. Rev. B 59, 2947 (1999)

Prediction of the Reconstruction & ECS for a given (T,P)

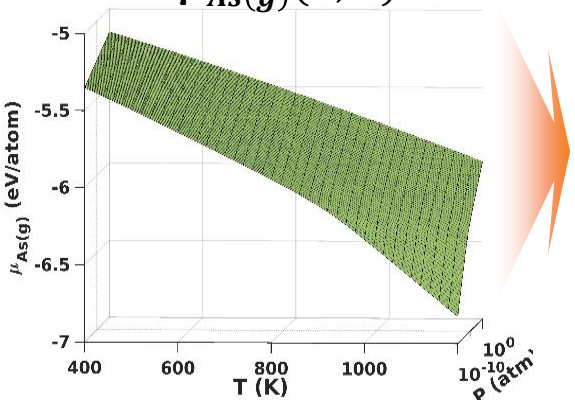
Surface energy γ(μ) to γ(T,P) by DFT

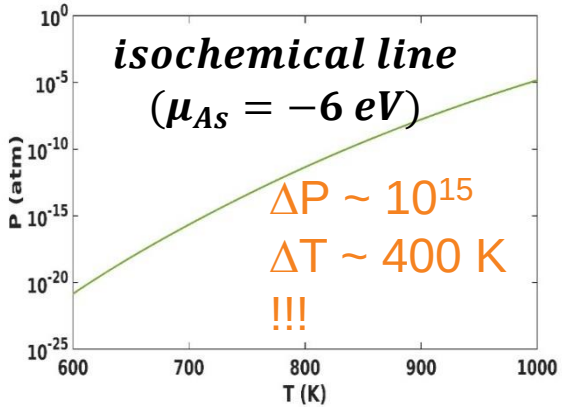
Previous DFT Study

$\gamma(\mu)$ Physical review letters **93**, 146102 (2004).



$\mu_{As(g)}(T, P)$





isochemical line
$(\mu_{As} = -6\ eV)$

ΔP ~ 10^{15}
ΔT ~ 400 K
!!!

Gap between thermodynamic variables; μ vs. (T,P)

This DFT Study

Surface energy(μ)

↓

Surface energy(T,P)

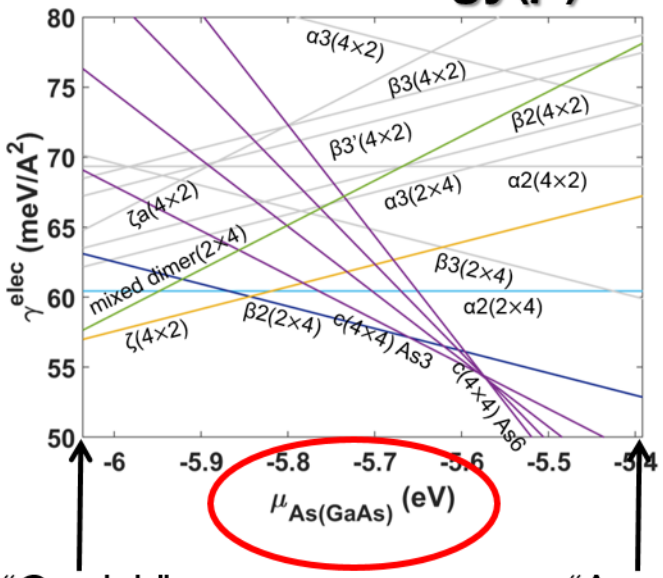
↓

Wulff shape(T,P)

Method 1: ab-initio thermodynamics

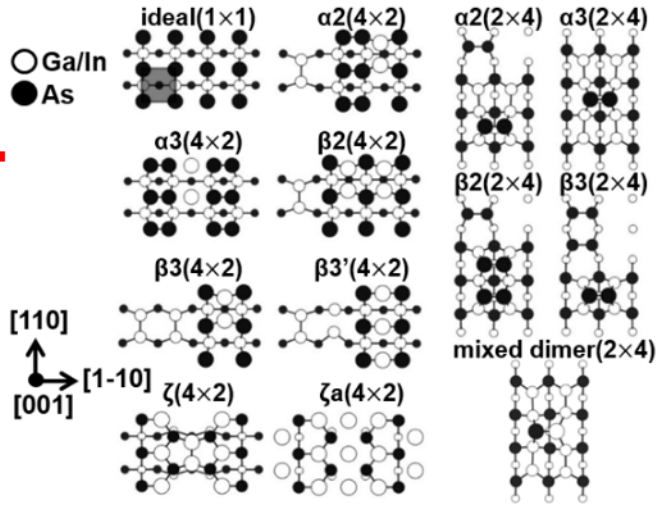
Continuum Property ← **DFT + Statistical calculation** ← **Atomic Structure**

Surface energy(μ)



DFT calculation

Surface reconstruction



"Ga-rich"
High T, Low P

"As-rich"
Low T, high P

Where is (768 K, 10^{-9} atm) ??

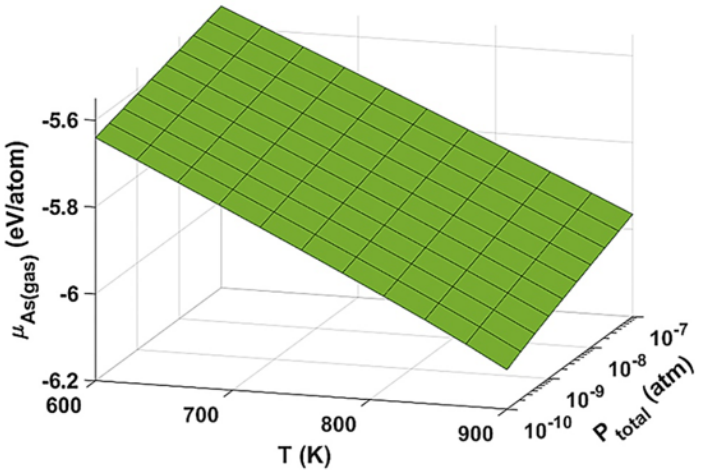
I. W. Yeu, Scientific Reports, 7, 10691 (2017)

