제 25회 한국반도체학술대회
세션: [WA1-C] Material Growth & Characterization

Surface reconstruction and equilibrium shape of Ⅲ−Ⅴ compound semiconductors as a function of pressure and temperature

2018. 02. 07

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- **Modeling of GaAs Crystal shape**
  - Surface energy
  - Wulff construction
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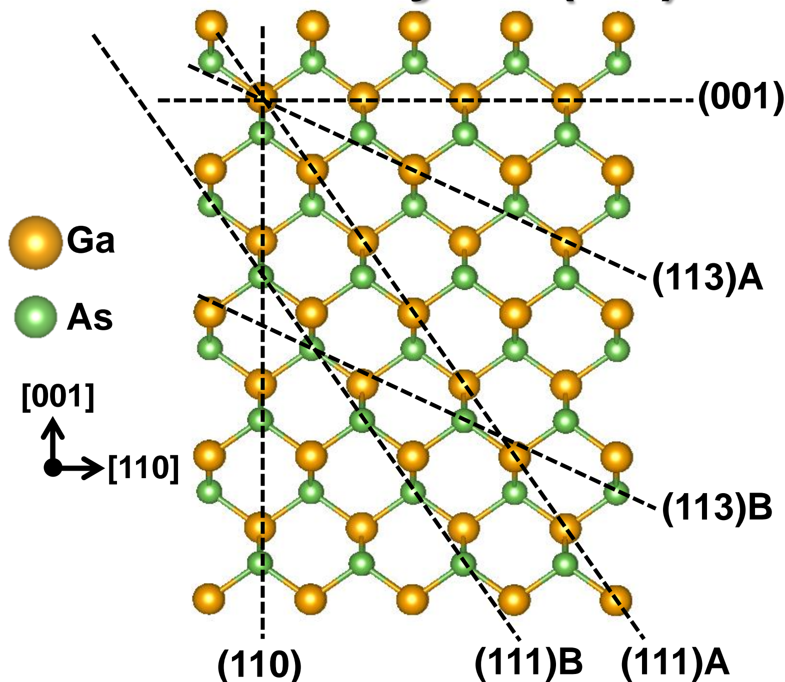
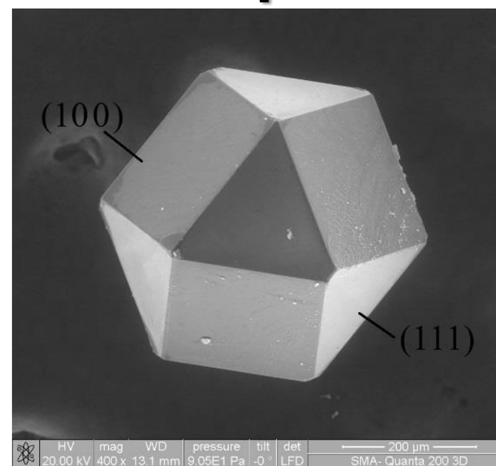
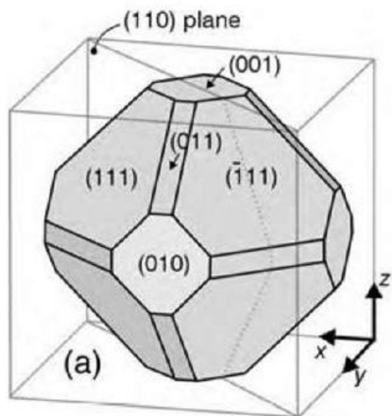
Equilibrium crystal shape(ECS)

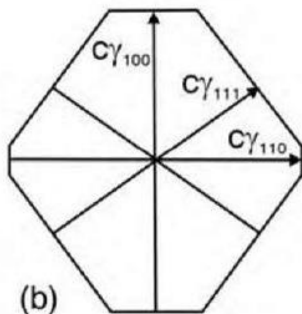
GaAs crystal(ZB)



Anisotropic facets







Wulff construction(ECS):

minimization of the total surface free energy for the given thermodynamic conditions

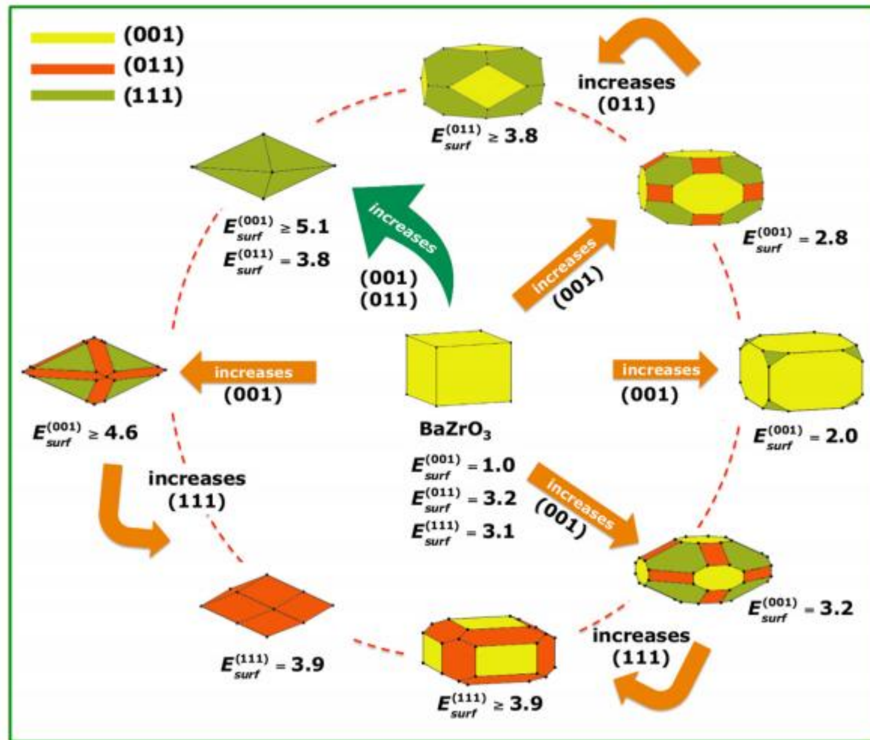
$$\frac{\gamma^{(n)}}{h^{(n)}} = constant,$$

