IUMRS-ICEM 2018
S4H-Nano Structure & Surface Engineering Ⅱ

T-P surface phase diagram of GaAs(100) and Equilibrium crystal shape of GaAs by ab-initio thermodynamics

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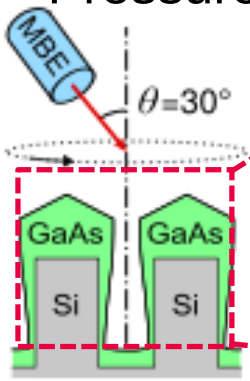
- **Summary**

Surface engineering of Ⅲ-Ⅴ

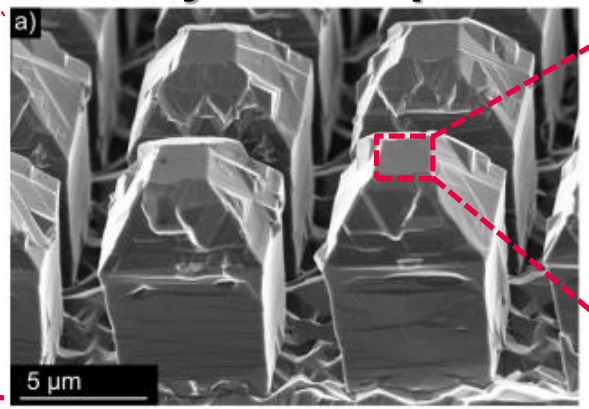
Continuum Property → **Experimental measurements** → **Atomic Structure**

Growth Variable:
Temperature,
Pressure



SEM

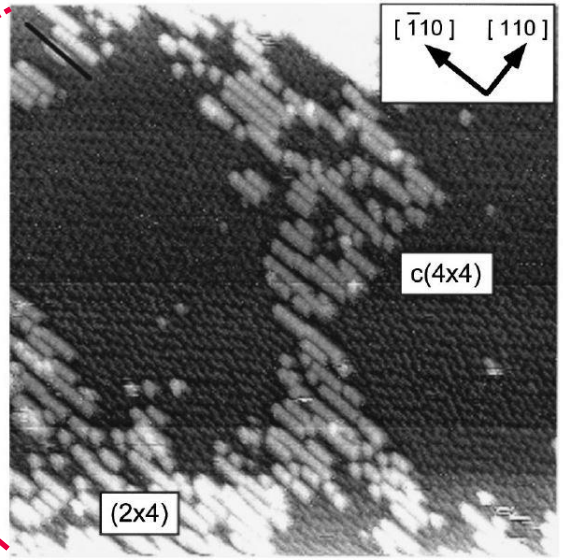
Crystal shape



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

STM

Surface reconstruction



Temperature: 768 K
Pressure: ~10^{-9} atm
Phys. Rev. B 59, 2947 (1999)

Variation of GaAs(100) reconstructions

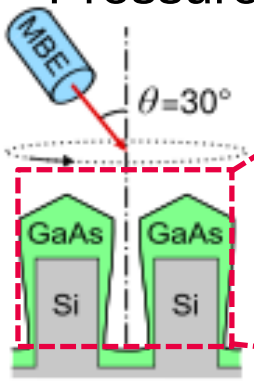
~760 K ***~850 K***

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

Surface engineering of Ⅲ-Ⅴ

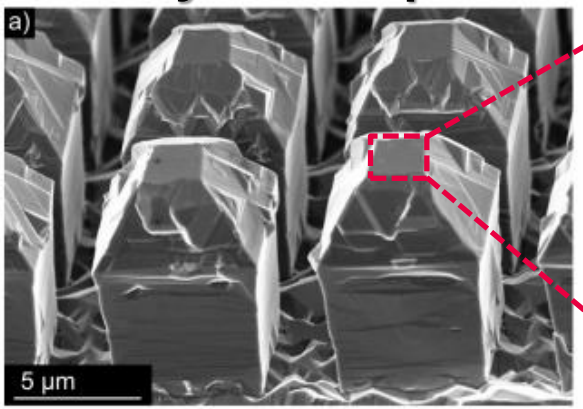
Continuum Property → **Experimental measurements** → **Atomic Structure**

Growth Variable:
Temperature,
Pressure



SEM

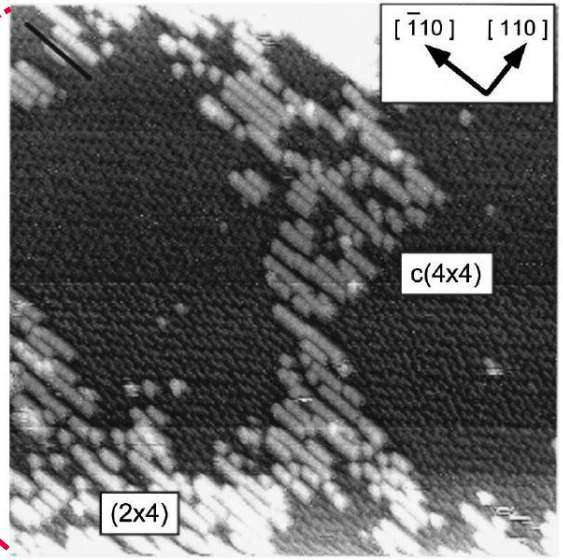
Crystal shape



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

STM

Surface reconstruction



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

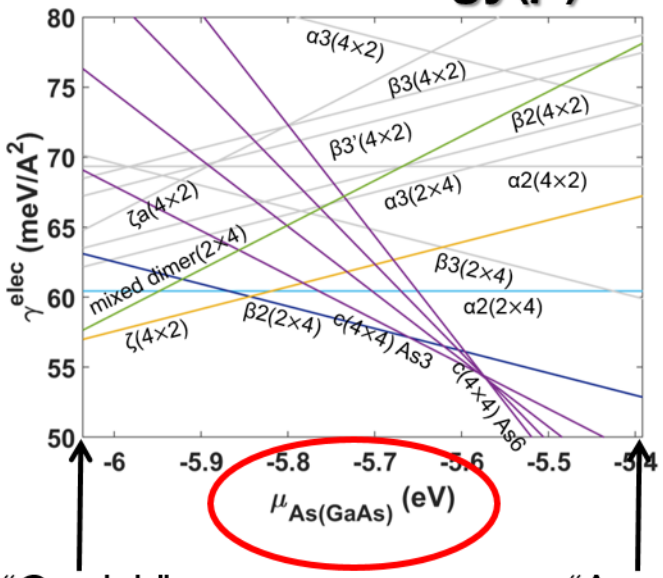
Phys. Rev. B 59, 2947 (1999)

