Atomistic Modeling for the Vapor-Phase Growth of GaAs Nanowires: from DFT to Growth Kinetics

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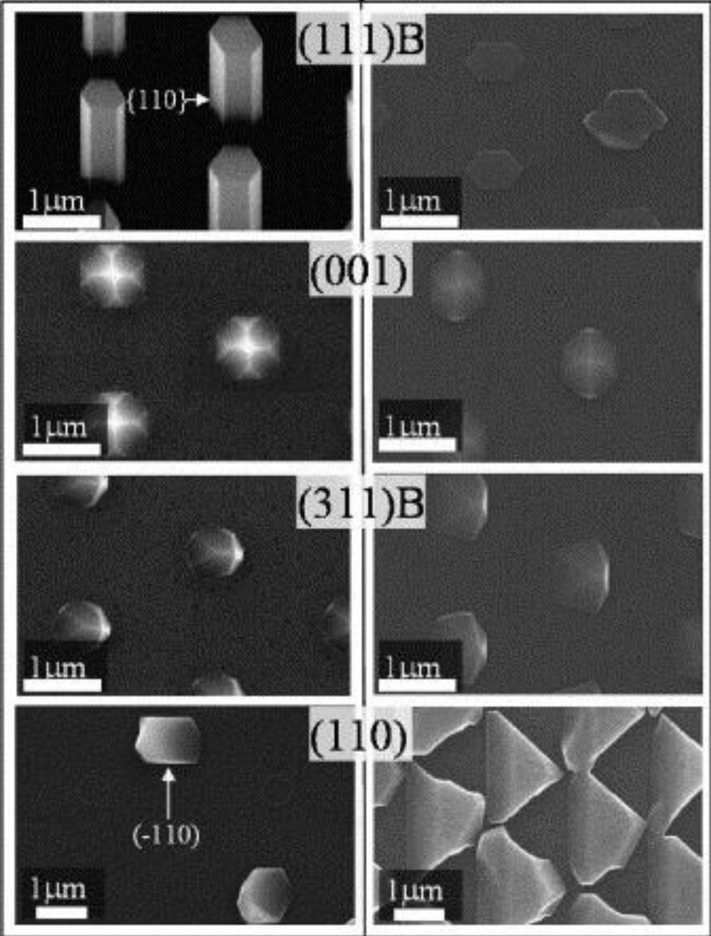
Computational Materials Design

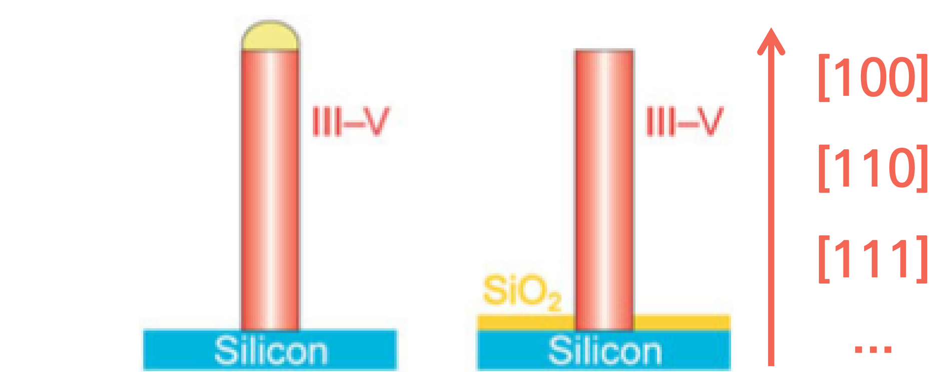
Tue, Mar 2 2021, 13:30-15:30, Poster **O 46.1**