$\gamma^{(n)}$=surface energy of specific orientation

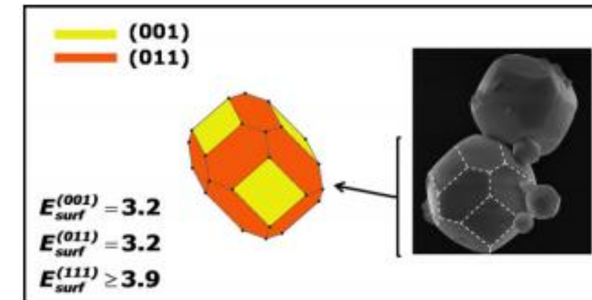
$h^{(n)}$=surface normal

Limitations on the previous ECS simulation Ⅰ

Adjusted Wulff shape



Experiments



Limitation:

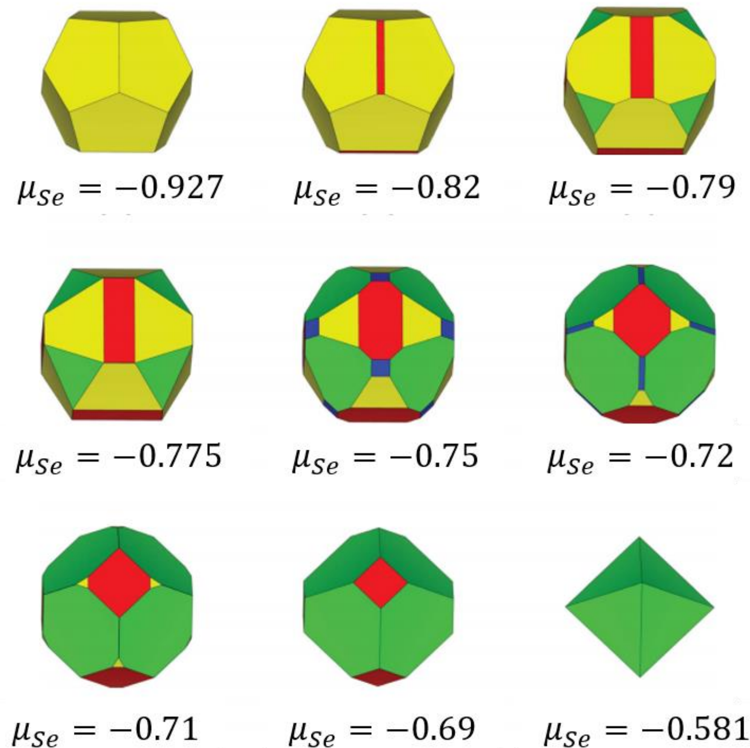
Available facet planes and their relative surface energies are adjusted for fitting to the experimental shape

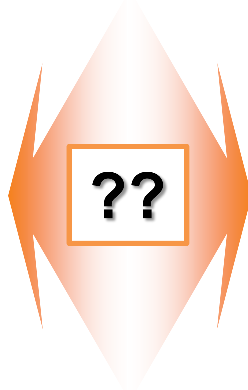
→ "Top-down approach"

Nanotechnology, 26, 405703(2015).

Limitations on the previous ECS simulation Ⅱ

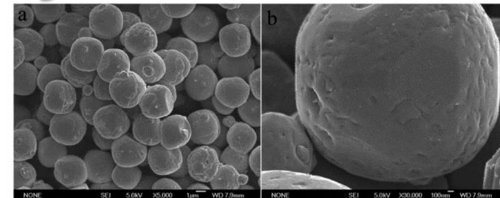
Wulff shape(μ_{Se}) from DFT



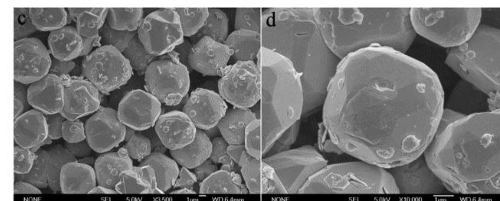


RSC Adv., 4, 13395 (2014).