Prediction of the Reconstruction &
Equilibrium crystal shape for a given (T,P)

Method 1: ab-initio thermodynamics

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

Surface energy(μ)

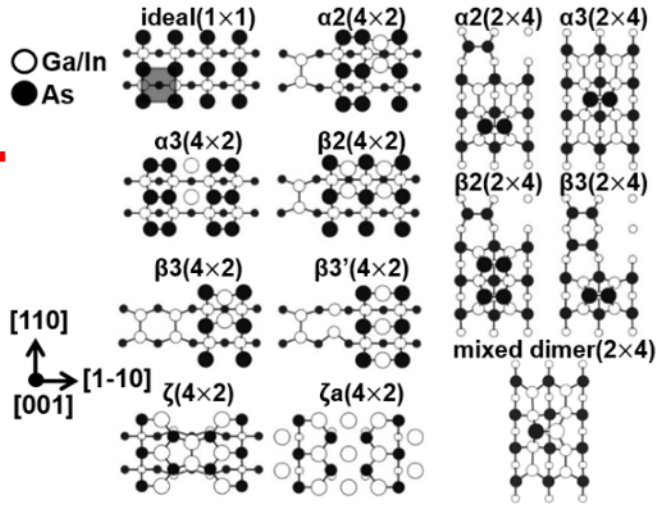


"Ga-rich"
High T, Low P

"As-rich"
Low T, high P

DFT calculation

Surface reconstruction



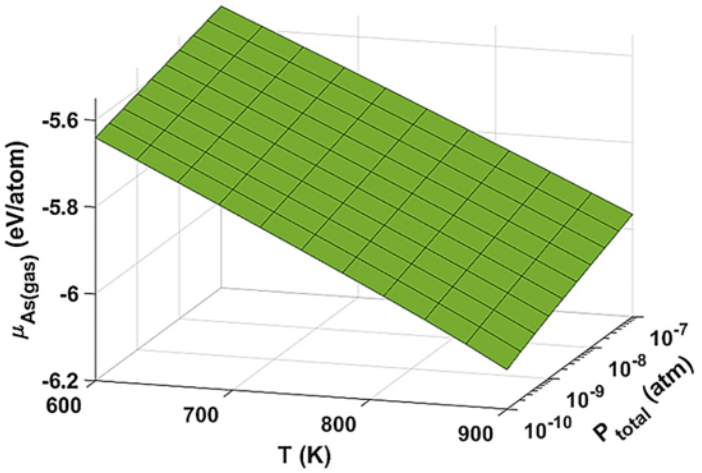
Where is (768 K, 10^{-9} atm) ??

Method 1: ab-initio thermodynamics

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

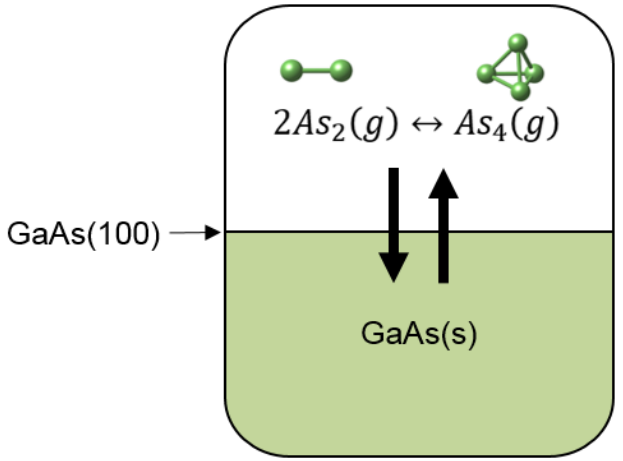
DFT calculation

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



Equilibrium

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

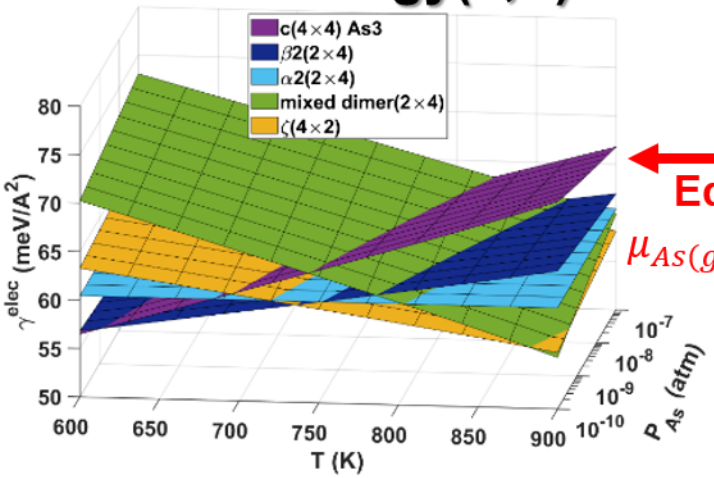


x-axis: $\mu_{As(GaAs)} = \mu_{As(g)}(T,P)$!!

Method 1: ab-initio thermodynamics

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

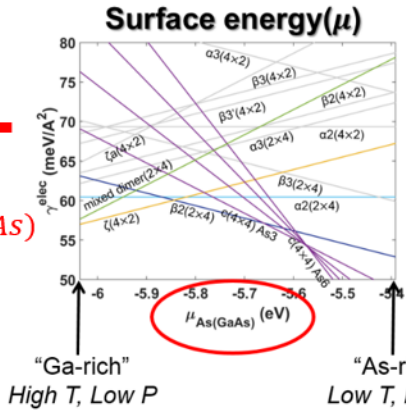
Surface energy(T,P)



Equilibrium

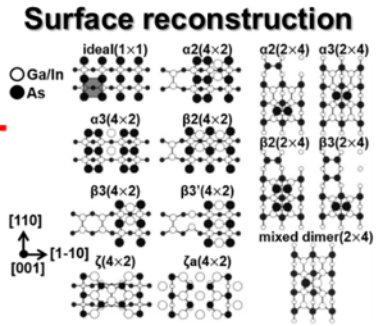
$\mu_{As(g)} = \mu_{As(GaAs)}$

Surface energy(μ)