Method 1: ab-initio thermodynamics

Continuum Property ← **DFT + Statistical calculation** ← **Atomic Structure**

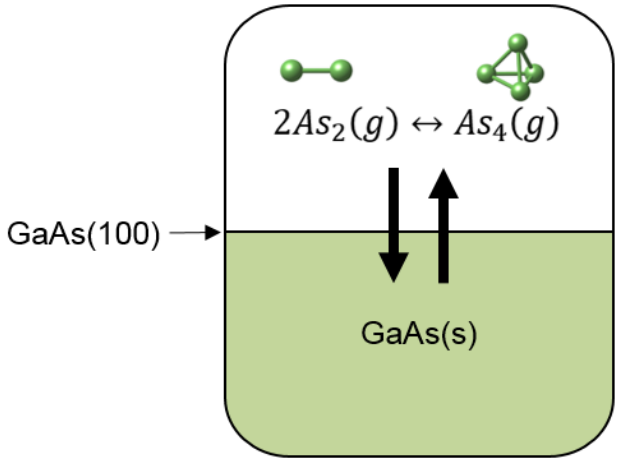
DFT calculation

$$\mu_{i(g)}(\mathrm{T},P) = \mu^{o}_{i(gas)}(T,P^{o}) + k_B T \ln \frac{P_{i(gas)}}{P^{o}}$$



Equilibrium

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

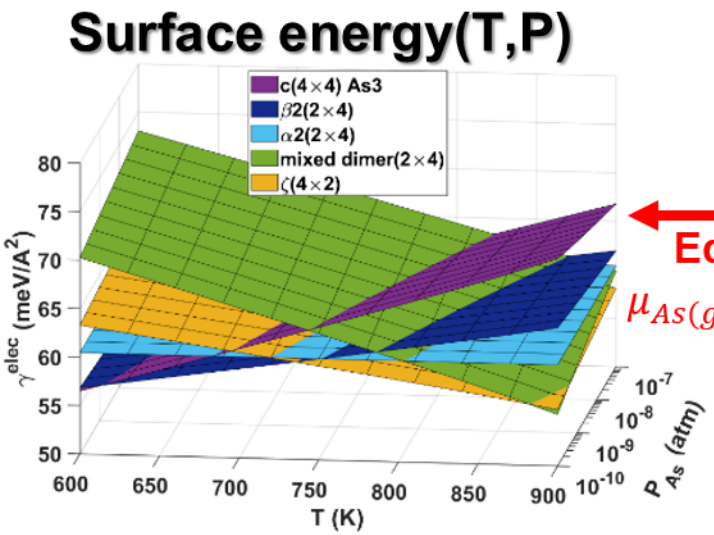


x-axis: $\mu_{As(GaAs)} = \mu_{As(g)}(T,P)$!!

I. W. Yeu, Scientific Reports, 7, 10691 (2017)

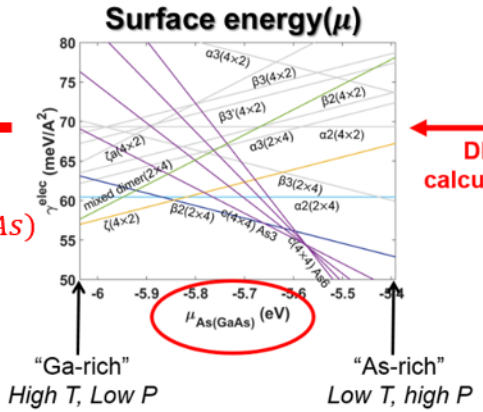
Method 1: ab-initio thermodynamics

Continuum Property ← **DFT + Statistical calculation** ← **Atomic Structure**

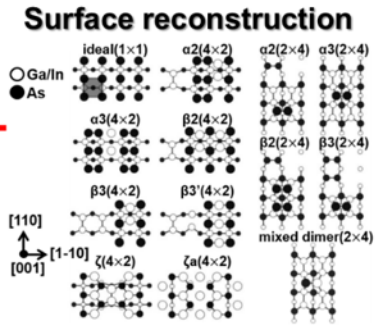


Equilibrium

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

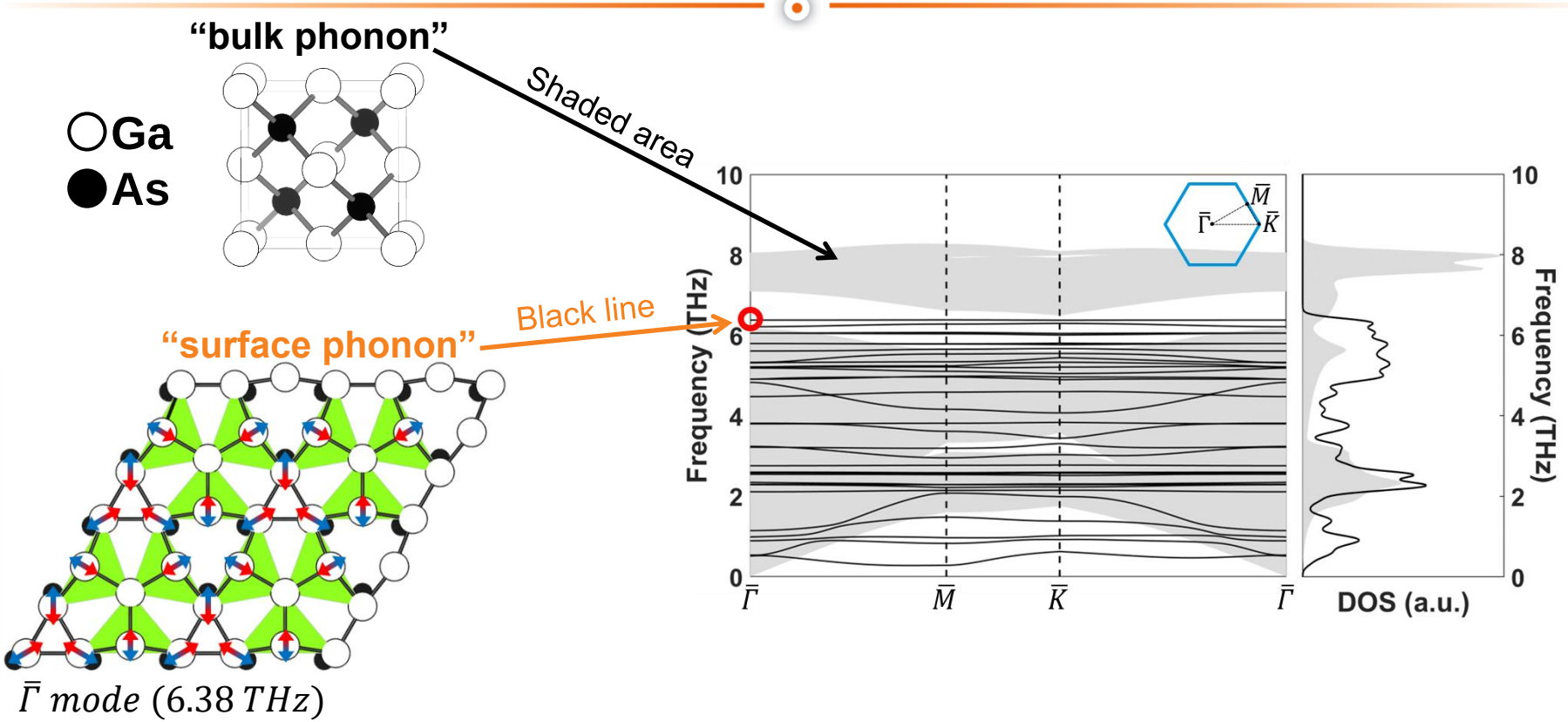


DFT calculation



Where is (768 K, 10^{-9} atm) ??