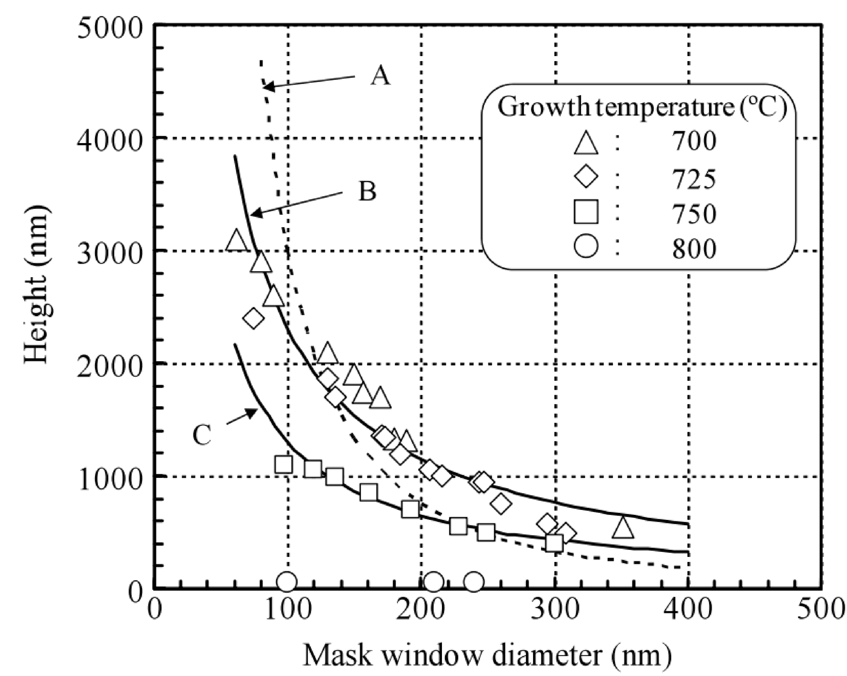
Introduction: GaAs nanowire (NW) growth

✓ Among various crystallographic directions, GaAs NWs prefers to grow along <111>B at narrow (T,P) range