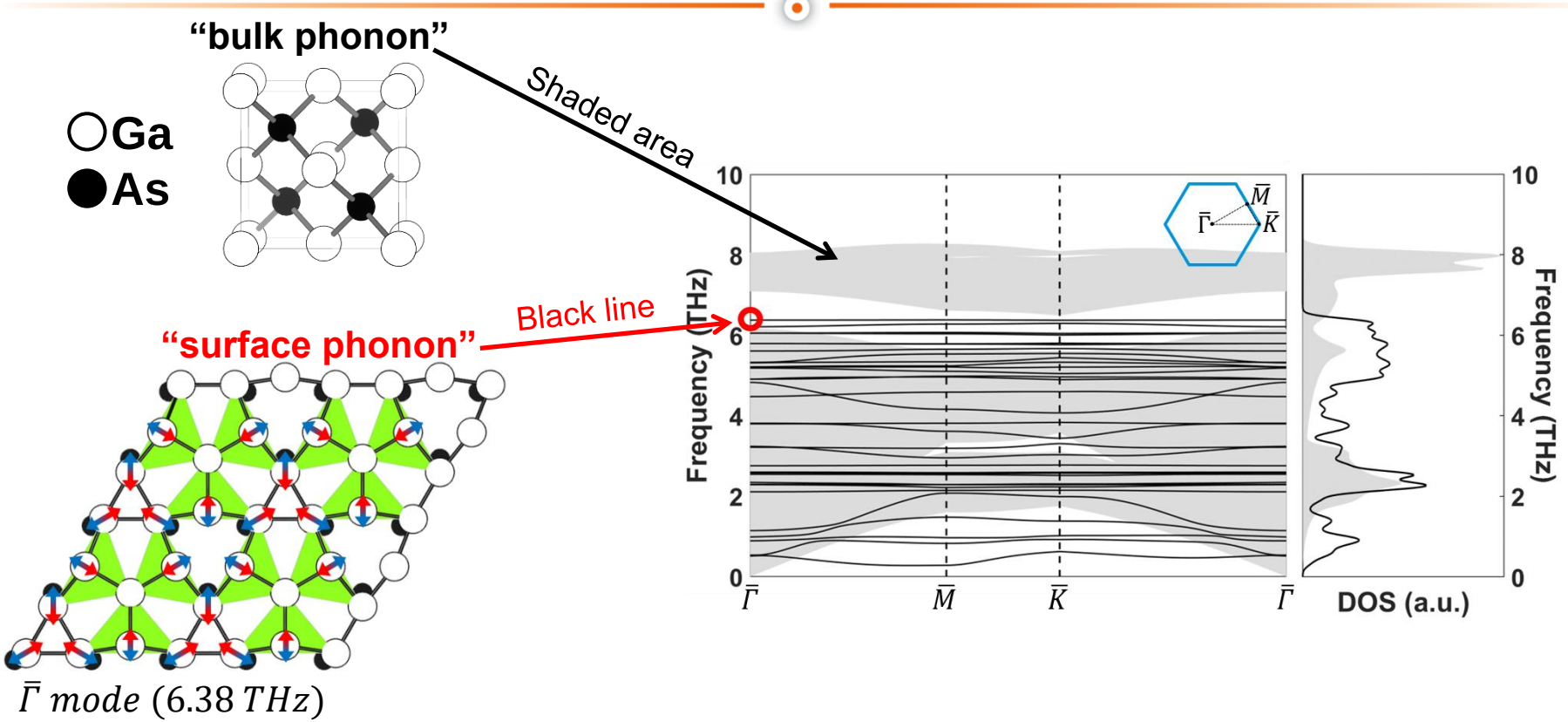
DFT calculation

Surface reconstruction



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

Method 2: vibrational effects



Surface vibration

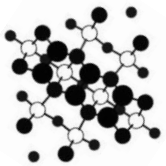
- Each reconstruction of GaAs has different bonding geometry and stoichiometry.
- Frequency of surface phonon is usually lower than bulk phonon.

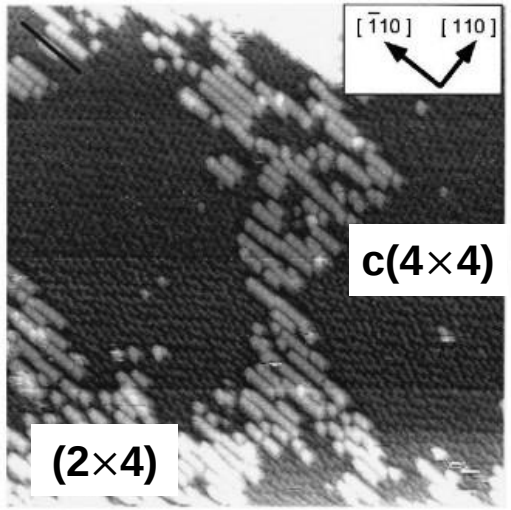
Method 3: configurational effects

~760 K

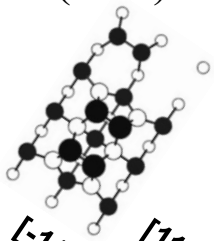
c(4×4) → mixture of c(4×4) with (2×4) → (2×4) → mixture of (2×4) with (4×2) → (4×2)

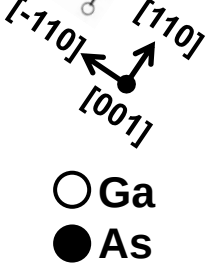
~850 K

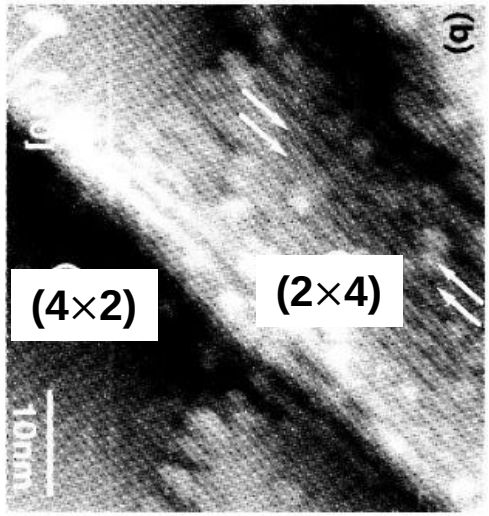




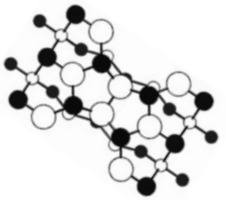
Phys. Rev. B 59, 2947 (1999)