Method 2: effects of surface vibration



Surface vibration

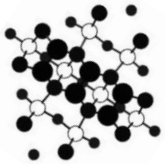
- Frequency of surface phonon is usually lower than that of bulk phonon.
- Each reconstruction has different surface phonon frequency due to different bonding geometry and stoichiometry.

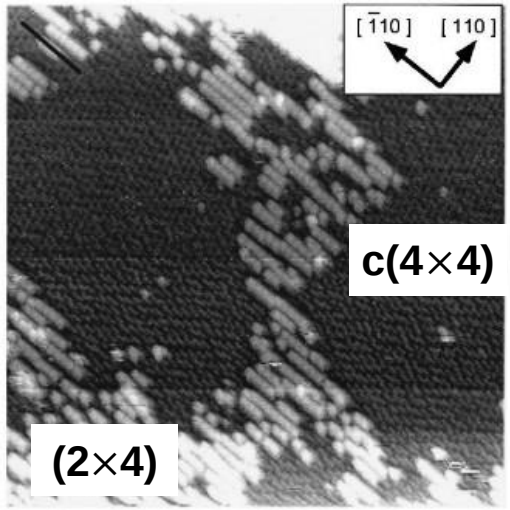
Method 3: configurational effects

~760 K

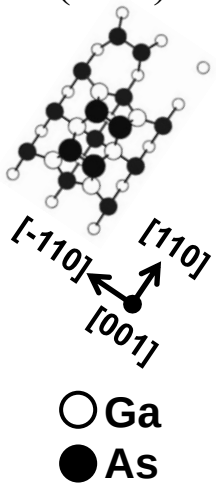
c(4×4) → mixture of c(4×4) with (2×4) → (2×4) → mixture of (2×4) with (4×2) → (4×2)

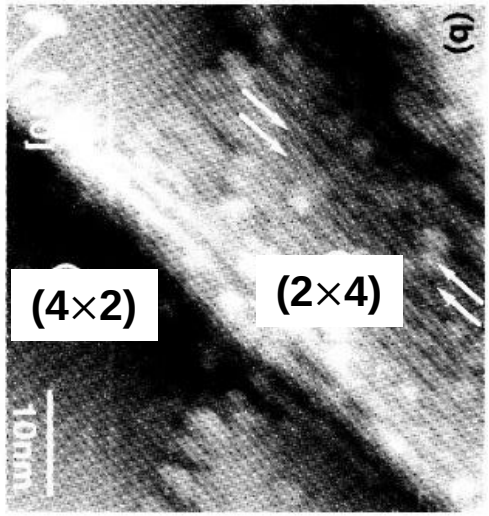
~850 K



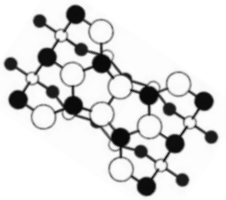


Phys. Rev. B 59, 2947 (1999)





Phys. Rev. B 51, 9836 (1995)



Mixed phase(coexistence)

- Real situation is not the ground state.
- Configurational entropy overcomes small energy difference at non-0 K.

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

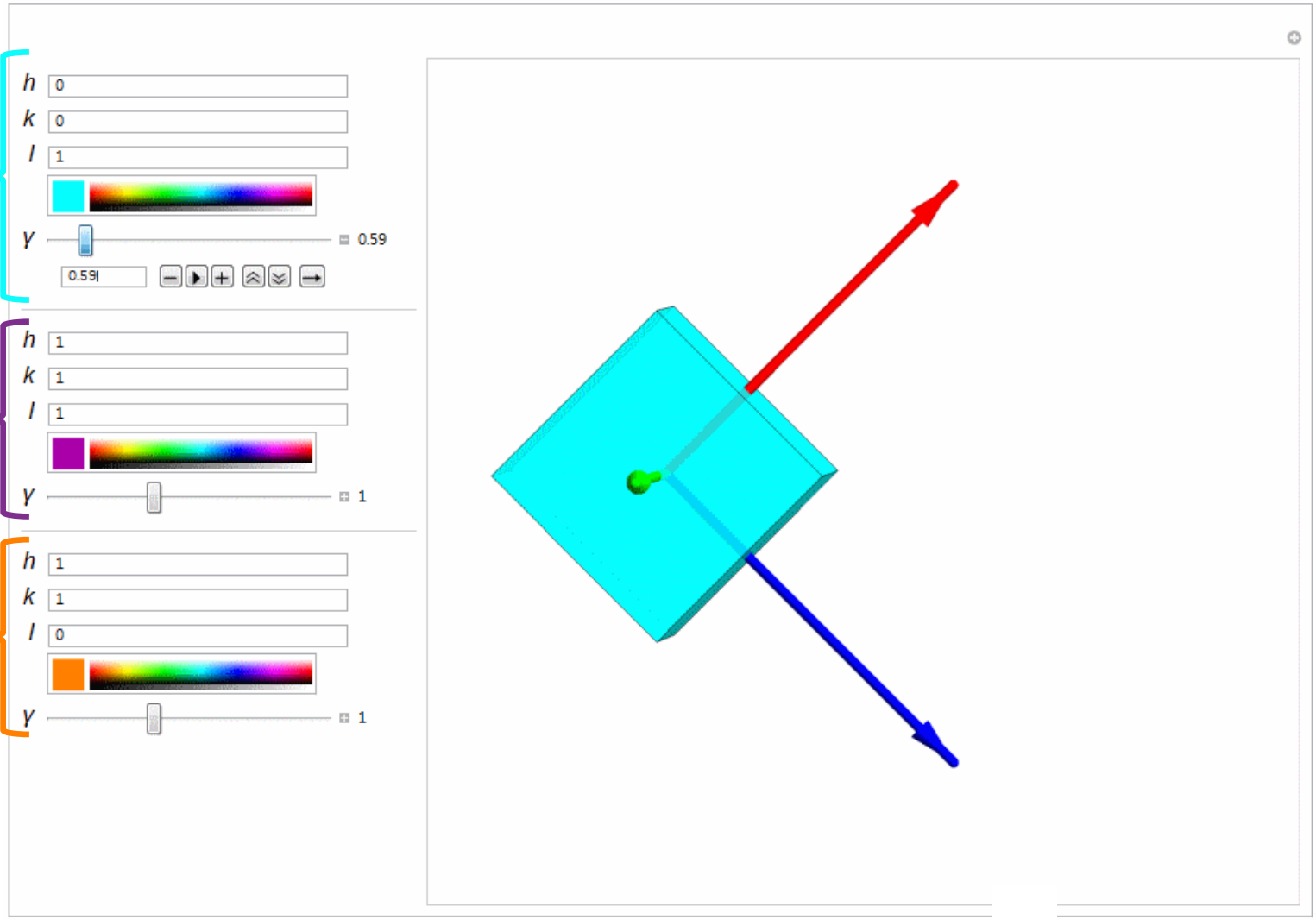
$$Z = \sum_i Z_i = \sum_i g_i \exp(-\frac{\gamma_i(T,P)A}{k_B T})$$

