Mathematical Aspects of Surface and Interface Dynamics 16

Lecture Hall / Room 056,
Graduate School of Mathematical Sciences,
The University of Tokyo

October 17-19, 2018

14:20 – 15:00

Influence of surface reconstruction on the impurity incorporation in GaN MOVPE

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NAGOYA UNIVERSITY

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Satoshi Yamamoto (MC 2017-)


Nagoya University

Kenji Shiraishi, Prof.
Atsushi Oshiyama, Designated Prof.

Poland



Michał Boćkowski, Prof. (UNIPRESS)
Stanisław Krukowski, Prof. (UNIPRESS)
Paweł Kempisty, Assistant Prof. (UNIPRESS)

OUTLINE

Introduction

- ✓ *Background* *~ Roles of crystal growth simulations ~*

Methodology

- ✓ *Ab initio based−approach*

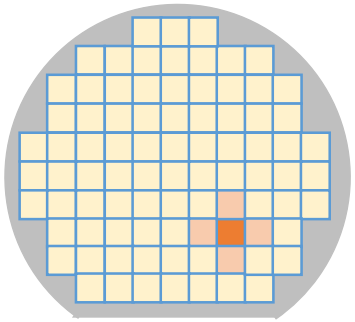
Results

- ✓ *Influence of growth orientation on InGaN composition*
- ✓ *Incorporation mechanism of C & O in GaN MOVPE*

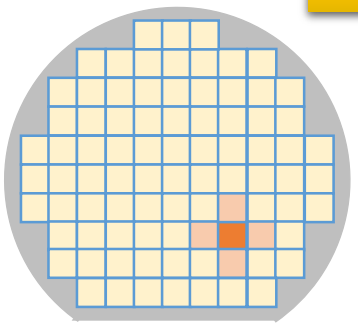
Summary

Background ~ Roles of crystal growth simulations ~

Experiments



Know-how



[*in situ analyses*]
- ✓ Surface measurements (Laser, X-ray, …)
- ✓ Strain measurements (Curvature)

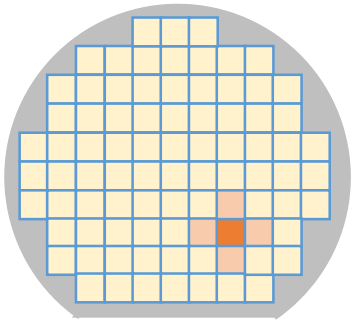
[*ex situ analyses*]
- ✓ Device properties
- ✓ TD distribution
- ✓ Impurity distribution *etc.*

- ➢ Physical model ☹
- ➢ Principles of crystal growth ☹

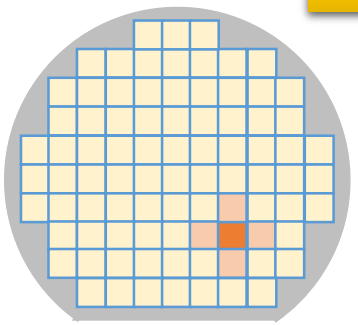
Background ~ Roles of crystal growth simulations ~

In situ DATA

Experiments



Know-how



[*in situ analyses*]
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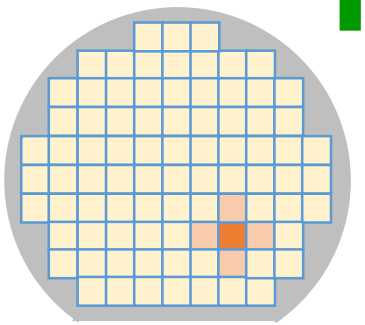
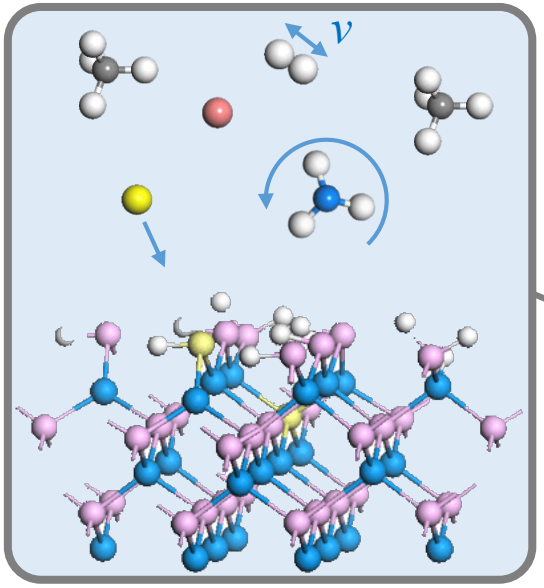


[*Multi-physics simulation*]
- ✓ Temperature distribution
- ✓ Growth rate *vs* Crystal orientation
- ✓ Impurity incorporation *etc.*

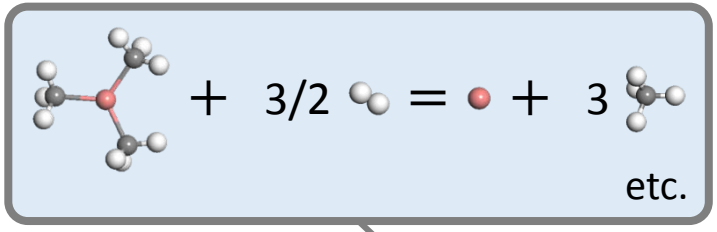
- ➢ Physical model, Principles of CG
- ➢ Acceleration of materials and device development