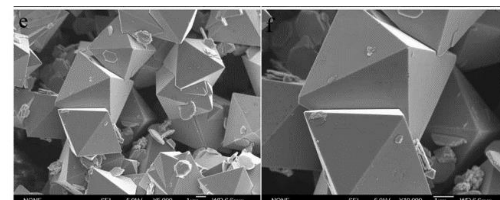
Synthesized $NiSe_2$



Temperature: 430 K with NH80:En=3:1



Temperature: 430 K with NH80:En=1:1

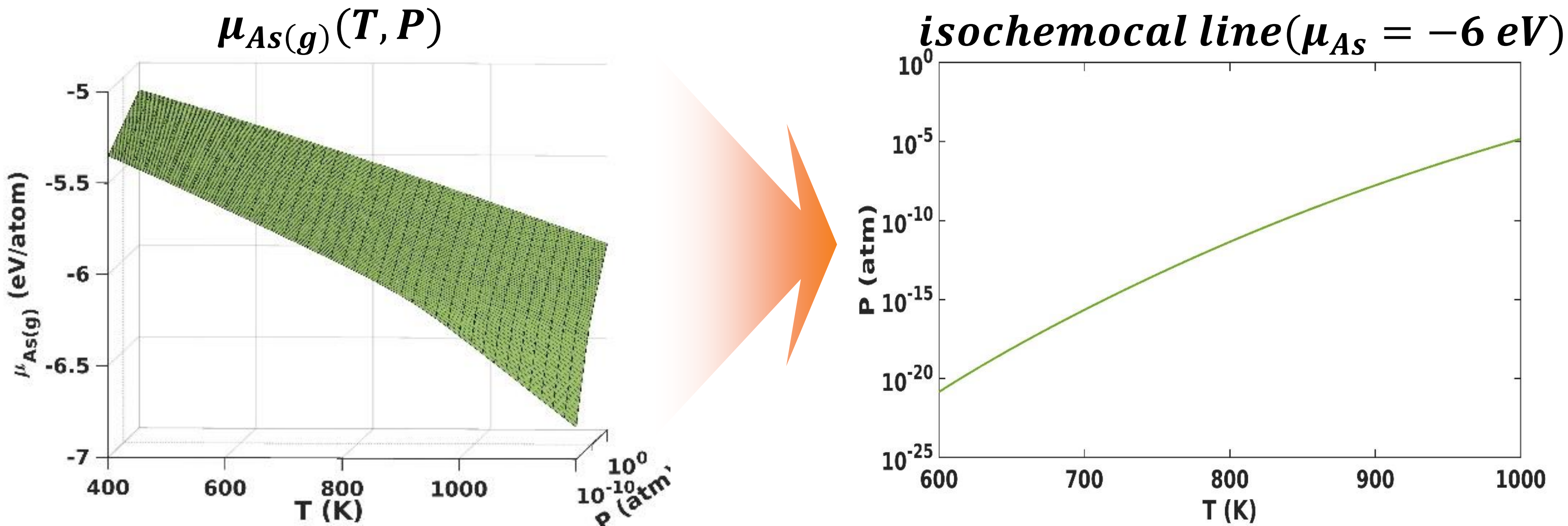


Temperature: 430 K with NH80:En=1:3

Limitation:

Density Functional Theory(DFT) gives absolute surface energy but the energy(wulff shape) is given as a function of μ → "Gap between thermodynamic variables; μ vs. (T,P)"

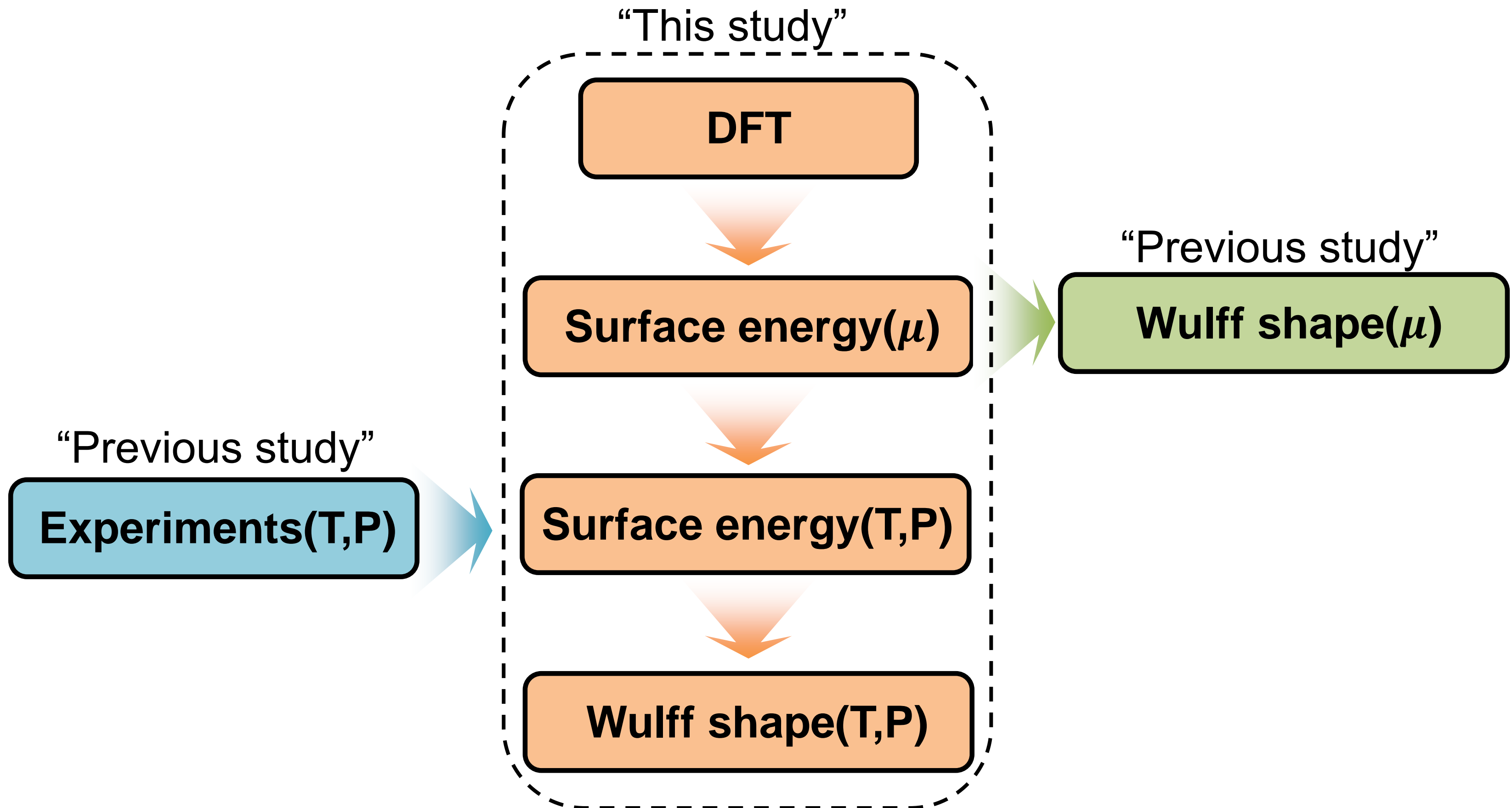
Relation between chemical potential and (T,P)