Method 4: Wulff construction

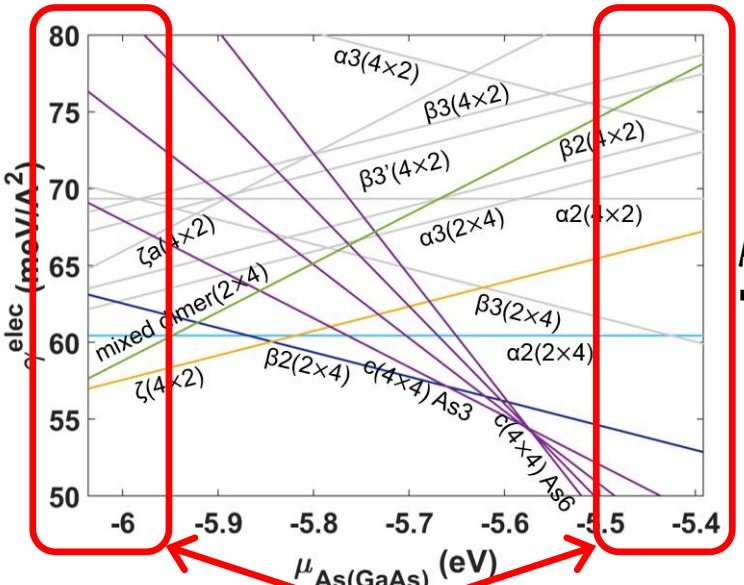
increasing $\gamma^{(100)}$

$\gamma^{(111)}$ is fixed

$\gamma^{(110)}$ is fixed

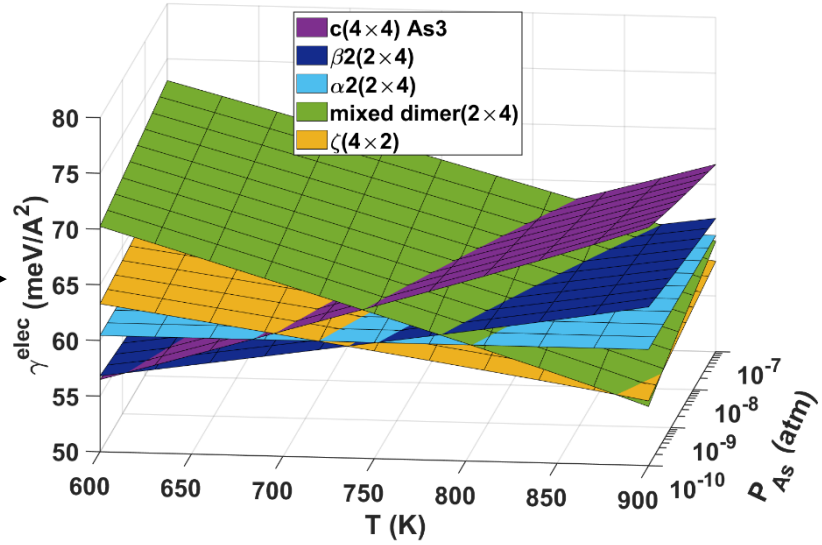


GaAs(100) phase diagram (T, P_{As})

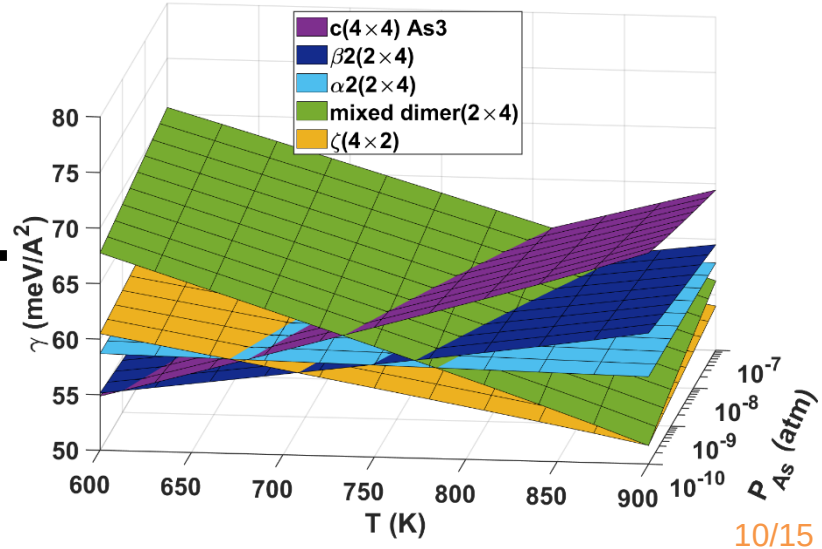


"Equilibrium"