III-Nitride MOVPE

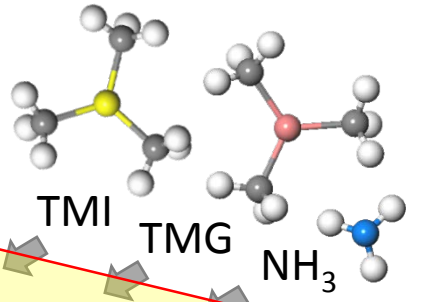
Surface reactions
& growth kinetics



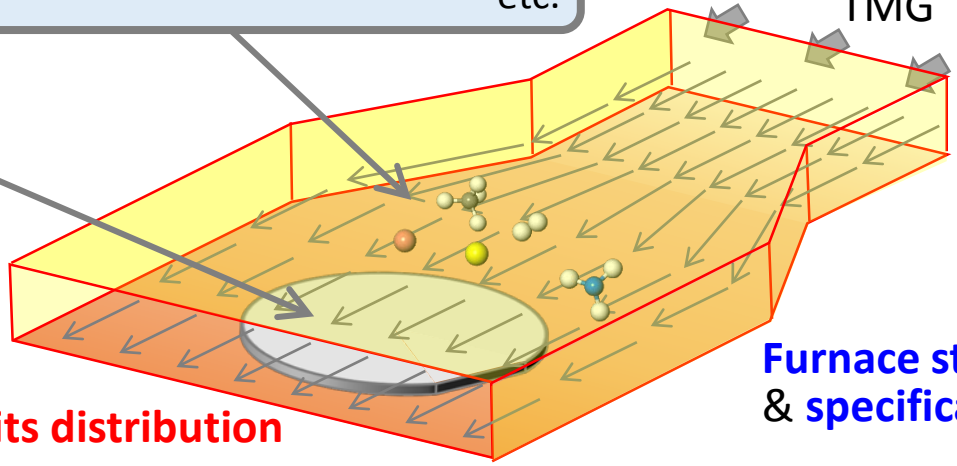
Gas flow rate
& gas phase reactions



Gas species
& their partial pressures (*p*)