J. Cryst. Growth 298, 616 (2007)

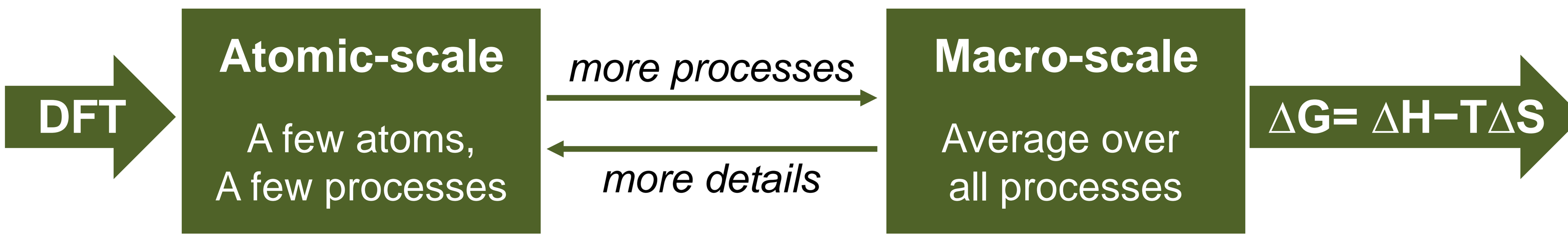


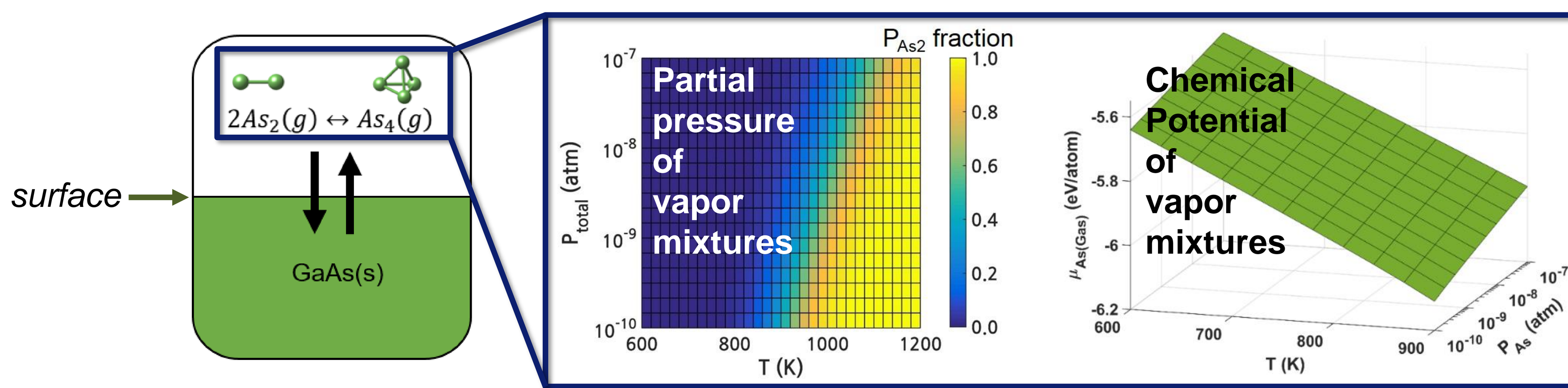


J. Mater. Res. 26, 2127 (2011)

Calculation methods

✓ Scale-bridging simulation approach to Vapor-Solid systems

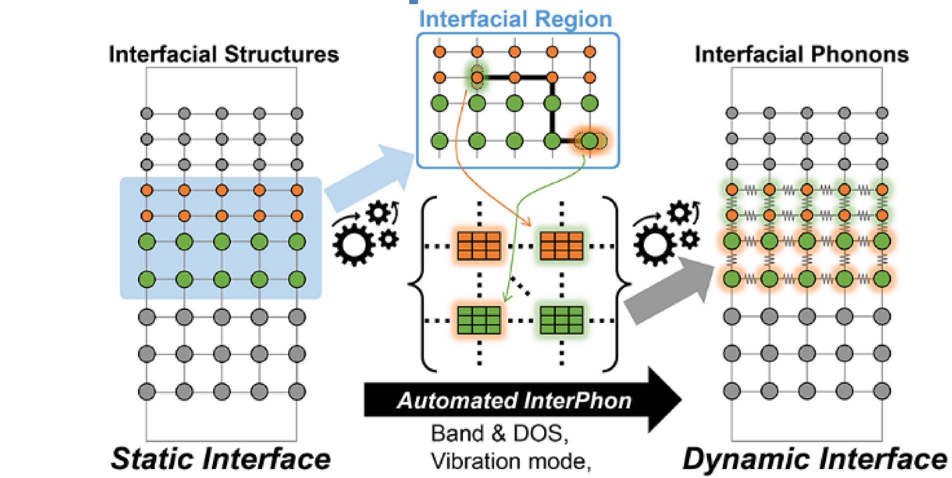




1) Surface structure depends on vapor environments, which can be described by μ_{vapor}(T,P)

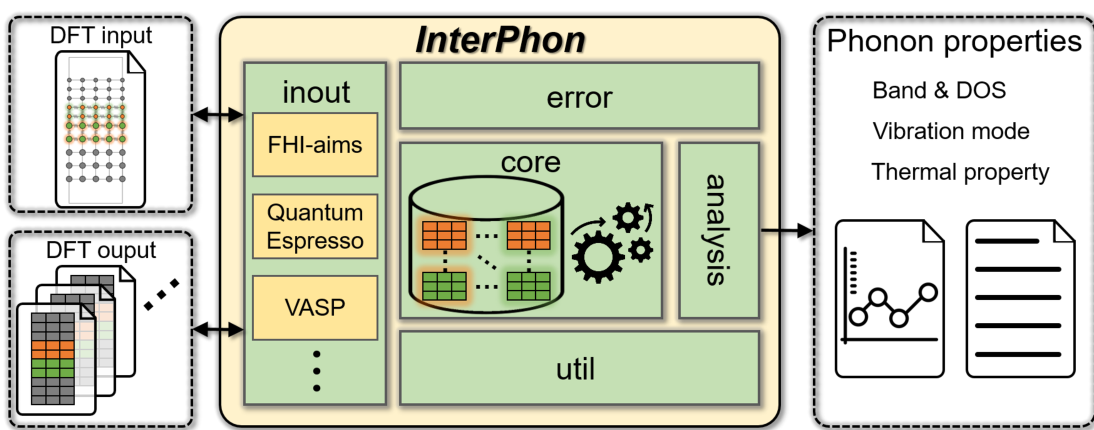
2) μ_{vapor}(T,P) was directly calculated by statistical mechanics taking into account the contributions from translational, rotational, vibrational, and electronic degrees of freedom