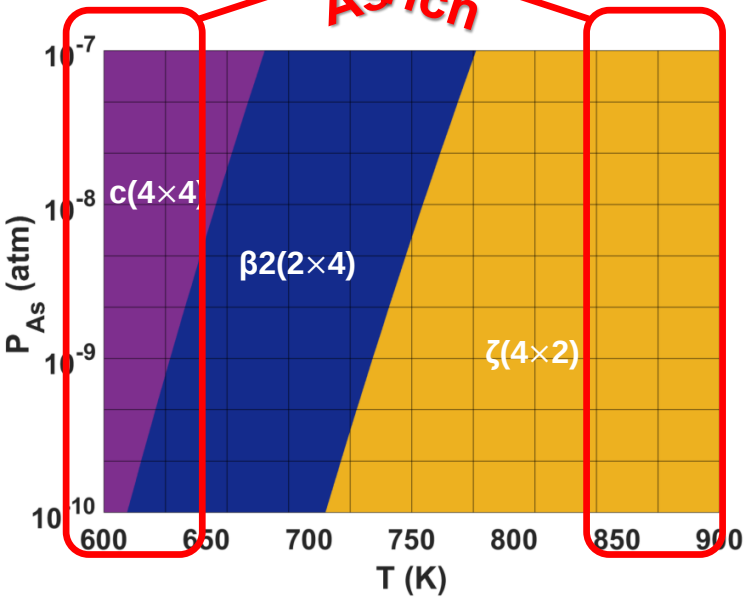
$\mu_{As(g)} = \mu_{As(GaAs)}$



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



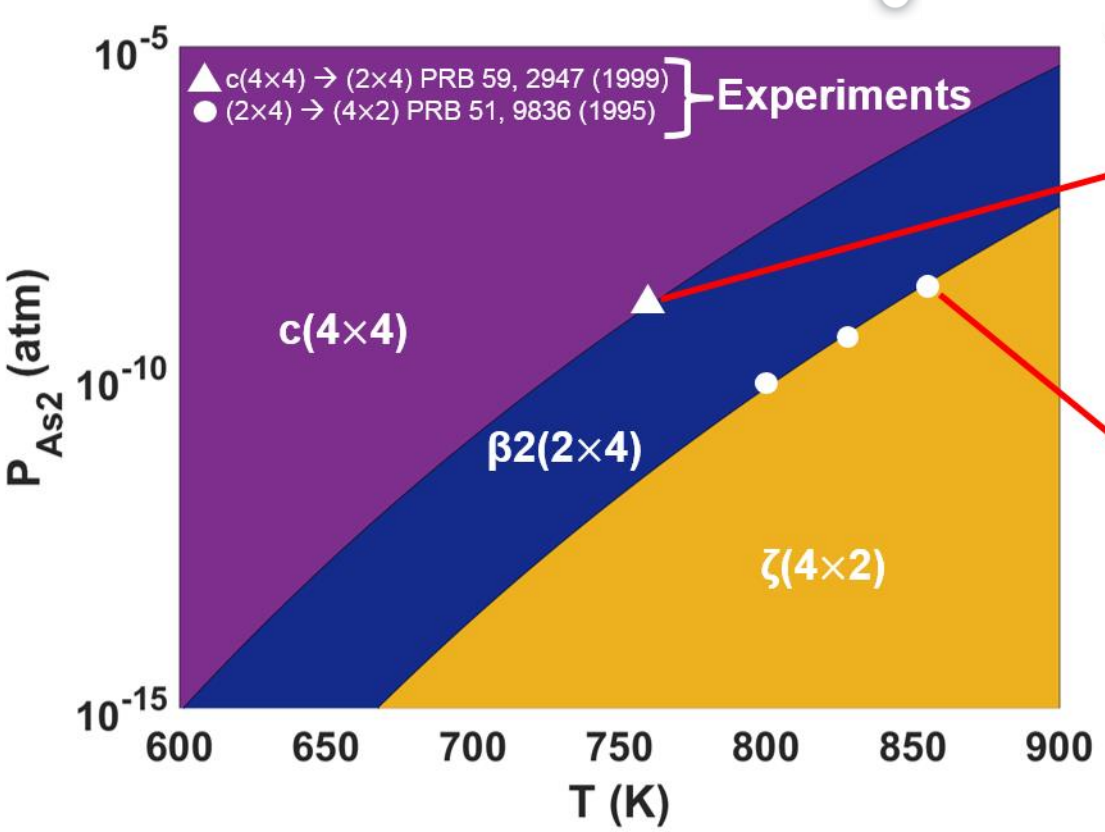
"Most stable"