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

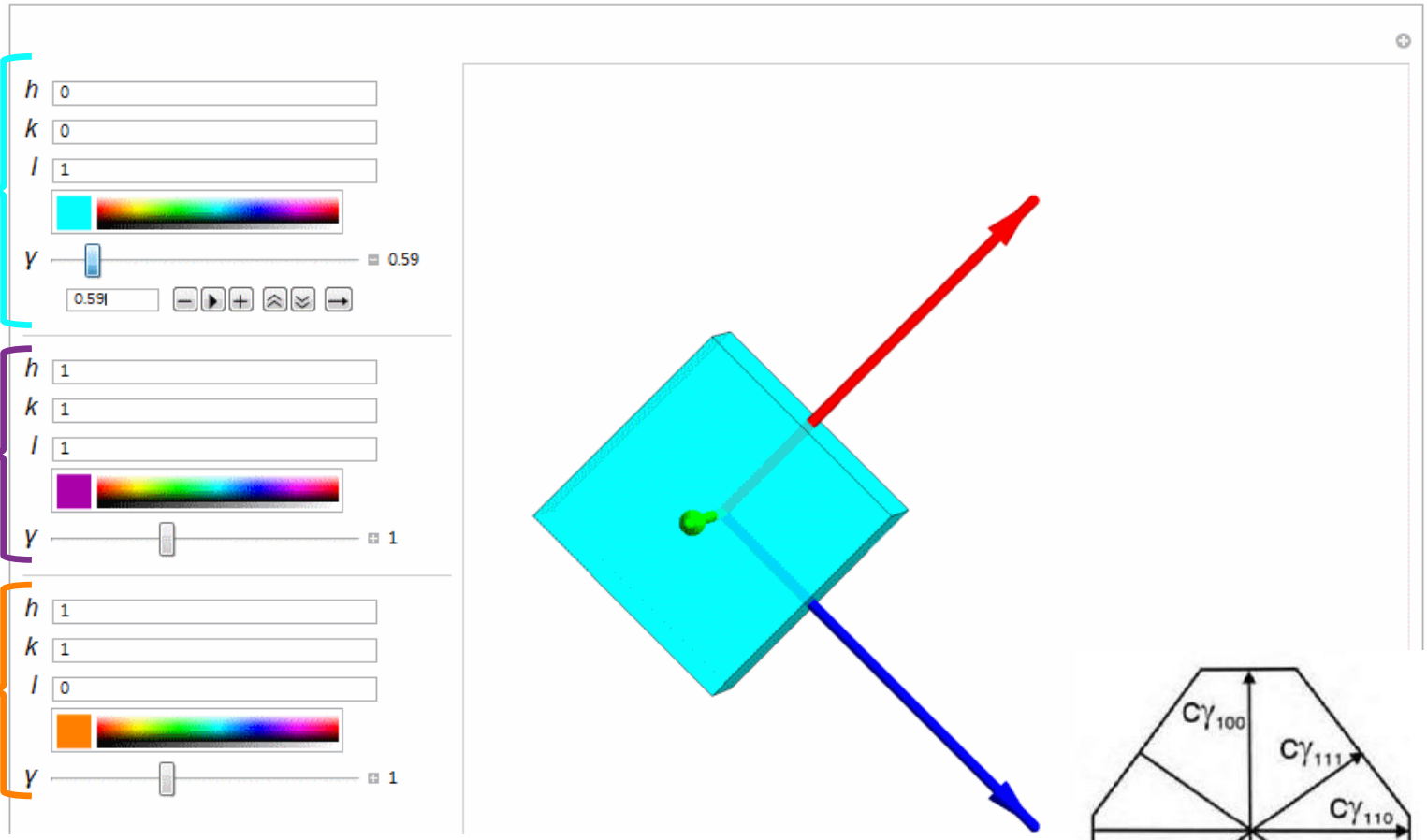
$$Z = \sum_i Z_i = \sum_i g_i \exp(-\frac{\gamma_i(T,P)A}{k_B T})$$

Method 4: Wulff construction

$\gamma^{(100)}$ is arbitrarily increasing

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

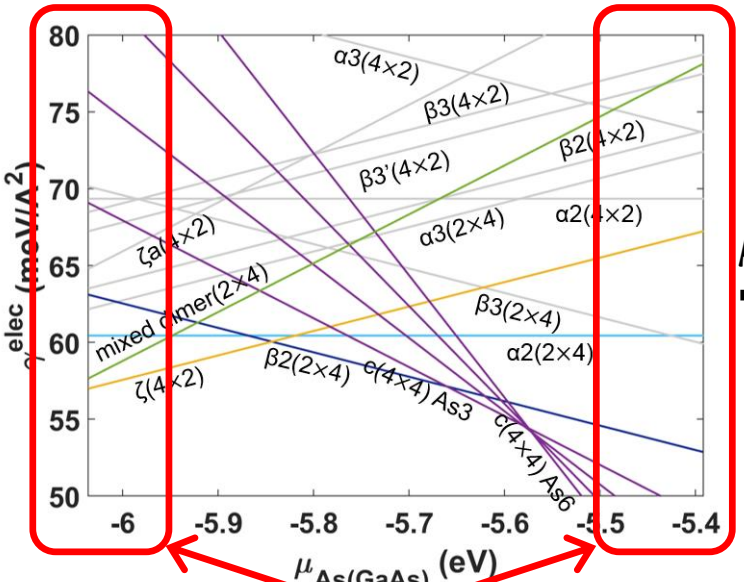
$\gamma^{(110)}$ is fixed



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

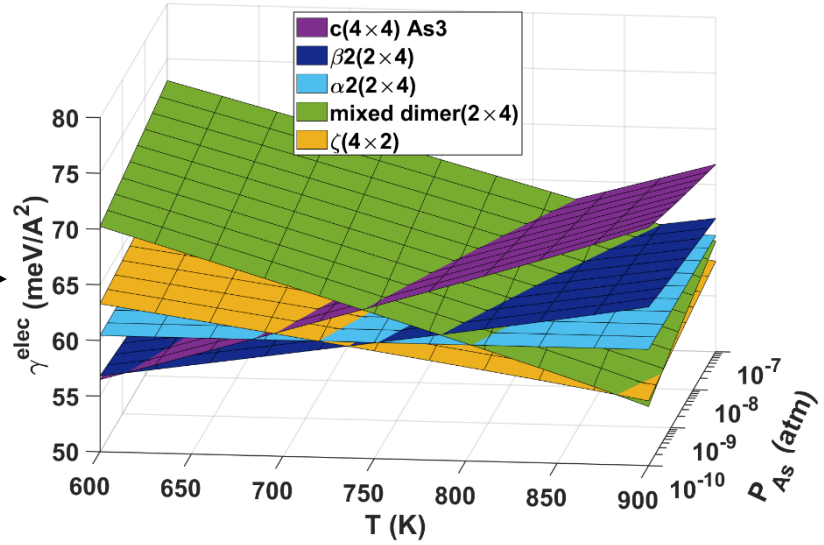
- This theorem makes the total surface energy minimum.
- The energy ratio between different surfaces determines the wulff shape.