with IG



Temperature (*T*) & its distribution

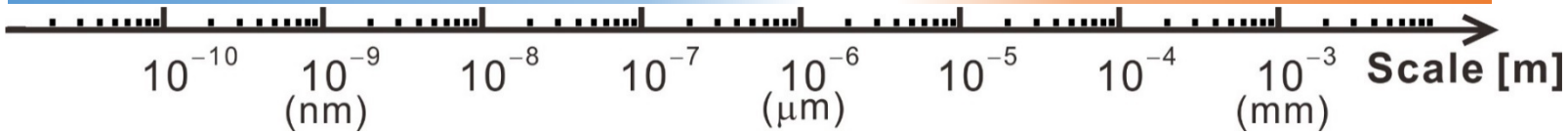
Furnace structures
& specifications

Scale of phenomena

Gas phase reactions,
Surface reactions,
Growth kinetics

Gas flow rate,
Temperature distribution

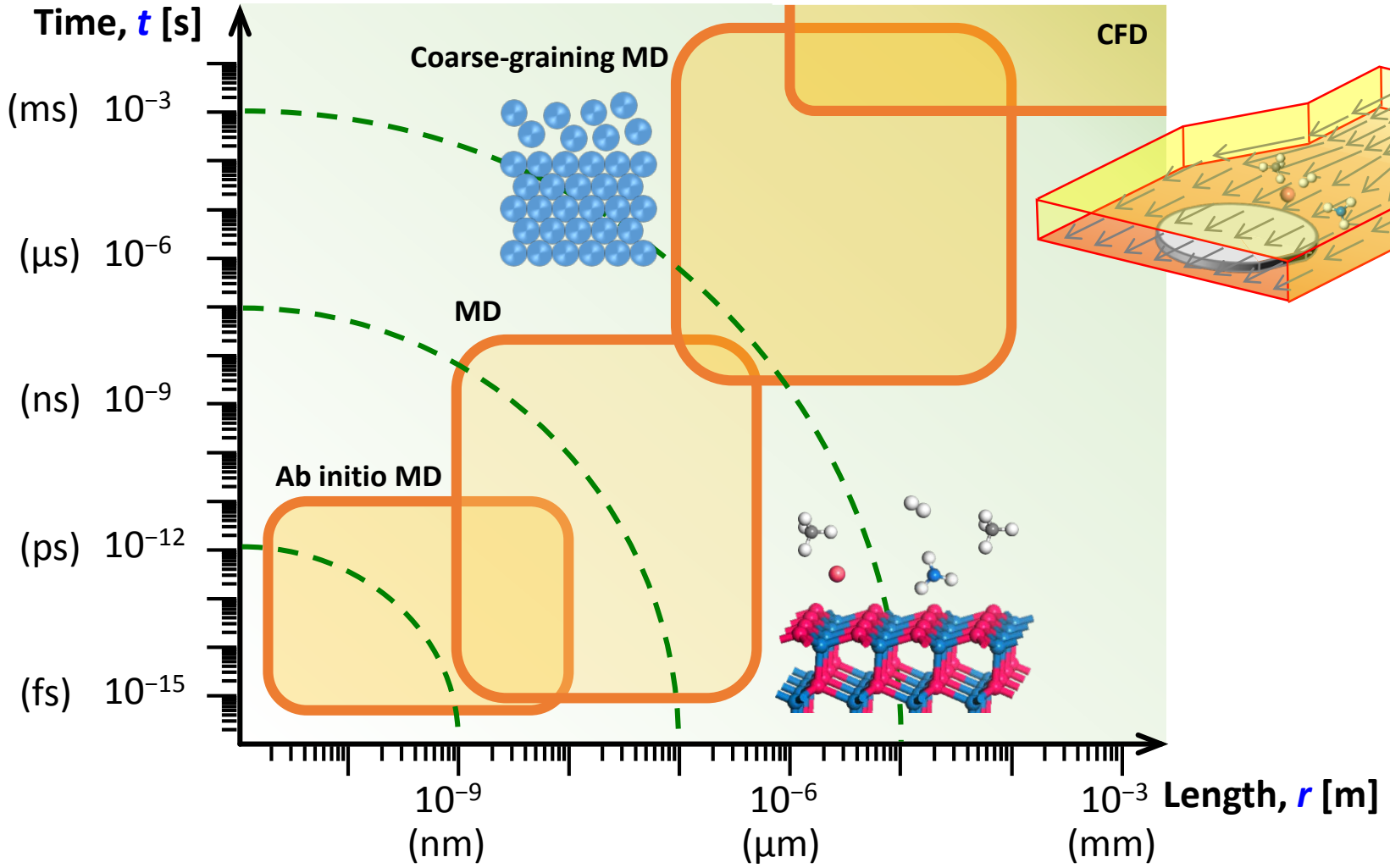
Dynamic range > 10^8



Background ~ Roles of crystal growth simulations ~

Conventional multi-scale simulation method

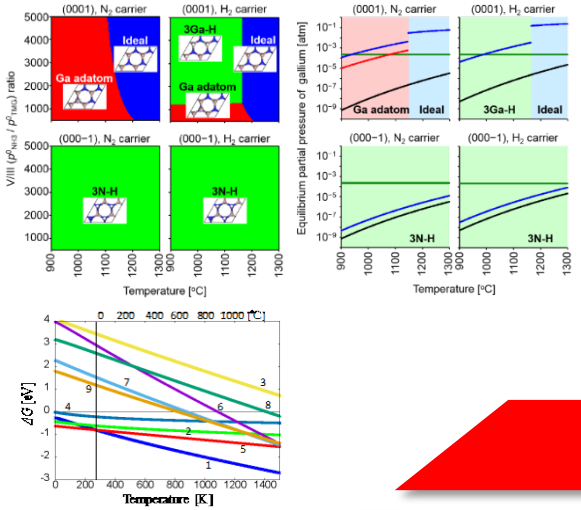
Missing links in *r* and *t*

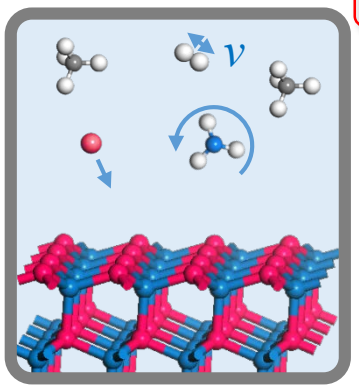


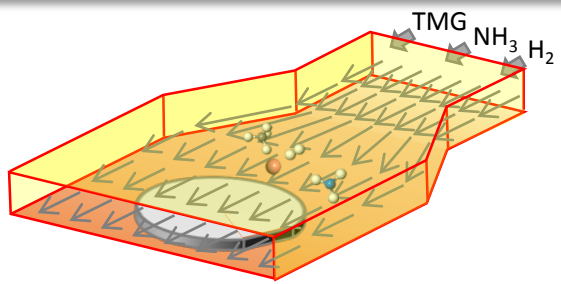
Background ~ Roles of crystal growth simulations ~

New concept

✓ **Paradigm shift:** from **r, t** to **p, T**







DATA Base

Exp.

prediction

upload

upload

p, T

install

install

comparison

Problem

Ab initio | **Thermodynamics** | **Fluid dynamics**

0 atm, Absolute zero

Pseudo equilibrium

Time [s]

(ms) 10^{-3}

10^{-9} (nm)

10^{-6} (μm)

10^{-3} (mm)

Length [m]

Nano – Macro scale relationship

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- ✓ *Incorporation mechanism of C & O in GaN MOVPE*