✓ Interfacial phonon calculations to obtain surface entropy



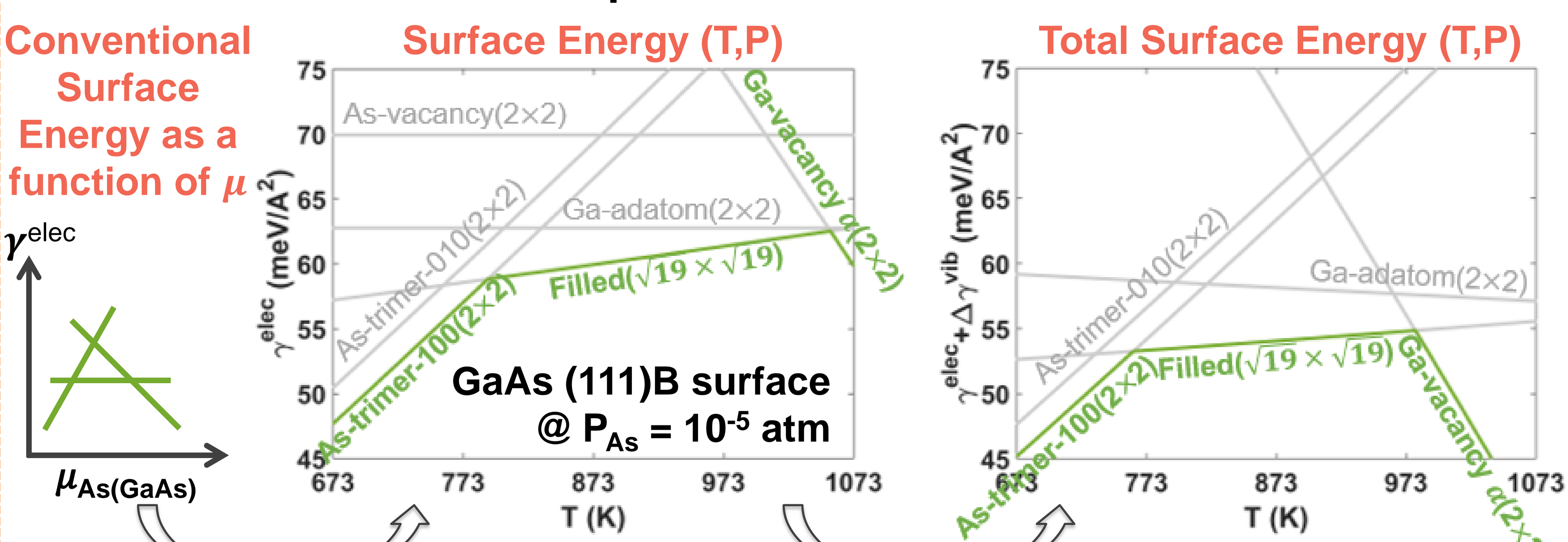
1) Surface introduces vibration patterns that differ from the bulk due to its distinct bonding state and stoichiometry

2) Within InterPhon code, phonon evaluation proceeds only in interface atoms, based on the fact that interfacial phonons are confined to the vicinity of interfacial regions



1) InterPhon: A Python Package for Ab initio Interface Phonon Calculations within a 3D Electronic Structure Framework
2) Source code: https://github.com/InWonYeu/interphon
3) Manual: https://interphon.readthedocs.io/
4) Reference paper: Yeu et al., arXiv:2012.04198 (2020)

✓ Prediction for T-P dependent surface structure transitions



$\mu_{As(Gas)} = \mu_{As(GaAs)}$ $\quad$ $\gamma = \gamma^{elec} + \Delta\gamma^{vib}$

Yeu et al., Sci. Rep. 7, 10691 (2017) $\quad$ Yeu et al., Sci. Rep. 9, 1127 (2019)

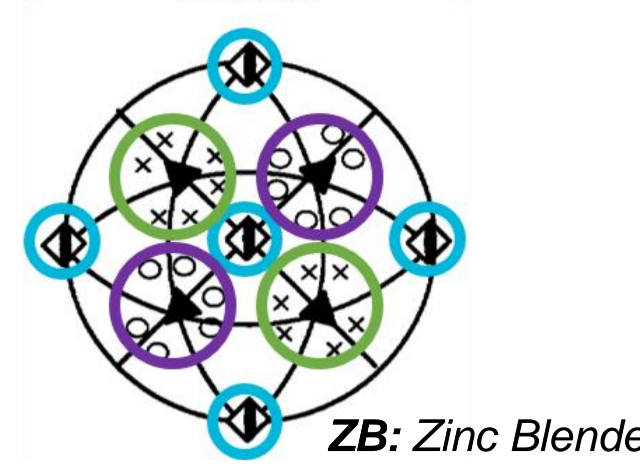
1) μ of surface and vapor will be the same If chemical equilibrium is reached