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

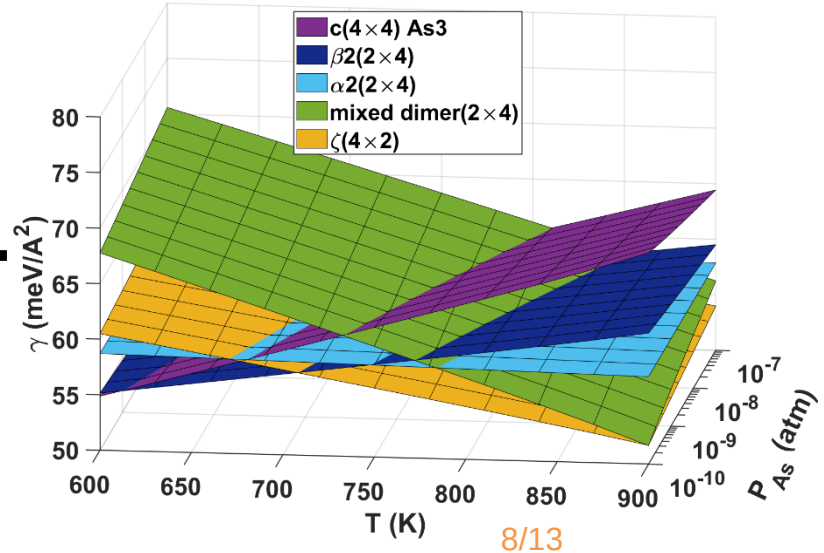


"Equilibrium"

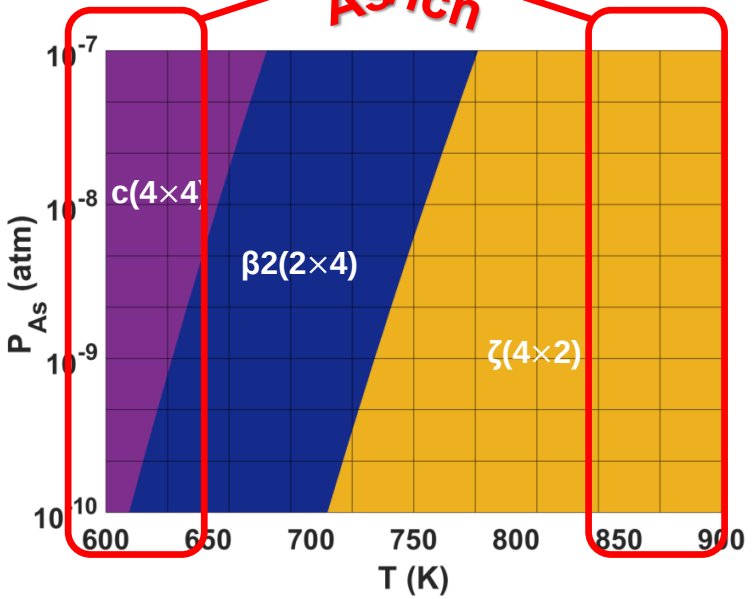
$\mu_{As(g)} = \mu_{As(GaAs)}$



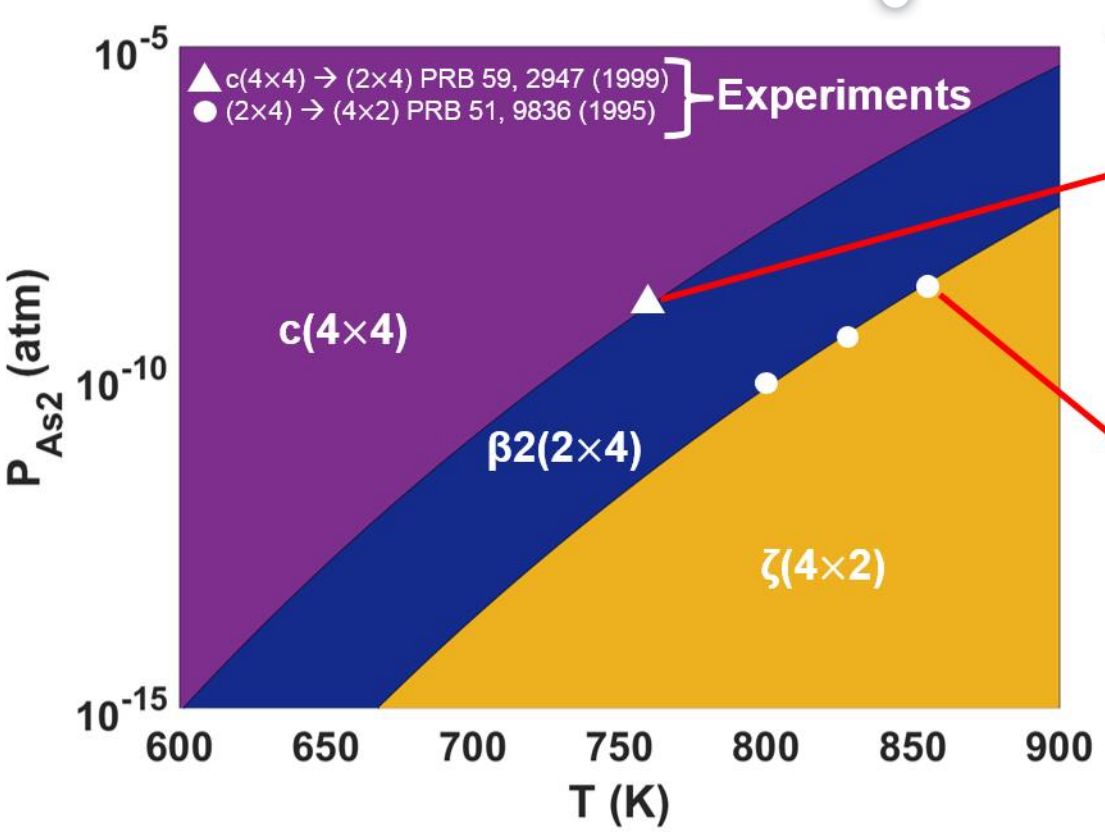
$\gamma = \gamma^{elec} + \Delta\gamma^{vib}$