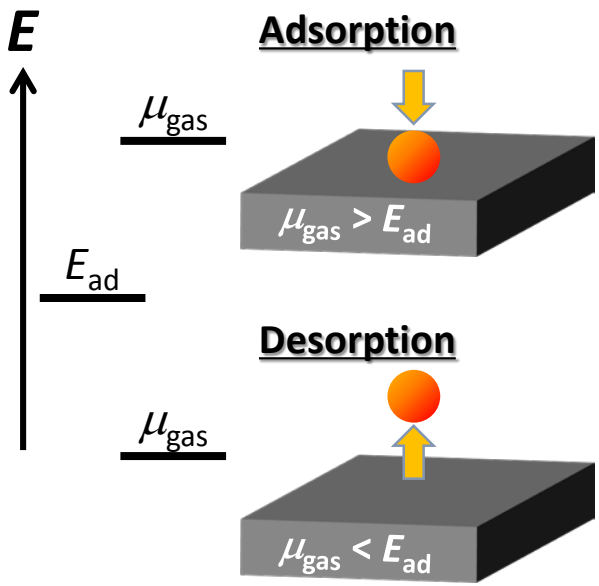
Summary

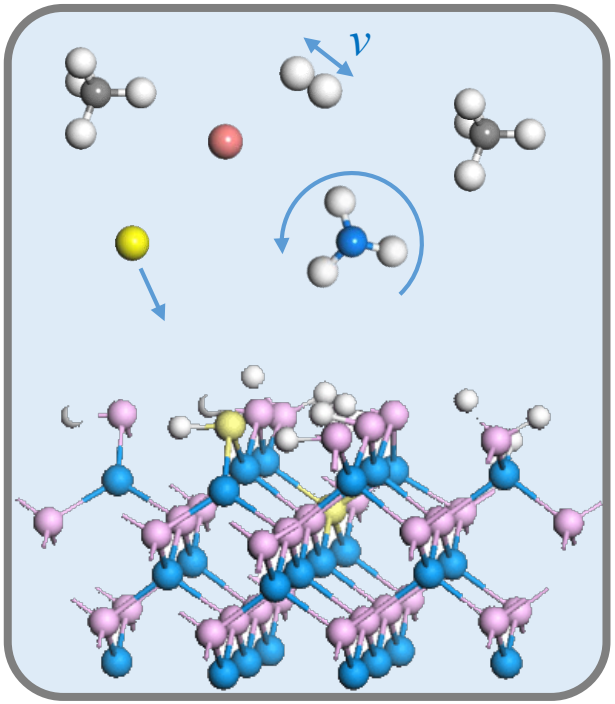
Ab initio based-approach

Paradigm shift

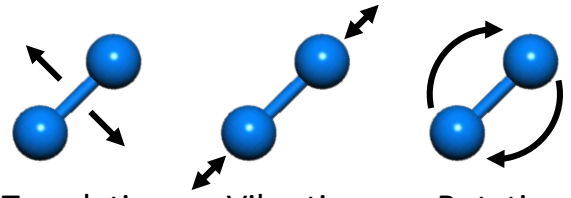
Ab initio **$\mu - E$** YK 2001 **$p - T$**

Ab initio-based approach





***eg.*, Entropy term of diatomic molecule**



$$\mu_{N2} = -k_B T \ln(g k_B T/p \times \zeta_{trans} \times \zeta_{rot} \times \zeta_{vibr}),$$

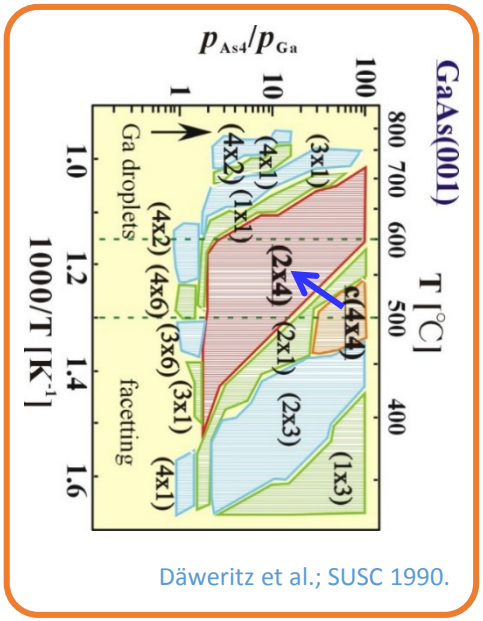
$$\zeta_{trans} = (2\pi m k_B T/h^2)^{3/2},$$
$$\zeta_{rot} = 8\pi^2 I k_B T/(\sigma h^2),$$
$$\zeta_{vibr} = \{1 - \exp(-h\nu/k_B T)\}^{-1}.$$

k_B: Boltzmann's const., ***T*: Temperature**,
***p*: partial pressure**, h: Planck's const.,
g: Degree of degeneracy of electron energy level,
m: Mass of a particle, σ: Symmetry factor,
I: Moment of inertia, ν: Frequency.

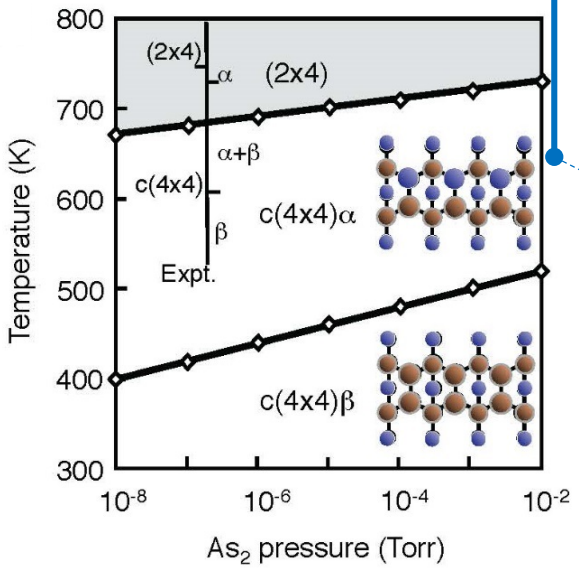
$$G = E_{slab}^{recon} - \left[E_{slab}^{ideal} + n_{Ga}^{ad}\mu_{Ga}^{gas} + \frac{1}{2}n_{N}^{ad}\mu_{N2}^{gas} + \frac{1}{2}n_{H}^{ad}\mu_{H2}^{gas}\right].$$