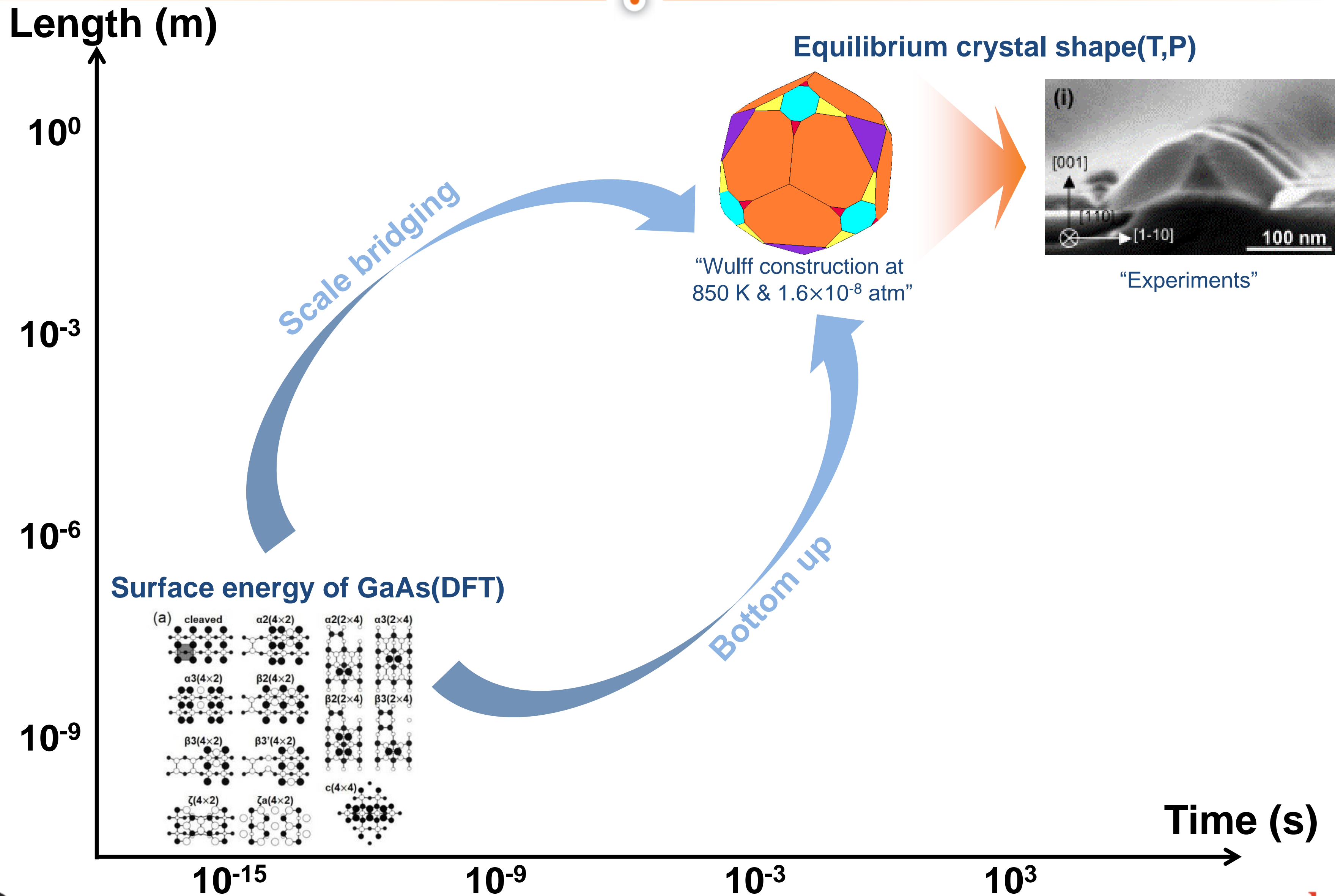
μ is determined by (T,P) but it is hard to experimentally control the μ by (T,P)

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

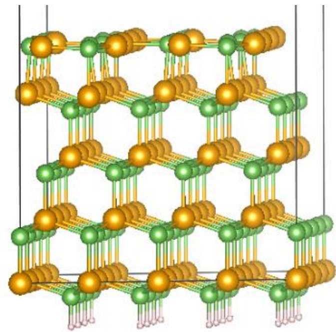
Purpose



Methodology by scale-bridging

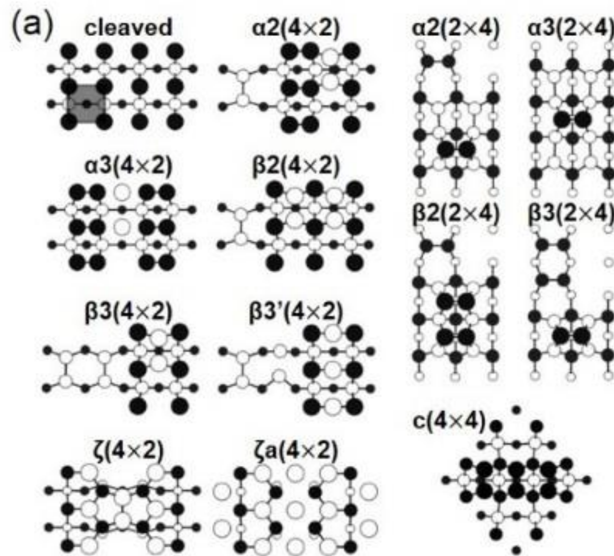


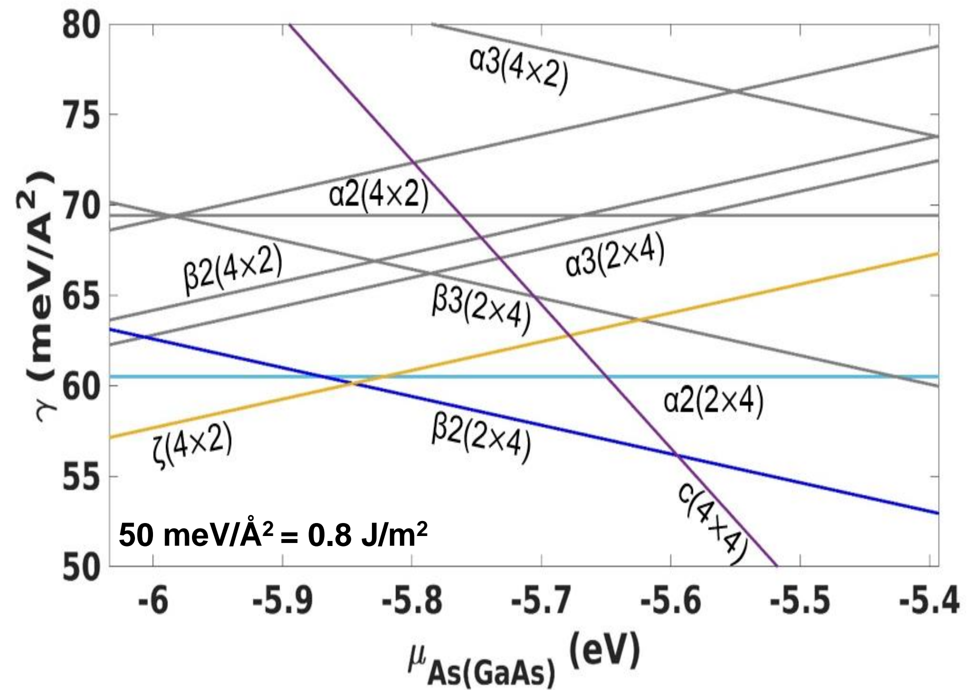
Surface energy(μ_{As}) of GaAs(001)