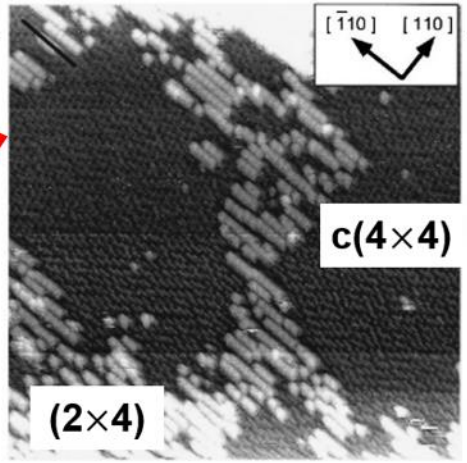


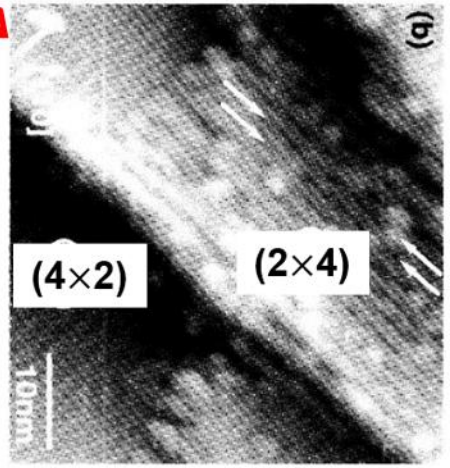
"Most stable"



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



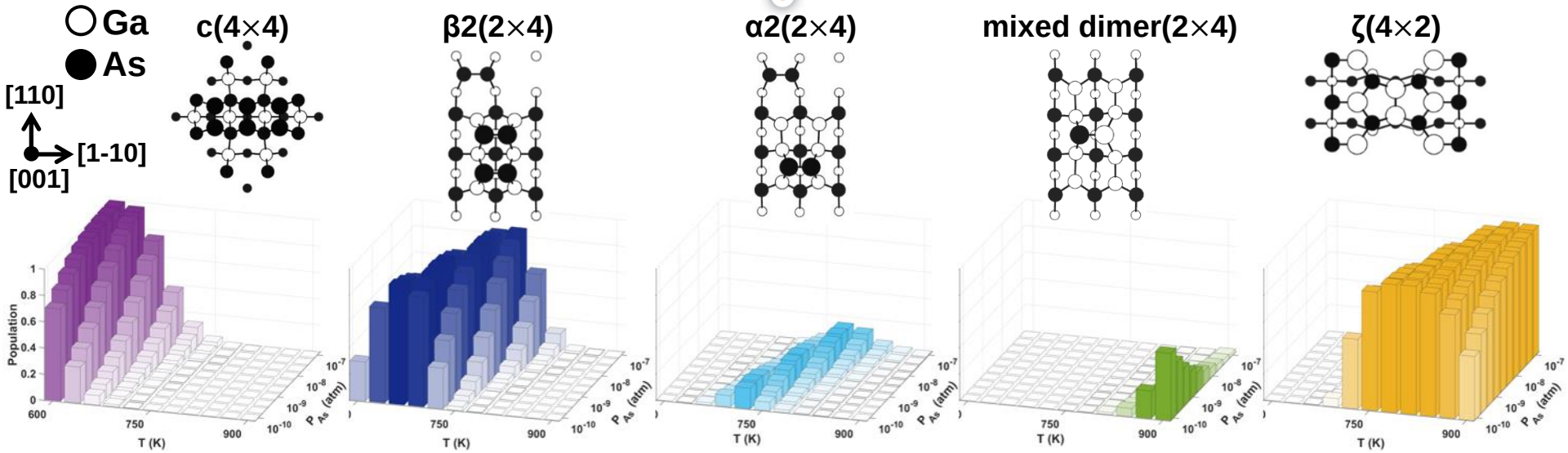




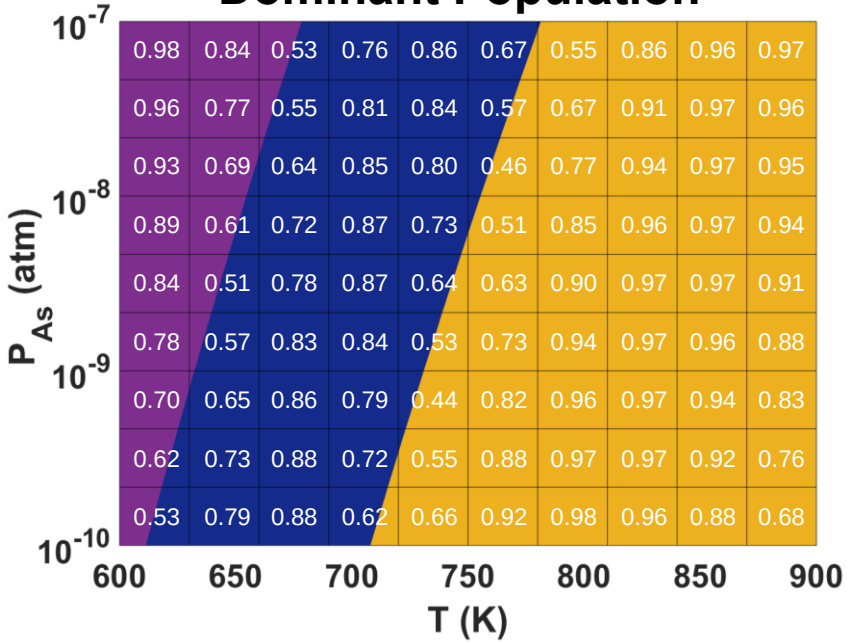
Transition Lines of GaAs(100)

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

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



"Dominant Population"