G: Gibbs free energy, ***n***: number of adatoms, ***μ***: chemical potential
(***μ*** is functions of ***p*** and ***T***)

Ab initio based−approach

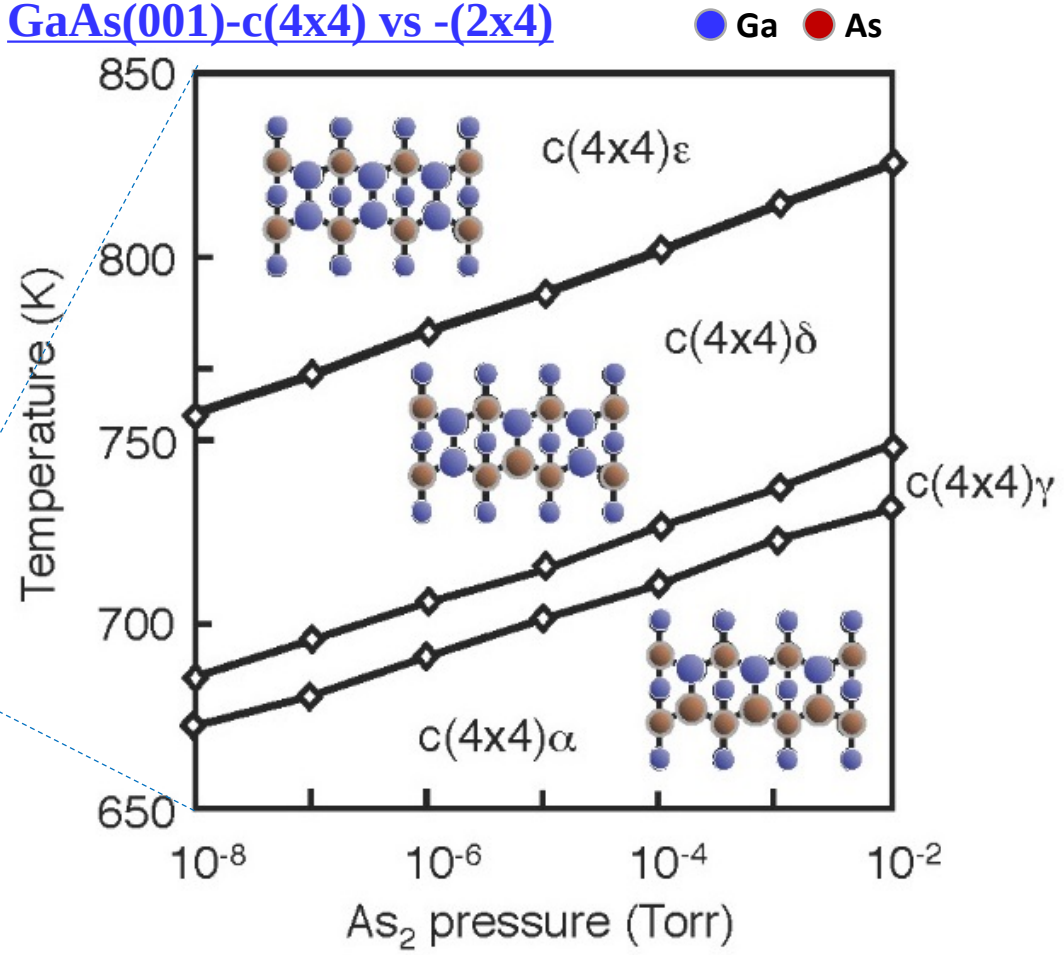


Däweritz et al.; SUSC 1990.



MBE

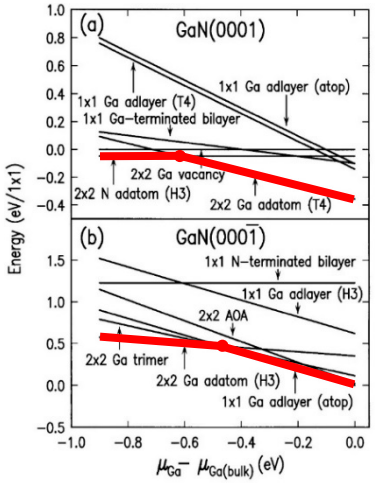
GaAs(001)-c(4x4) vs -(2x4)