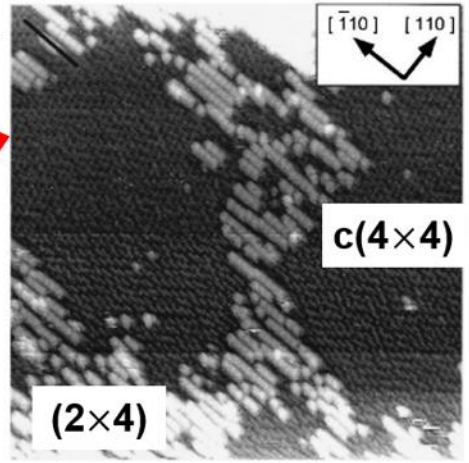


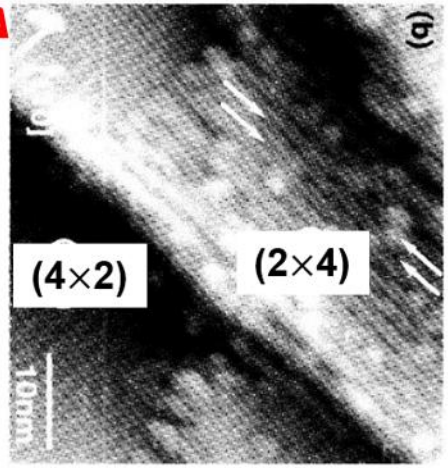
Ga-rich

As-rich

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



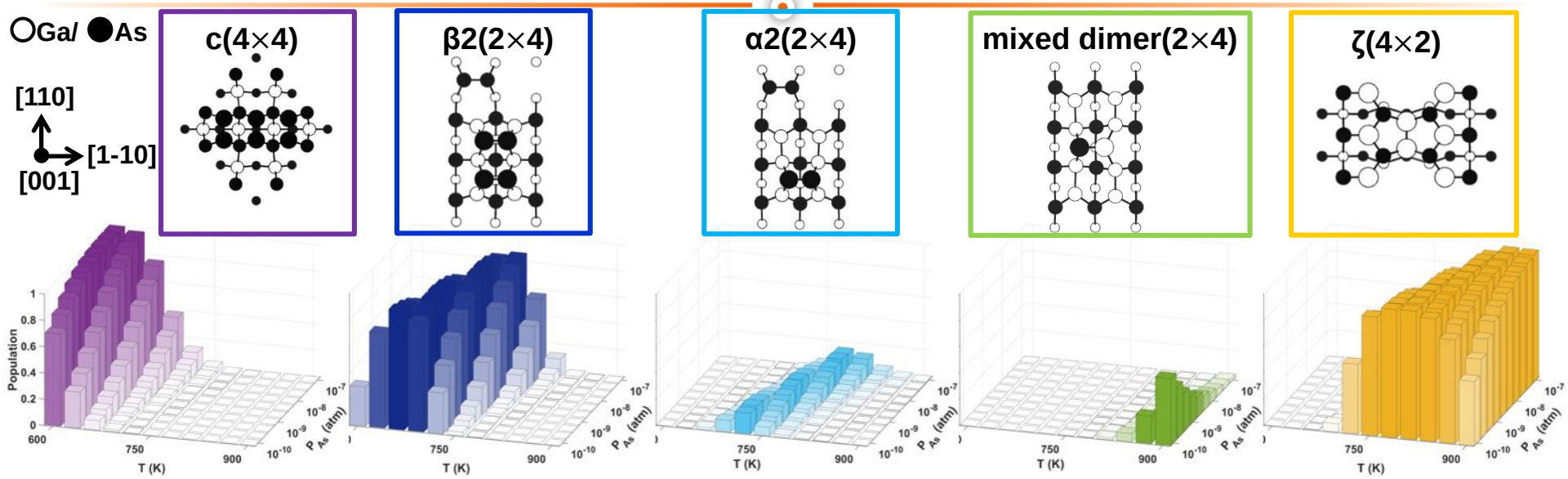




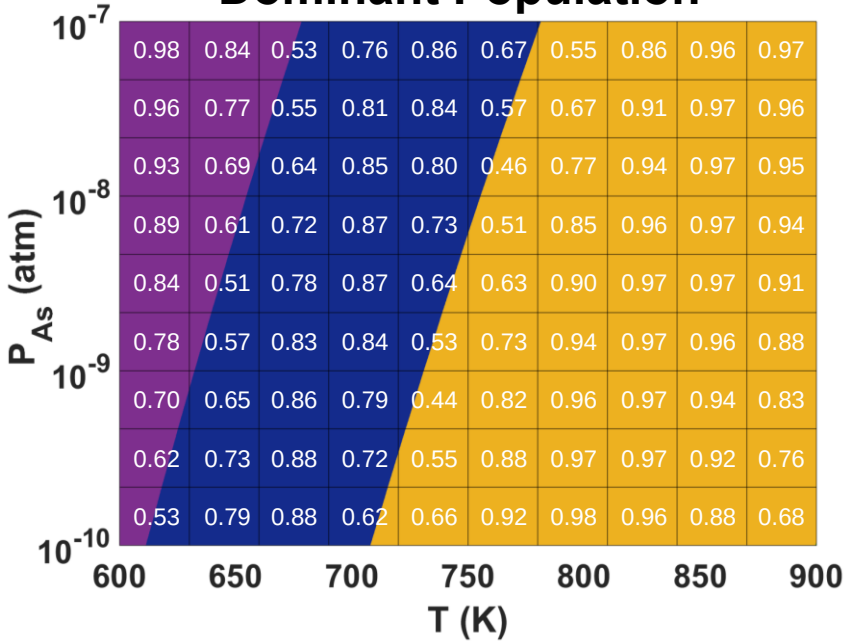
Transition Lines of GaAs(100)

- Calculated transition lines show good agreements with experimental transition (T,P) points.
- At around the transition lines, mixed phase occurs in experiments.

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



"Dominant Population"



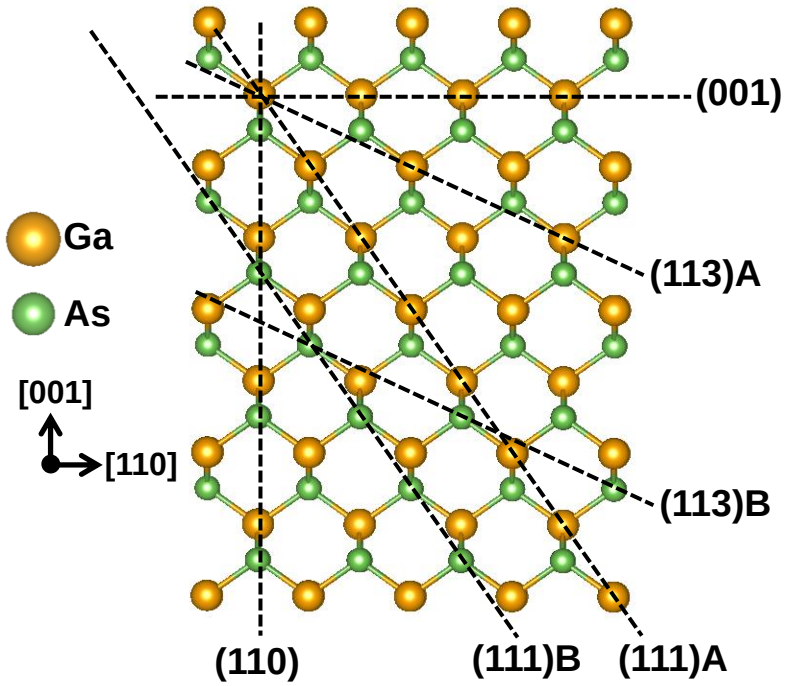
Population of reconstruction i:

$$c_i = \frac{Z_i}{Z} \; where \; i \in \{reconstructions\}$$

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

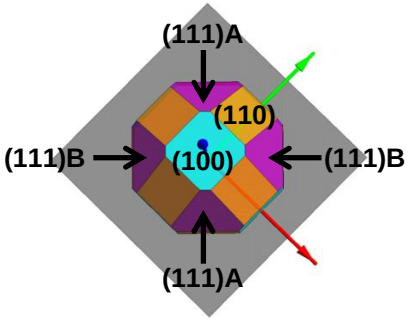
Various surfaces of GaAs

GaAs (Zinc Blende structure)

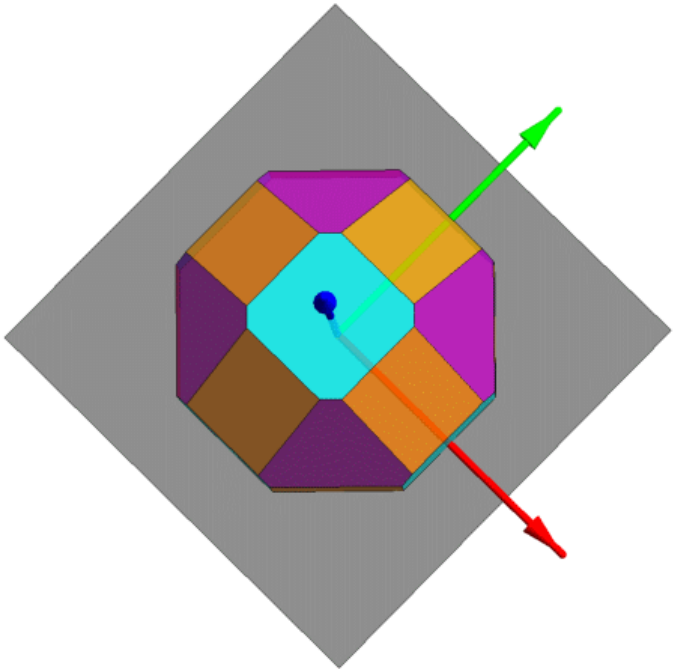


$Wulff\ construction$

$when\ \gamma^{(113)A} = \gamma^{(113)B} \gg \gamma^{(100)} = \gamma^{(110)} = \gamma^{(111)A} = \gamma^{(111)B}$