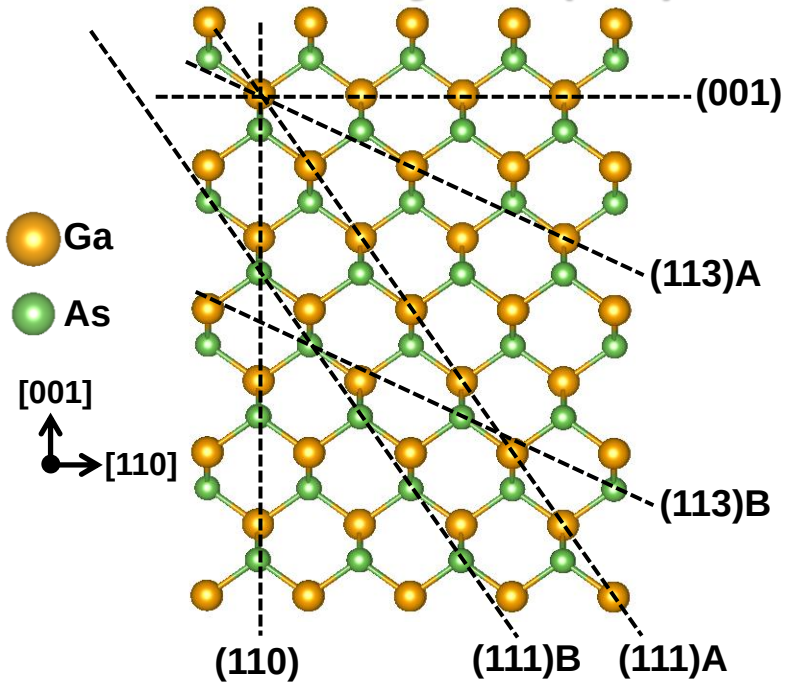
Population of reconstruction i:

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

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

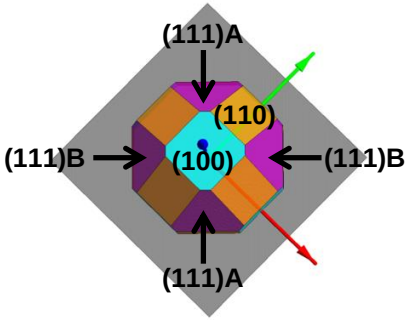
Various surfaces of GaAs

GaAs crystal(ZB)

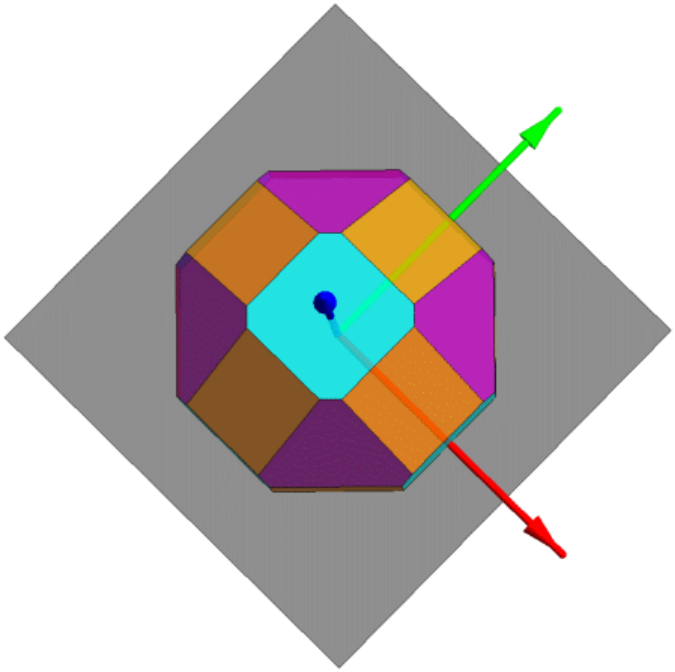


$Wulff\ construction$

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

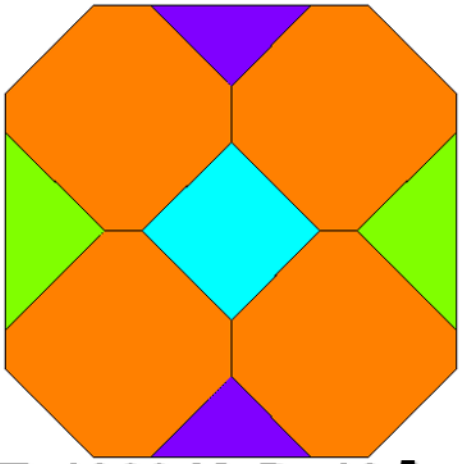


Wulff shape



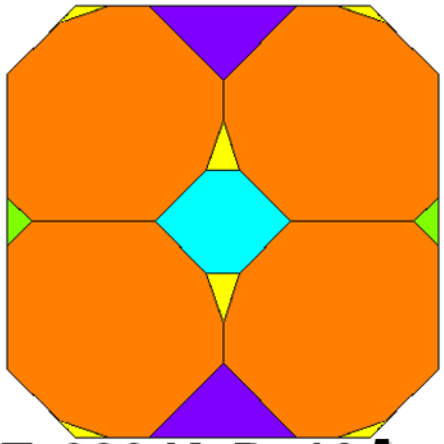
Wulff construction: $d^{(hkl)} \propto \gamma^{(hkl)}$

Equilibrium Crystal Shape (T, P_{As})