Calc.: T. Ito 2005, 2014,
Expt.: A. Ohtake 2002, 2004

Ab initio based-approach

Before 2000



A. R. Smith, PRL 79 (1997) 3934

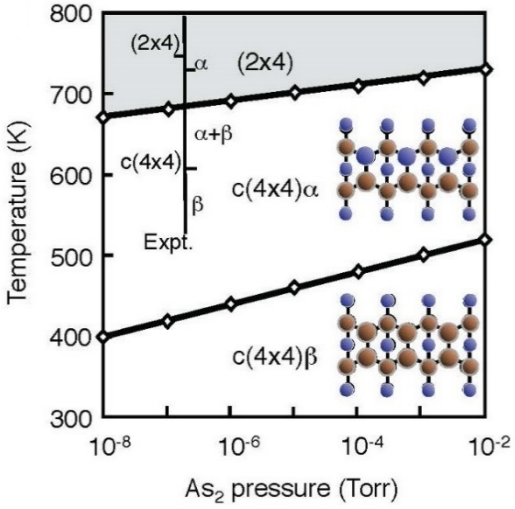
Theorists

$E, \mu_A, \mu_B, \mu_C, \ldots$

Experimentalists

$T, p_A, p_B, p_C, \ldots$

After 2001



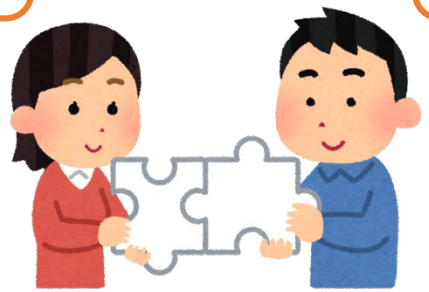
T. Ito & YK, 2014

Theorists

$T, p_A, p_B, p_C, \ldots$

Experimentalists

$T, p_A, p_B, p_C, \ldots$



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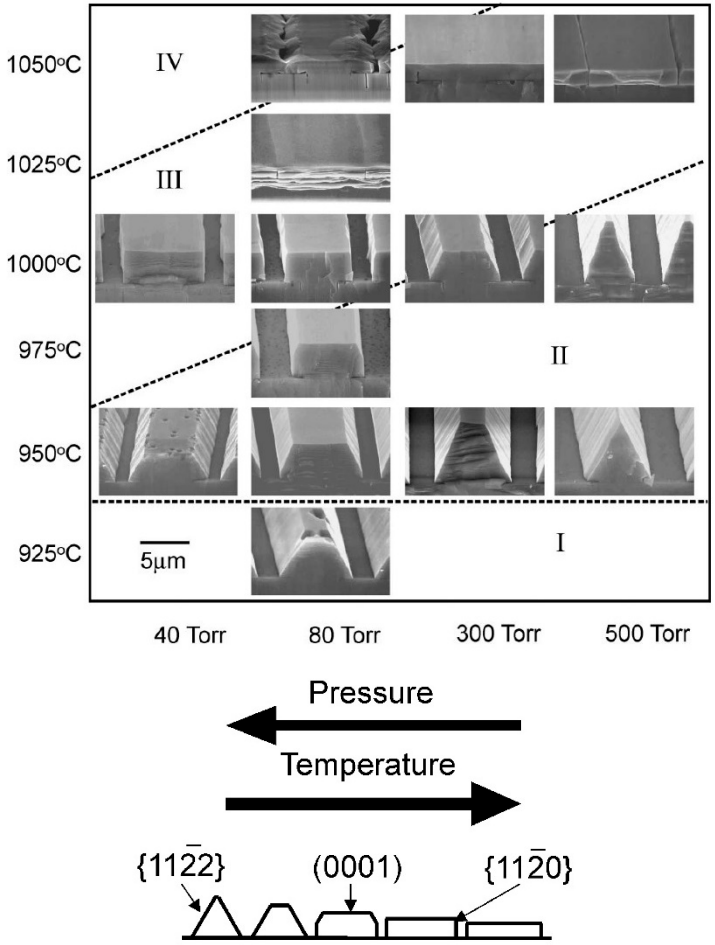
Summary

Influence of growth orientation on InGaN composition

GaN(0001)-MOVPE *Influence of growth orientation*

<1$\bar{1}$00> stripes

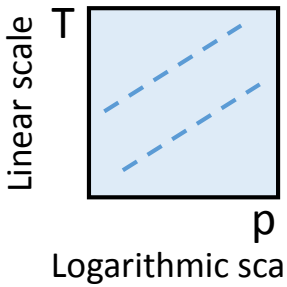


K. Hiramatsu et al., JCG 221 (2000) 316.

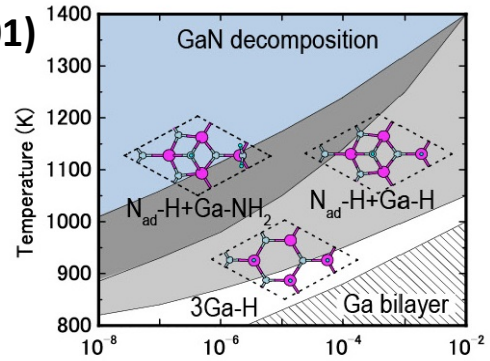
Ab initio

Similar trend

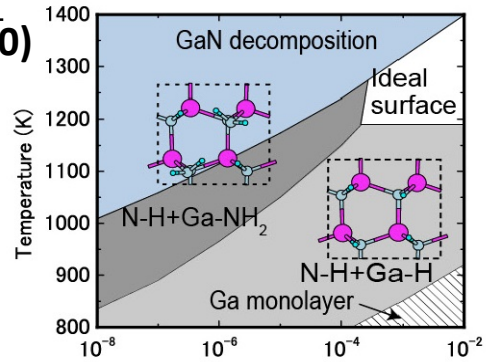
Up to the right boundary



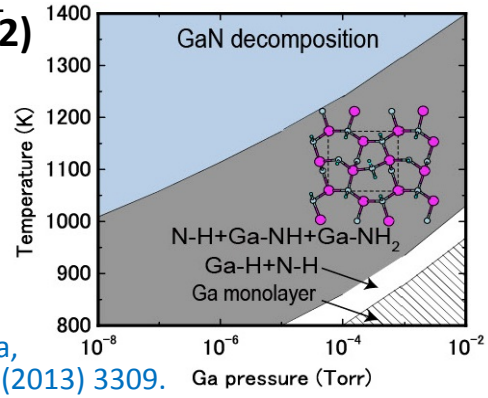
(0001)