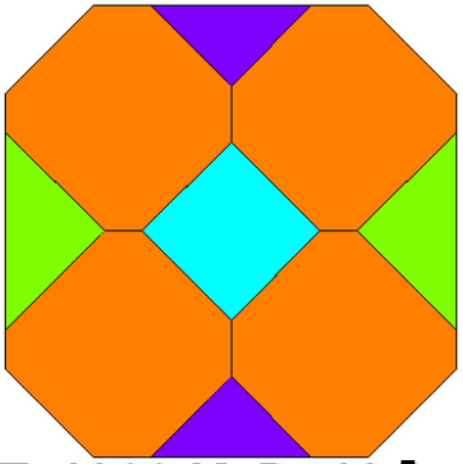


Wulff shape



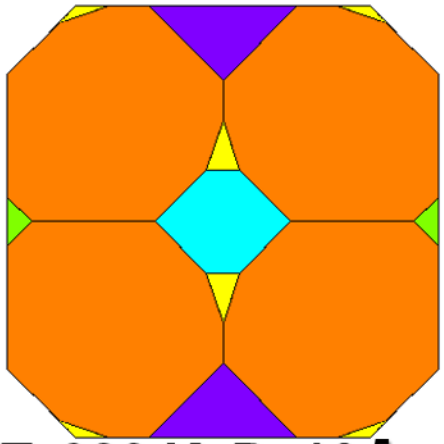
Wulff construction: $d^{(hkl)} \propto \gamma^{(hkl)}$

Equilibrium Crystal Shape (T, P_{As})



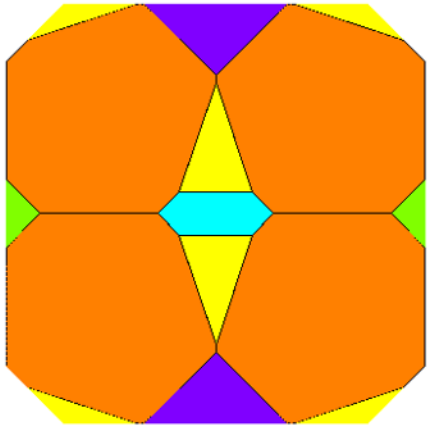
T: 1023 K, P: 10^{-5} atm

$\mu_{As(g)} = -6.04$



T: 923 K, P: 10^{-5} atm

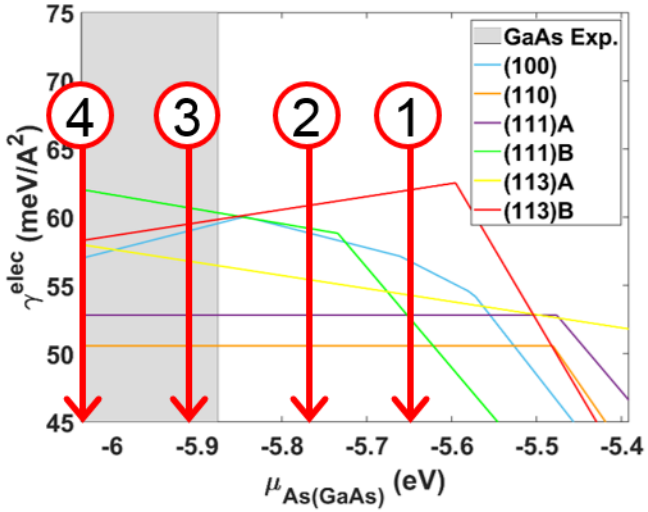
$\mu_{As(g)} = -5.91$



T: 823 K, P: 10^{-5} atm

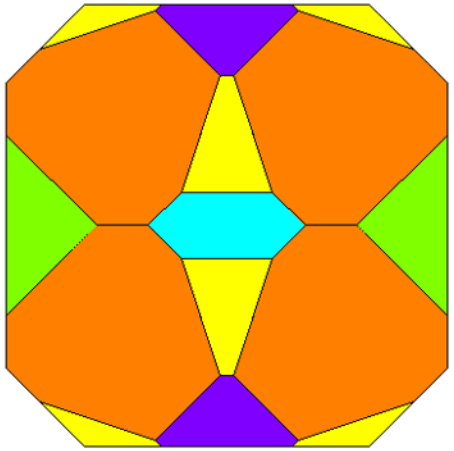
$\mu_{As(g)} = -5.77$

4 — 3 — 2 — 1



[110]
[1-10]
[001]

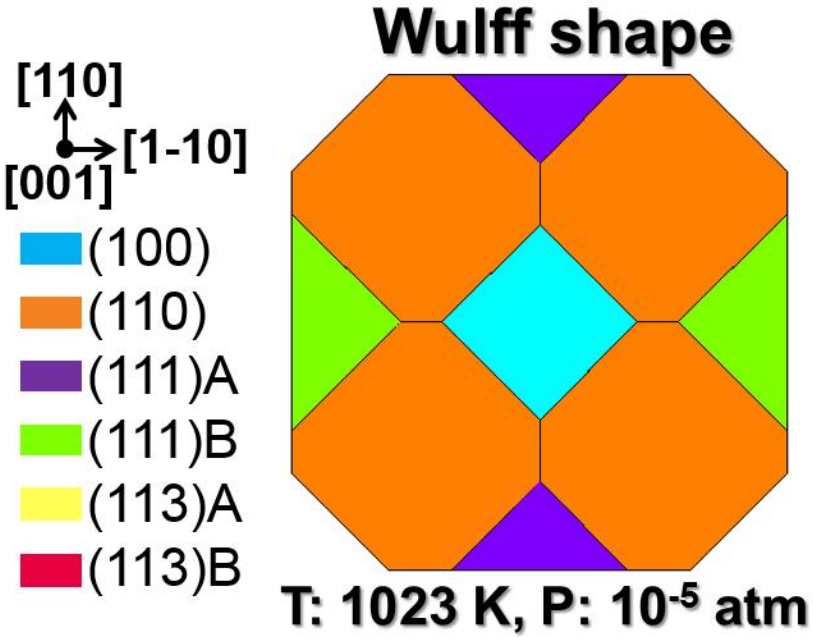
(100)×6
(110)×12
(111)A×4
(111)B×4
(113)A×12
(113)B×12