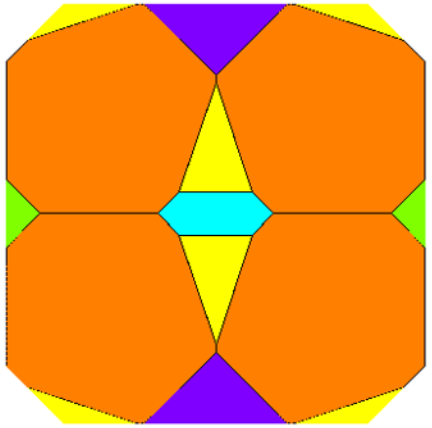
T: 1023 K, P: 10^{-5} atm

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



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

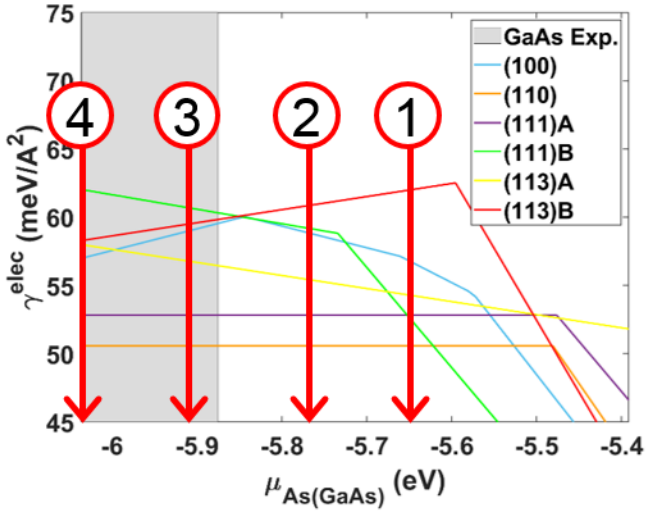
$\mu_{As(g)} = -5.91$

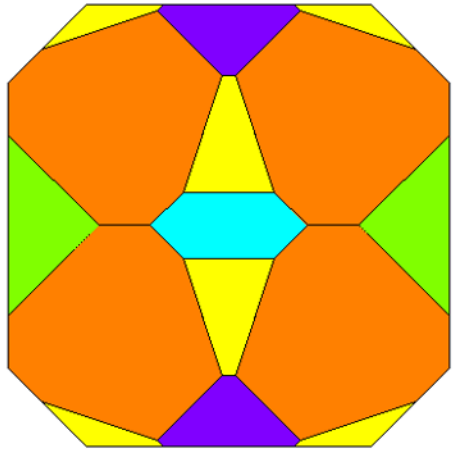


T: 823 K, P: 10^{-5} atm

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

4 — 3 — 2 — 1

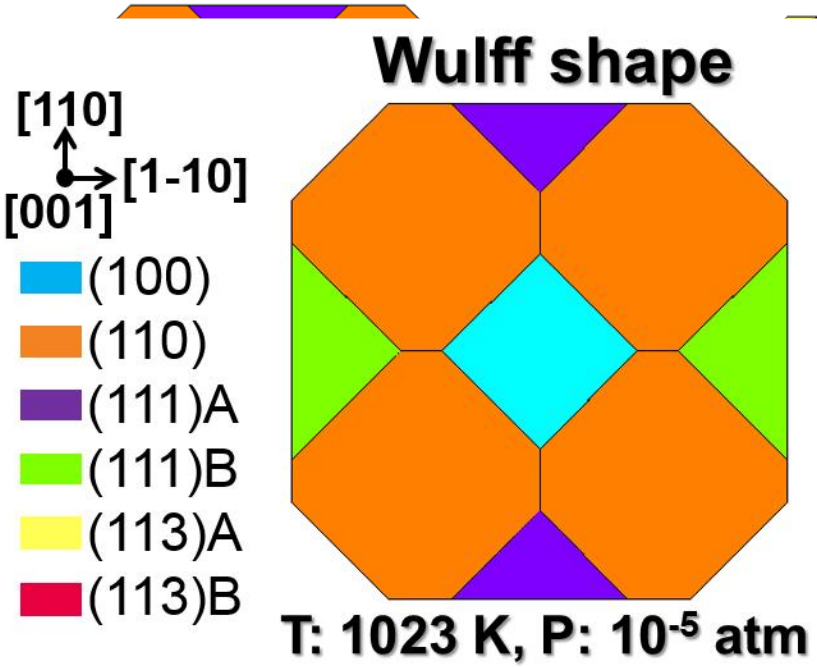


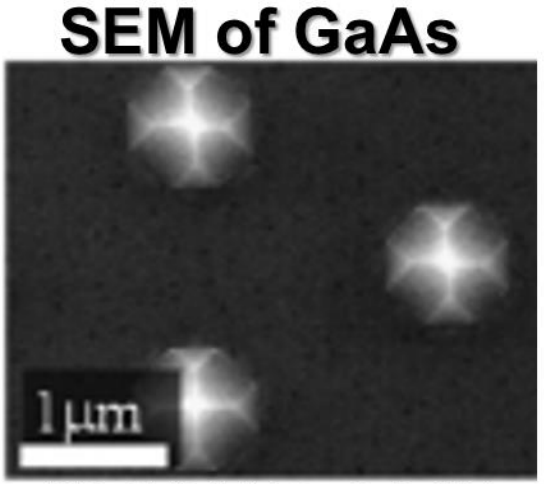


T: 723 K, P: 10^{-5} atm

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

Equilibrium Crystal Shape (T, P_{As})



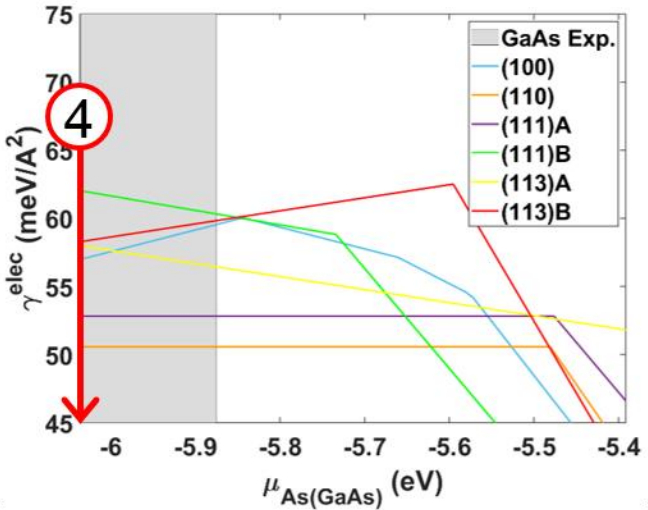


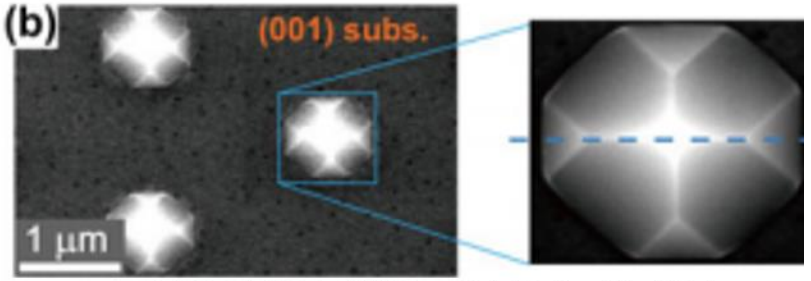
MOCVD(TMGa & AsH_3)

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 phase diagram(T,P)** of GaAs(100) shows good agreements with experimental transition points.

- **Surface population(T,P)** of GaAs(100) simulates the mixed phase of different reconstructions.

- **Equilibrium Crystal Shape(T,P)** shows coincidences with experimental crystal shapes.

- Consideration of the **equilibrium condition and entropy effects** makes the calculation comparable to the experiments.

- This calculation method is also **applicable to other Ⅲ-Ⅴ compounds.**