(11$\bar{2}$0)



(11$\bar{2}$2)



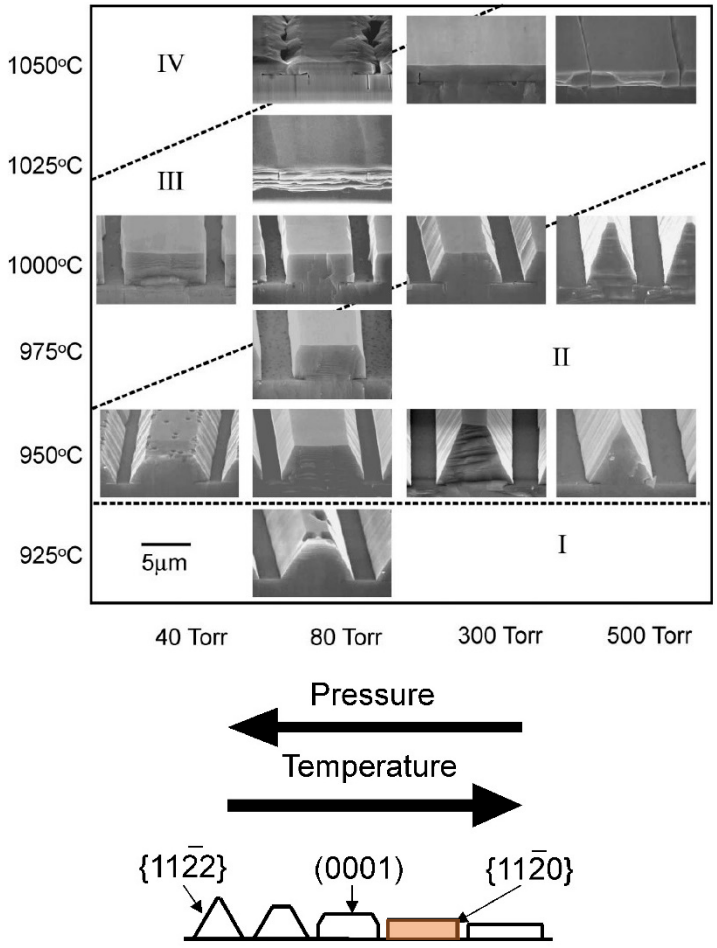
YK, T. Akiyama, T. Ito, K. Shiraishi, T. Nakayama, Materials 6 (2013) 3309.

(p_{H2} = 76 Torr)

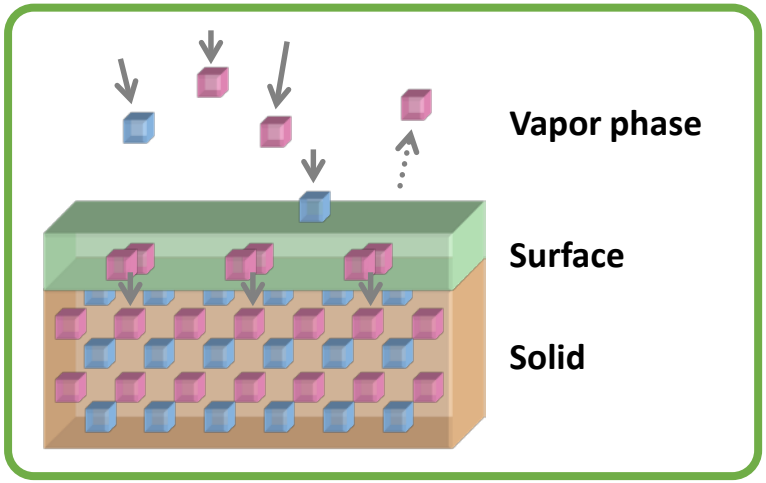
Influence of growth orientation on InGaN composition