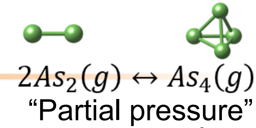
$$\gamma = \frac{\left(E^{elec}_{surf} + F^{vib}_{surf}\right) - N_{In}(E^{elec}_{Ga} + F^{vib}_{Ga}) - N_{As}(E^{elec}_{As} + F^{vib}_{As})}{A}$$

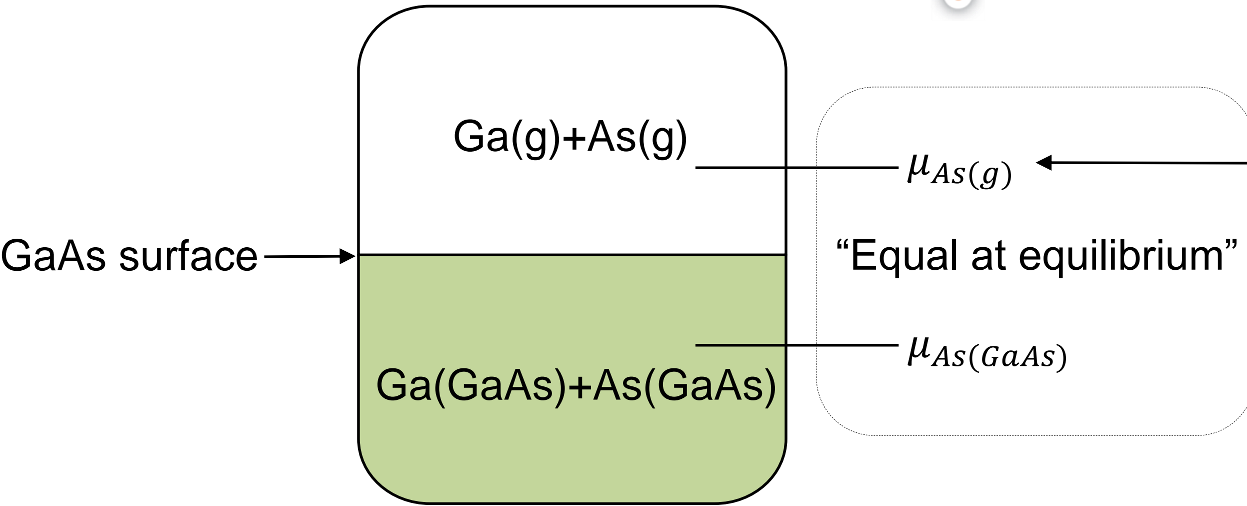
$$F^{vib} = \frac{1}{N_k}\sum_{k\in BZ}\sum_{i}^{M}\{\frac{\hbar w_i(k)}{2} + k_B T \ln(1 - e^{-\frac{\hbar w_i(k)}{k_B T}})\}$$





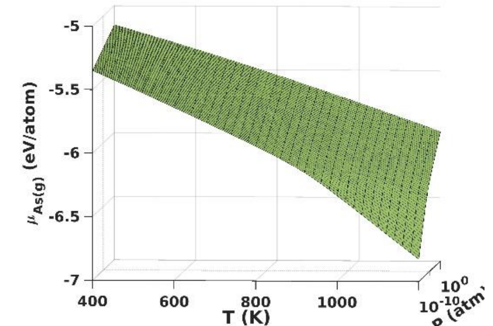
μ_{As}(T,P)

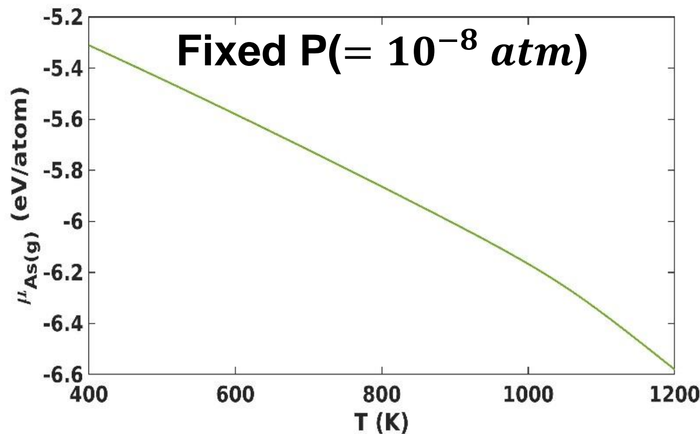


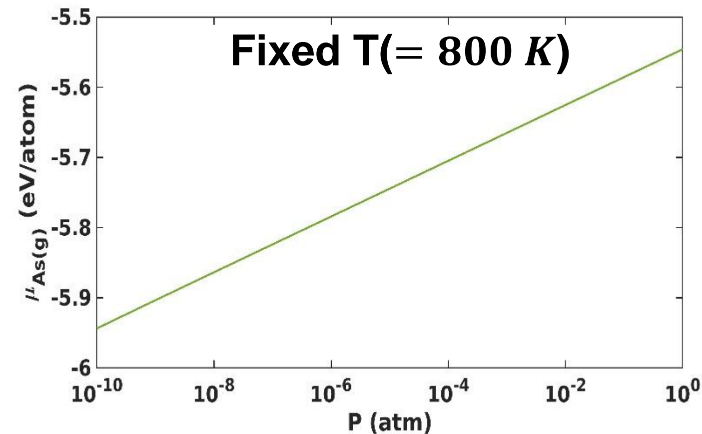


$$\mu_{i(g)}(\mathrm{T}, P) = \mu^{o}_{i(gas)}(T, P^{o}) + k_B T \ln \frac{P_{i(gas)}}{P^{o}}$$

"Translational motion"
"Rotational motion"
"Vibrational motion"







Surface energy(T,P) of GaAs(001)