2) $\Delta\gamma^{vib}$ comes from the difference in vibrational entropy between surface and bulk

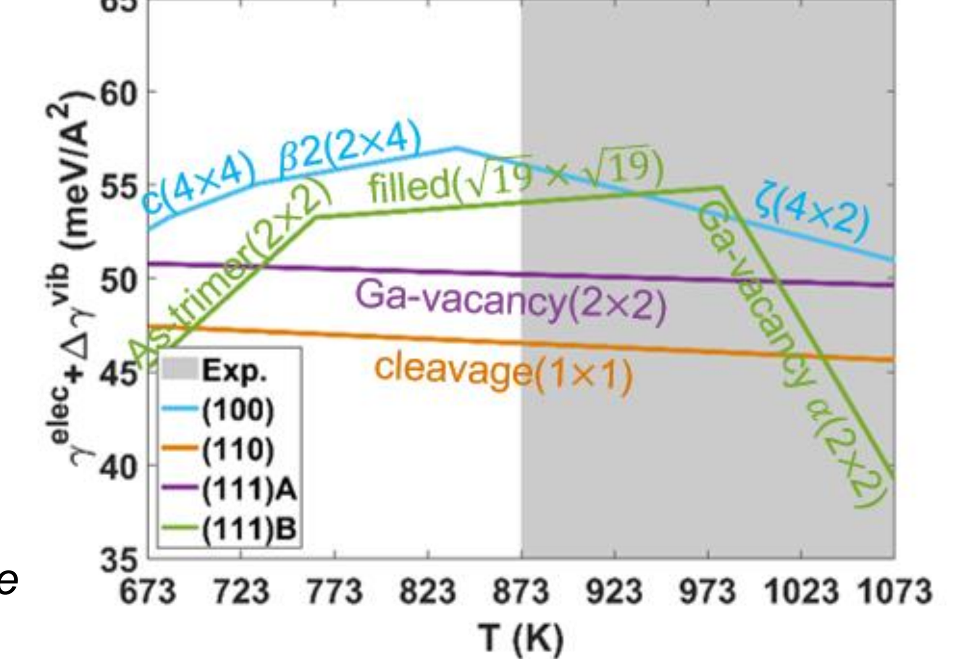
Results 1: Anisotropic growth of GaAs NW

✓ Why is the growth of GaAs NWs allowed selectively along <111>B at narrow (T,P) range?