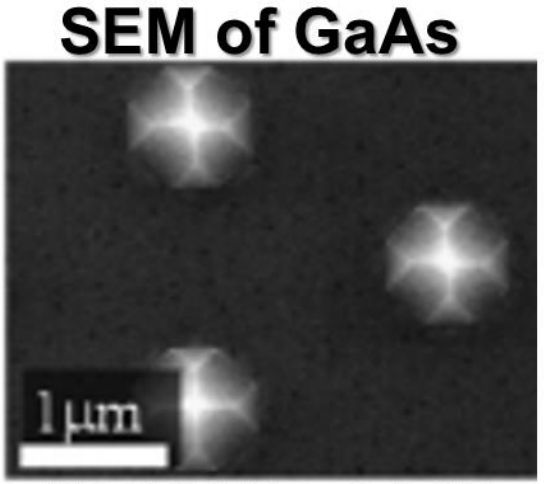


T: 723 K, P: 10^{-5} atm

$\mu_{As(g)} = -5.65$

Equilibrium Crystal Shape (T, P_{As})



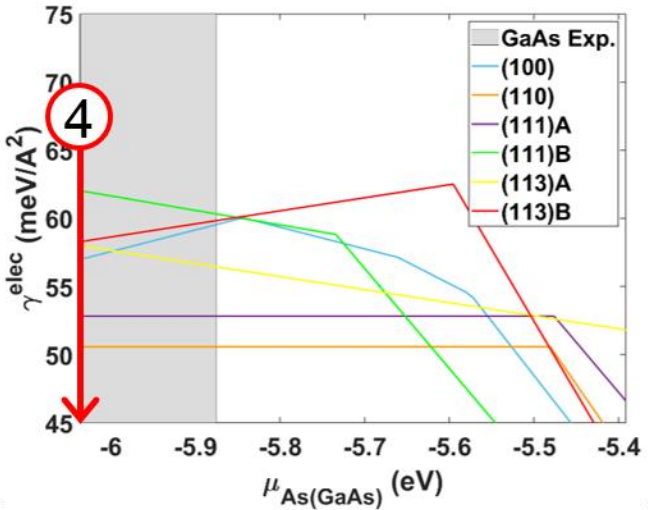


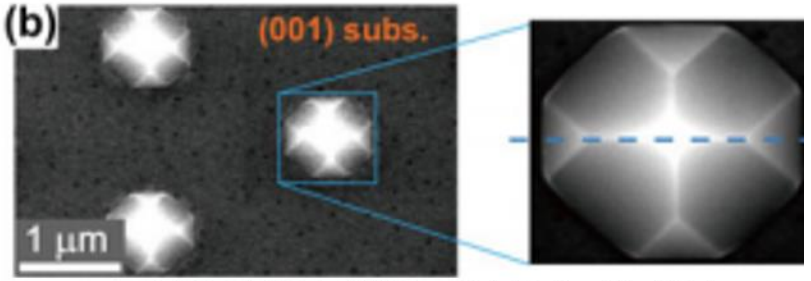
MOCVD(TMGa & AsH_3)

T: 1023 K

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

$\mu_{As(g)} = -6.04$





MOCVD(TMGa & TBAs/AsH_3)

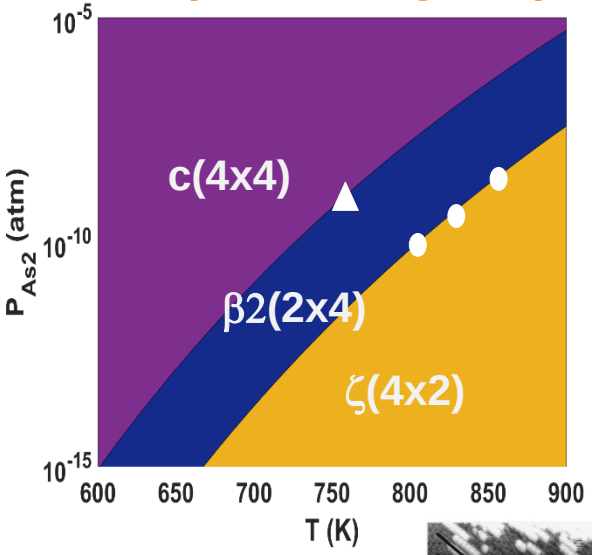
T: 973~1023 K

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

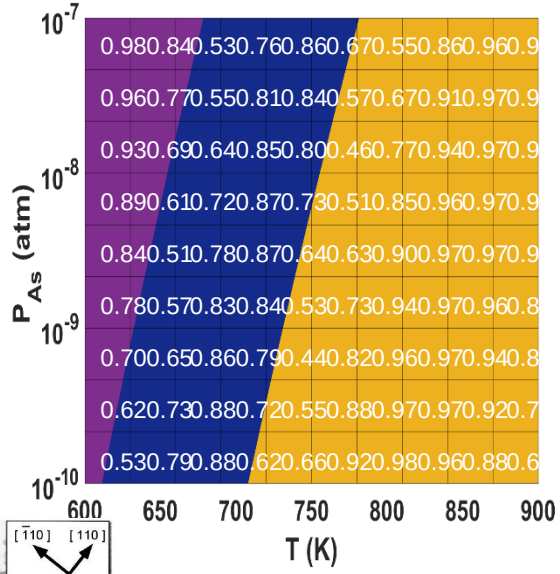
Summary

Surface energy(T,P) → **Wulff shape(T,P)**

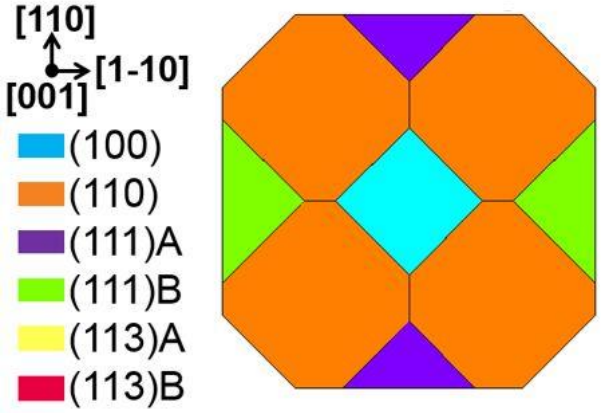
Surface phase diagram(T,P)

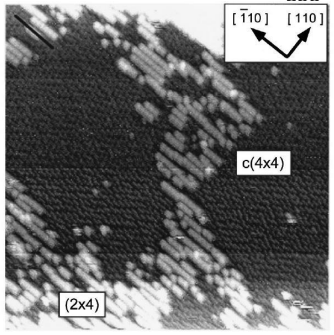


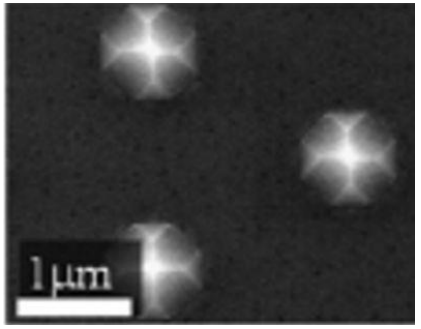
Surface population(T,P)



ECS(T,P)







→ can be applicable to other systems.