"0 K electronic energy difference"

$$\gamma = \frac{(E_{surf}^{elec}) - N_{In}(E_{Ga}^{elec}) - N_{As}(E_{As}^{elec})}{A}$$

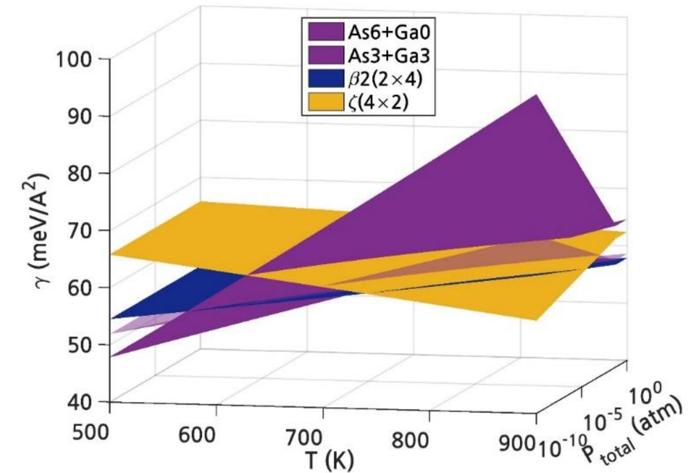
"High T → weak bonding → lower γ"

"Electronic + thermal energy difference"

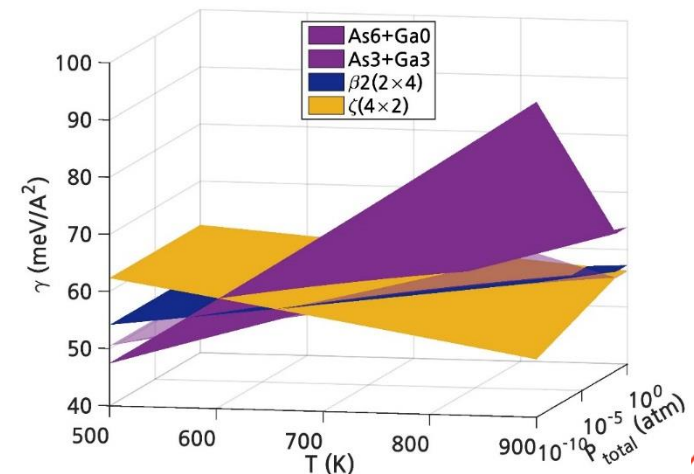
$$\gamma = \frac{(E_{surf}^{elec} + F_{surf}^{vib}) - N_{In}(E_{Ga}^{elec} + F_{Ga}^{vib}) - N_{As}(E_{As}^{elec} + F_{As}^{vib})}{A}$$

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

Without surf. vib.



With surf. vib.



Scientific Reports, 7, 10691 (2017).

Wulff shape(T,P)

$$\gamma^{(001)}(T,P) = min\{\gamma_{i\in(001)\ reconstructions}^{(001)}\}.$$

$$\gamma^{(110)}(T,P) = min\{\gamma_{i\in(110)\ reconstructions}^{(110)}\}.$$

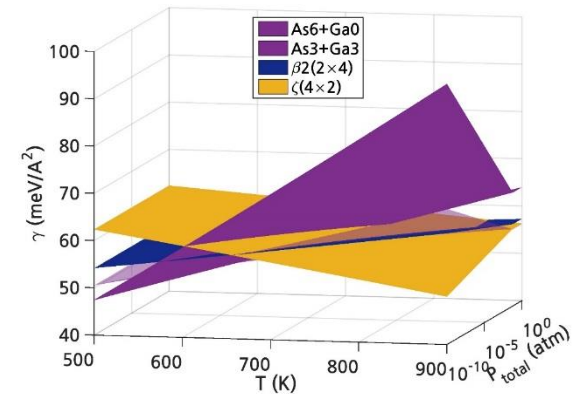
$$\gamma^{(111)A}(T,P) = min\{\gamma_{i\in(111)A\ reconstructions}^{(111)A}\}.$$

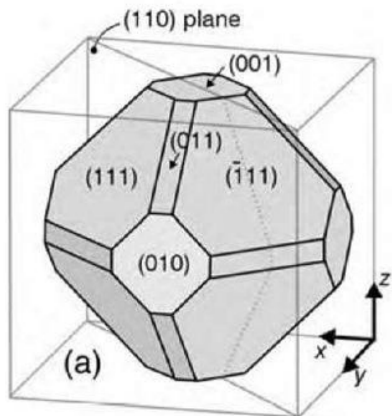
$$\gamma^{(111)B}(T,P) = min\{\gamma_{i\in(111)B\ reconstructions}^{(111)B}\}.$$

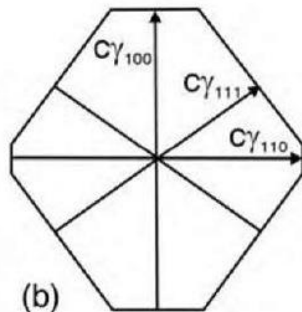
$$\gamma^{(113)A}(T,P) = min\{\gamma_{i\in(113)A\ reconstructions}^{(113)A}\}.$$

$$\gamma^{(113)B}(T,P) = min\{\gamma_{i\in(113)B\ reconstructions}^{(113)B}\}.$$

$$\gamma_{i\in reconstructions}^{(001)}$$







Wulff construction:

minimization of the total surface free energy for the given thermodynamic conditions

$$\frac{\gamma^{(n)}}{h^{(n)}} = constant,$$

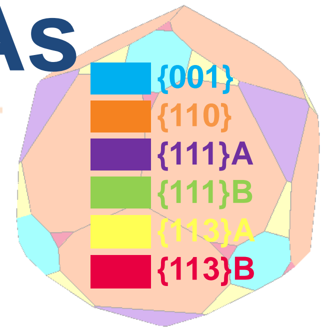
$\gamma^{(n)}$=surface energy of specific orientation

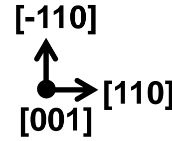
$h^{(n)}$=surface normal

KIST Korea Institute of Science and Technology

Wulff shape(T,P) of GaAs

Simulation





P_{As} (atm)