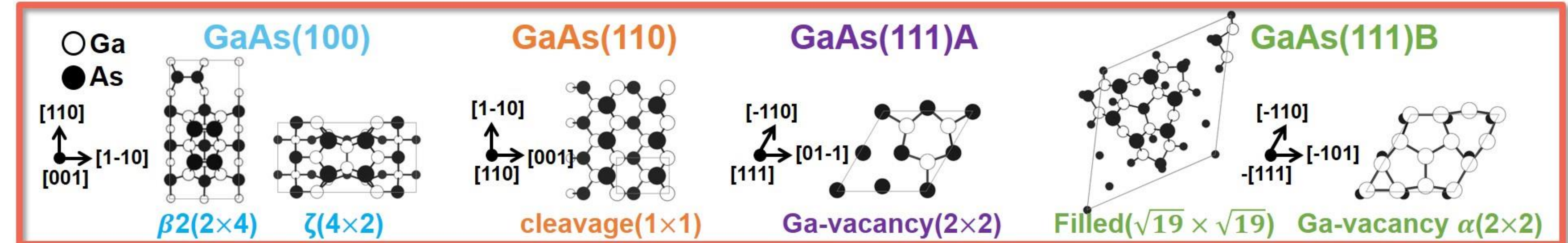
Stereographic Projection of ZB



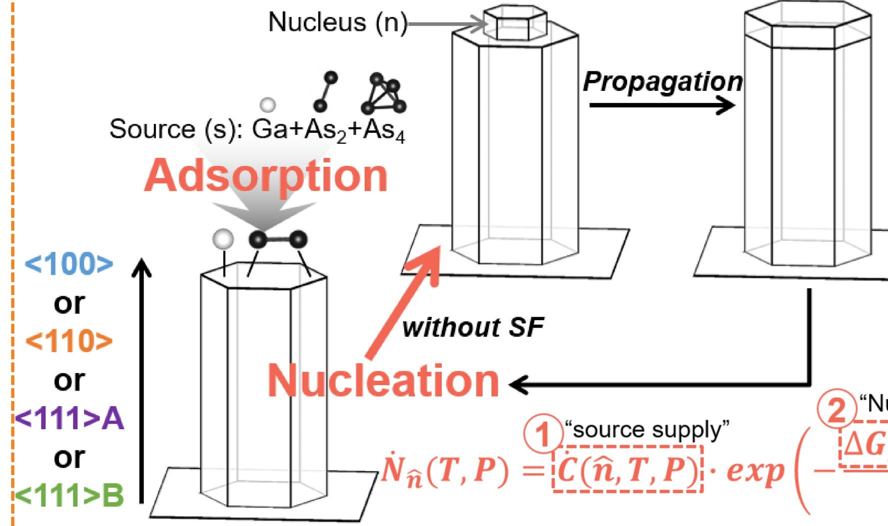
Anisotropic Transition of Surface Structure



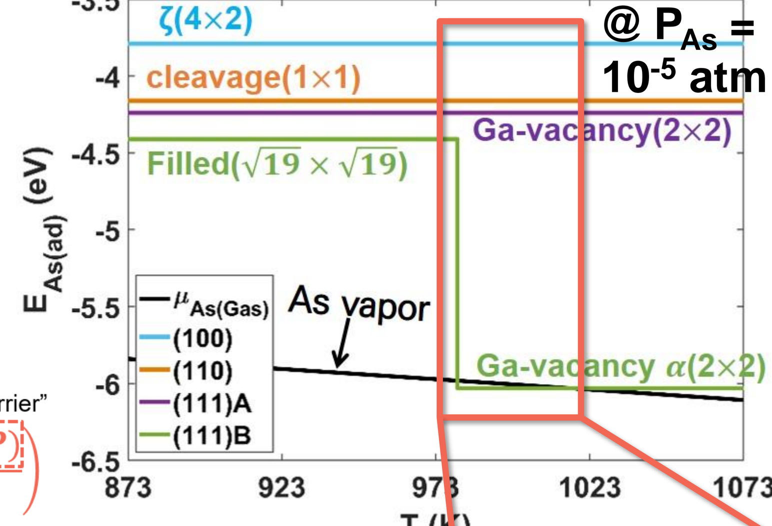
Most Stable Reconstructions of Each Surface Orientation



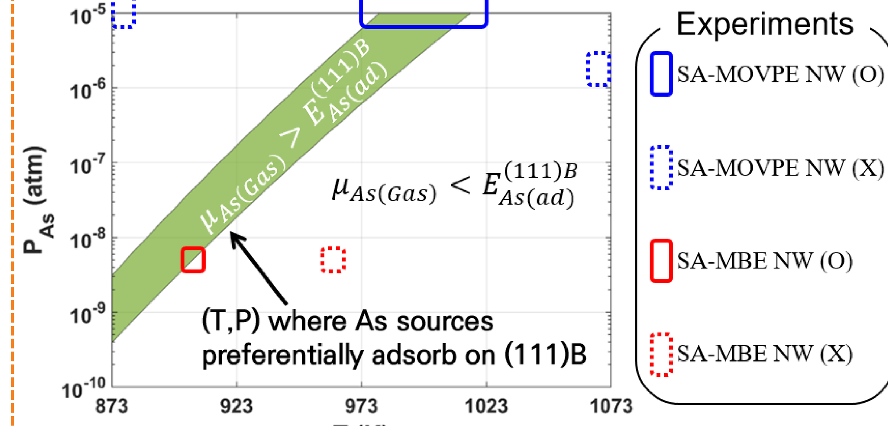
Schematic of Nucleation and Growth

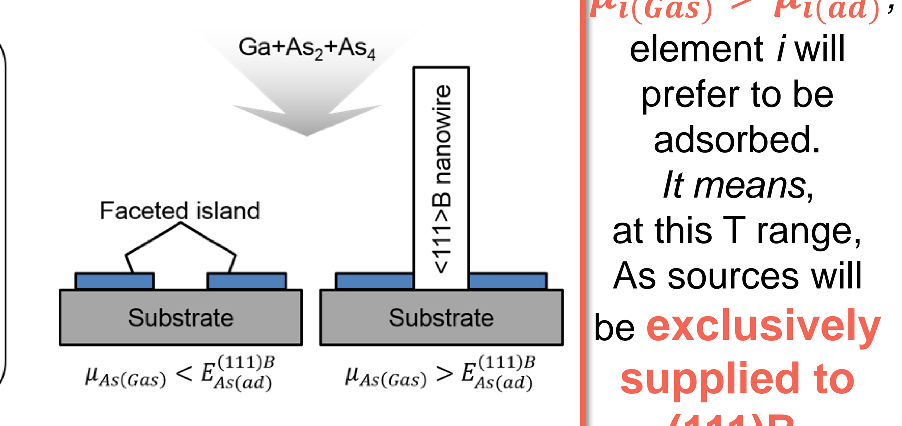


Anisotropic Adsorption of Sources



Preferential Adsorption → Preferential Nucleation → <111>B NW



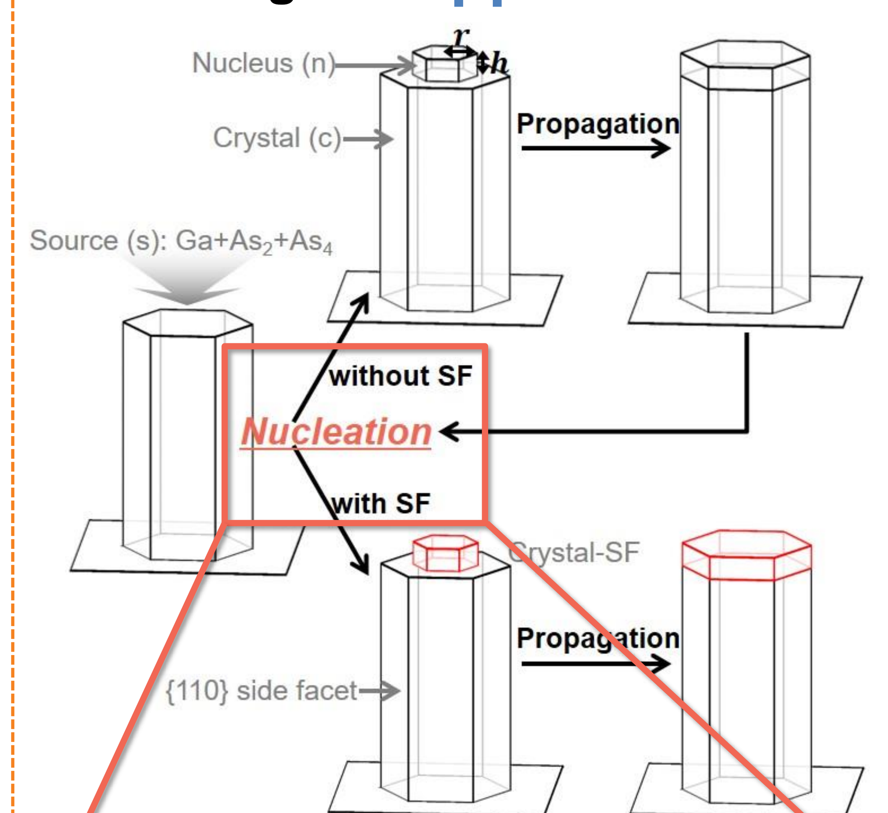


If $\mu_{i(Gas)} > \mu_{i(ad)}$, element i will prefer to be adsorbed. It means, at this T range, As sources will be exclusively supplied to (111)B.