4.6×10^{-8}

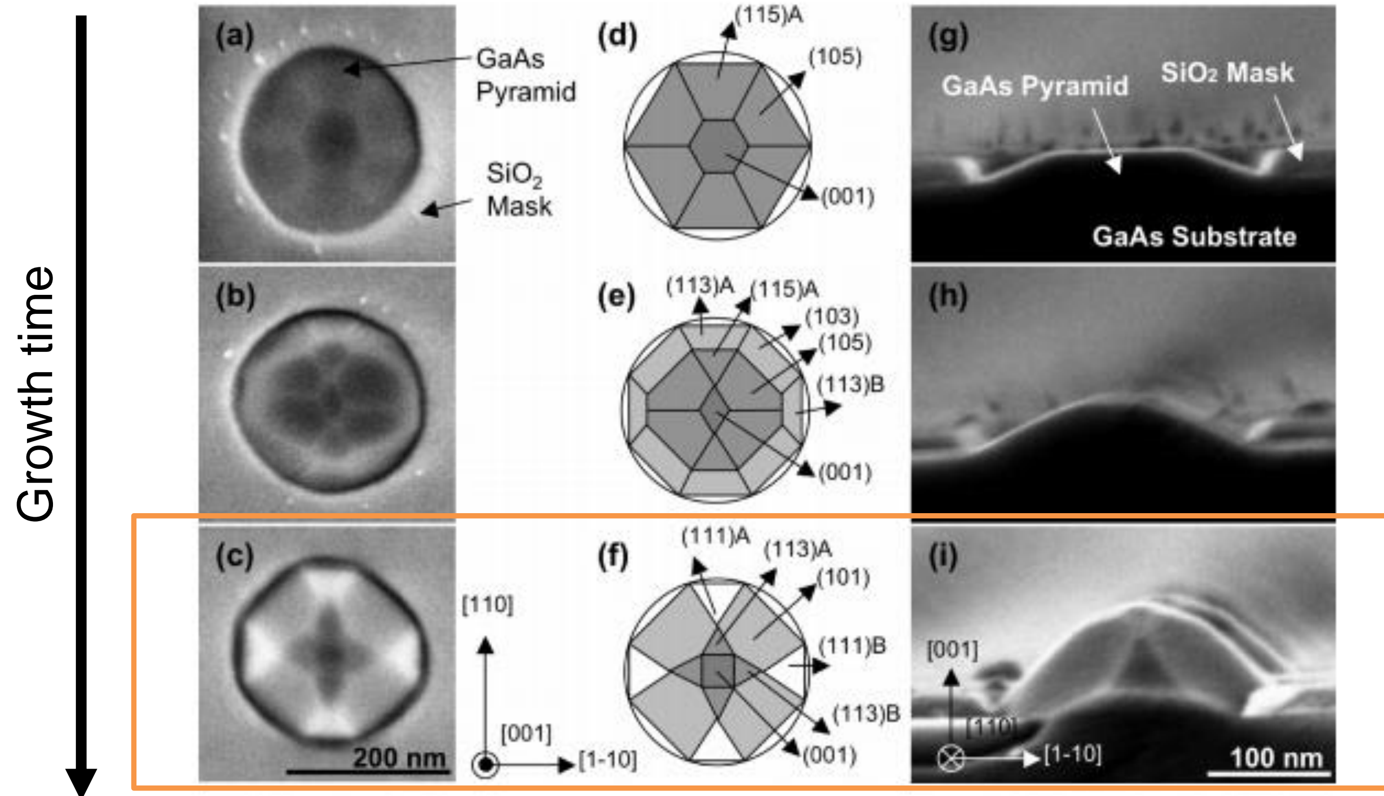
4.6×10^{-9}

T (K)

600 750 900

Homo-Epitaxy of GaAs on GaAs(001)

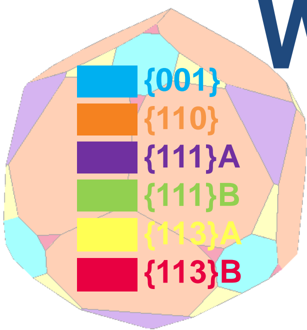
Experiments

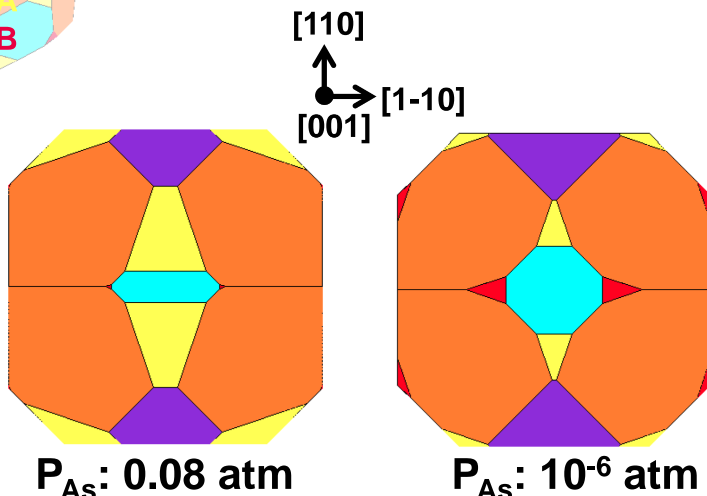
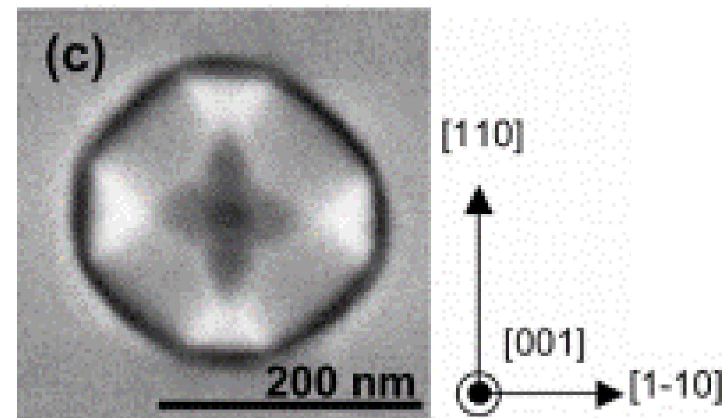
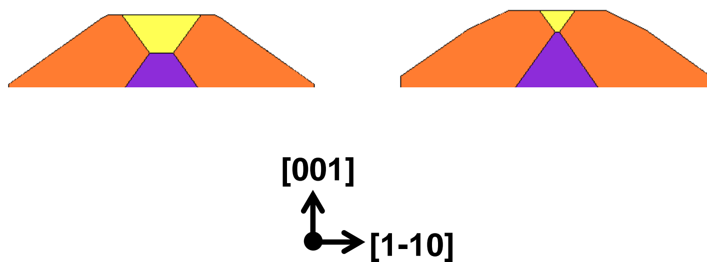
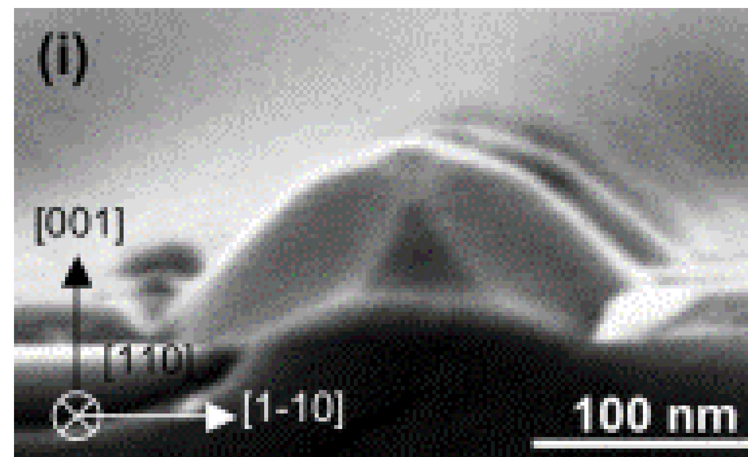