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

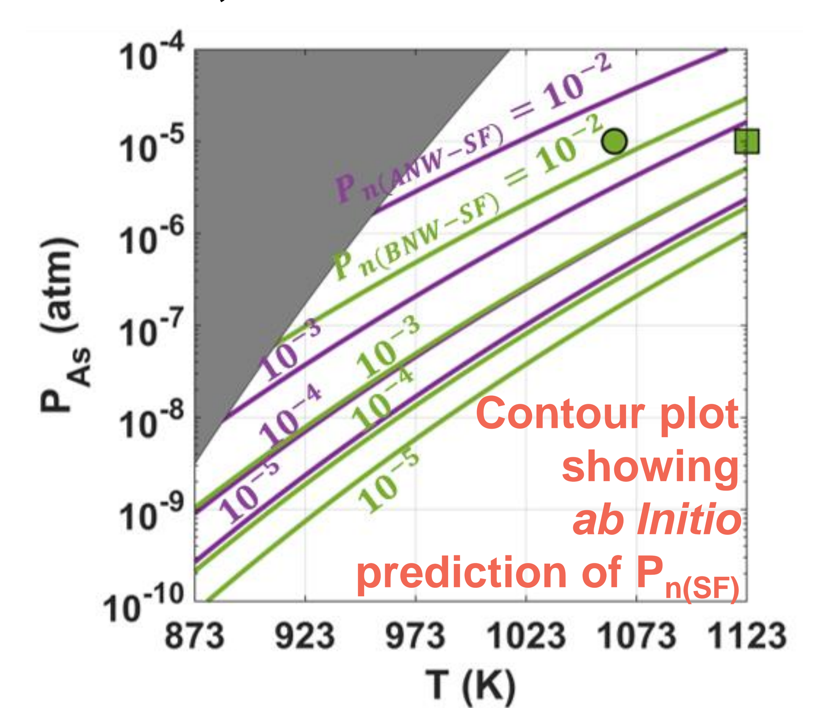
Results 2: Asymmetric stacking of GaAs NW

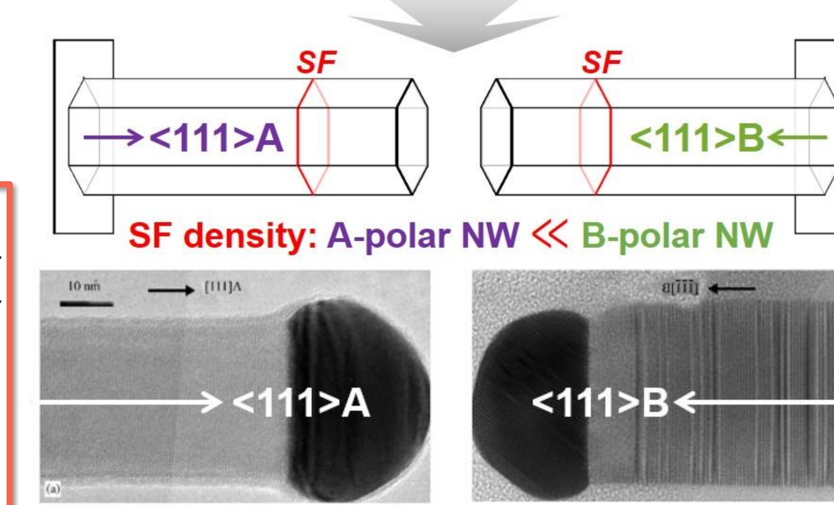
✓ Why is the SF in GaAs NWs formed asymmetrically along two opposite directions of <111>, <111>A & <111>B?



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

ZB: Zinc Blende
SF: Stacking Fault
$P_{n(SF)}$: SF probability





J. Cryst. Growth 287, 5004 (2006)

Yeu et al., Nanoscale 12, 17703 (2020), Outside Front Cover

Summary

1) Considering the surface transitions, the change in Gibbs free energy was calculated as a function of T and P at each growth stage on surfaces: adsorption and nucleation.

2) The mechanism of extreme anisotropic growth of GaAs (spontaneous NW formation): preferential adsorption of vapor sources on (111)B surface, allowed at narrow T-P range.

3) The mechanism of asymmetric formation of stacking sequence: different nucleation behavior on the different polar surfaces, (111)A and (111)B.

DPG-Frühjahrstagung (DPG Spring Meeting) of the Surface Science Division, Mar 1st ~ 4th, 2021

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