1. MOCVD with trimethyl-Ga and tertiarybutyl-Arsine
2. Temperature: 970 K
3. Pressure: 0.08 atm with V/III ratio of 12.5

Wulff shape vs. Growth shape

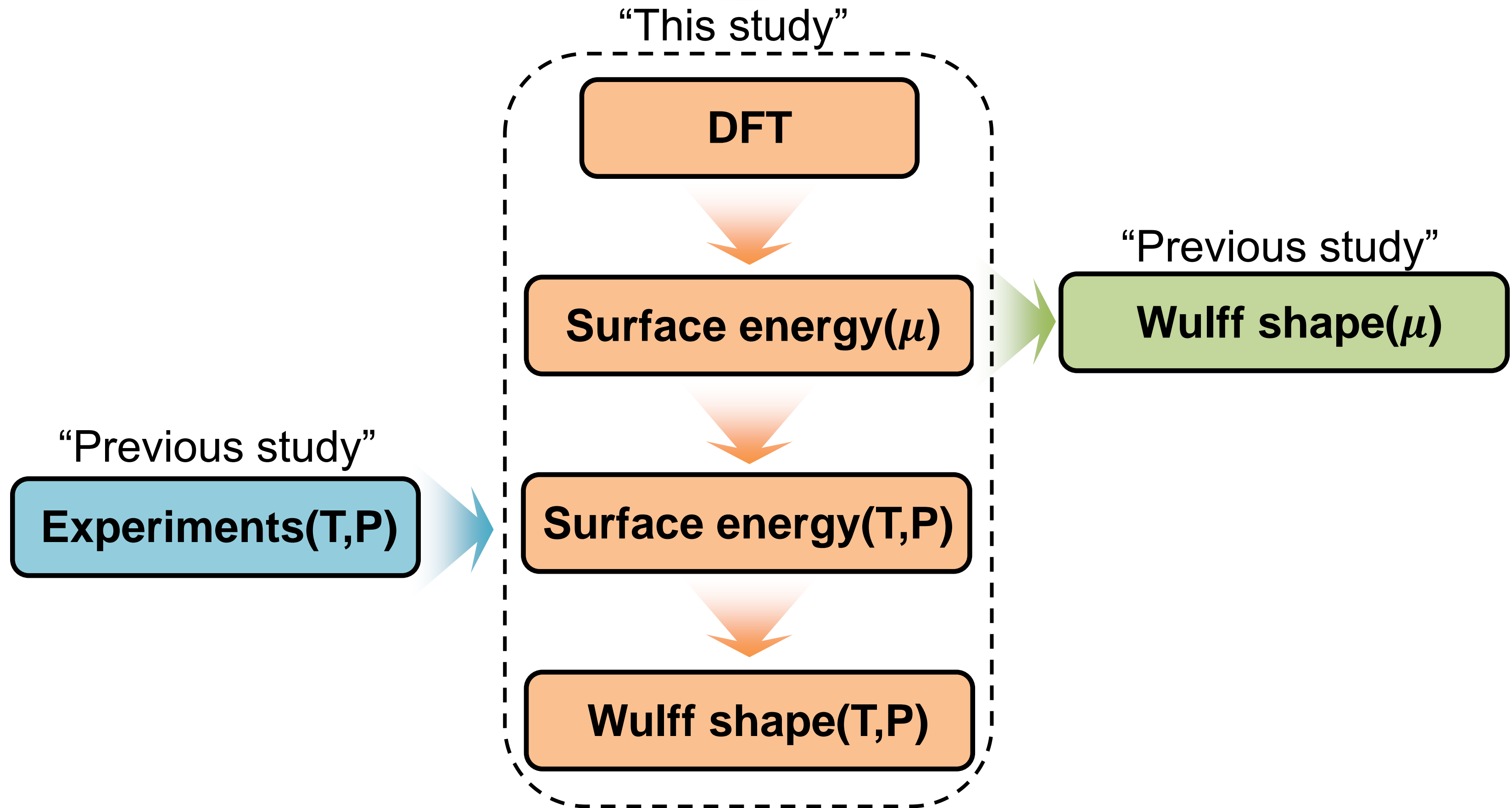
T: 970 K,
P: 0.08 atm



	Simulation	Experiments
Top View		
Side View		

Crystal Growth & Design, 10(6), 2509 (2010).

Summary



1. **Comparable ECS of GaAs is determined by (T,P)**
2. **This method can be applied to other Ⅲ-V**