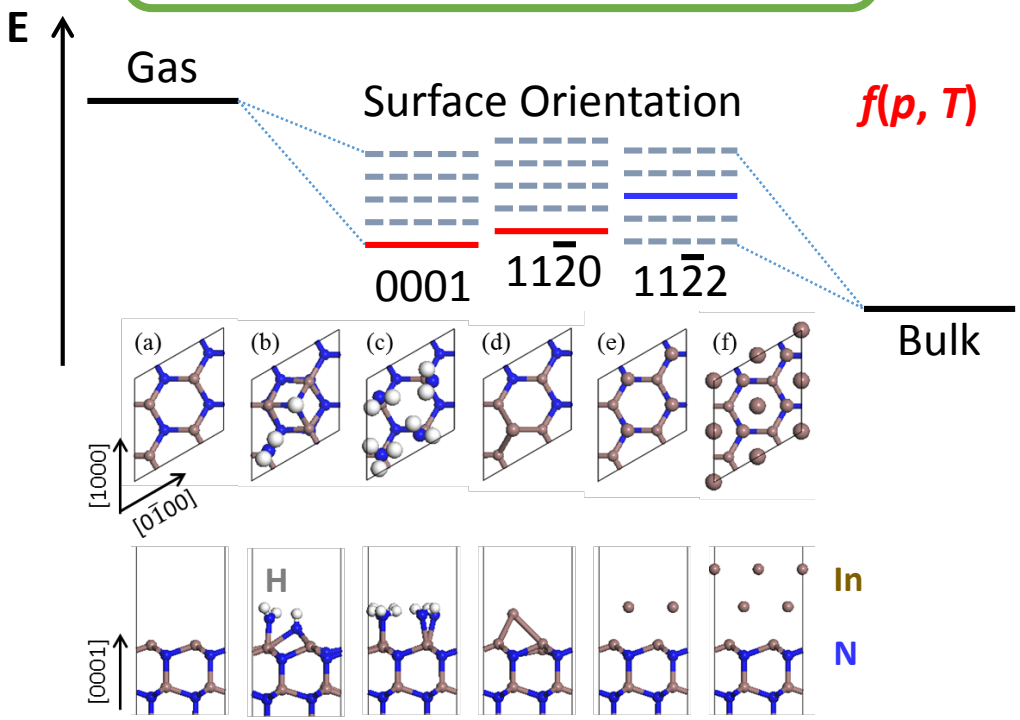
GaN(0001)-MOVPE

<1$\bar{1}$00> stripes



K. Hiramatsu et al., JCG 221 (2000) 316.





Influence of growth orientation on InGaN composition

GaN(0001)-MOVPE

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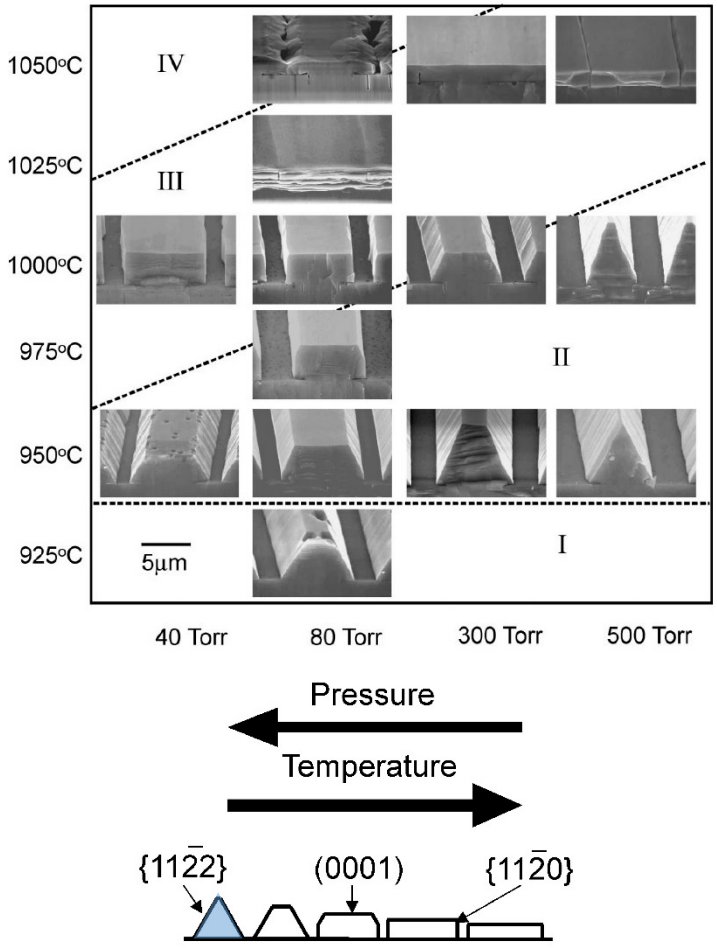

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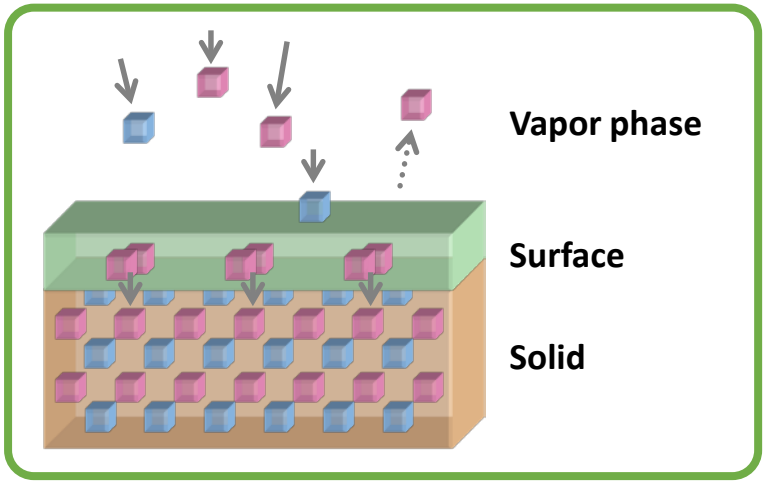
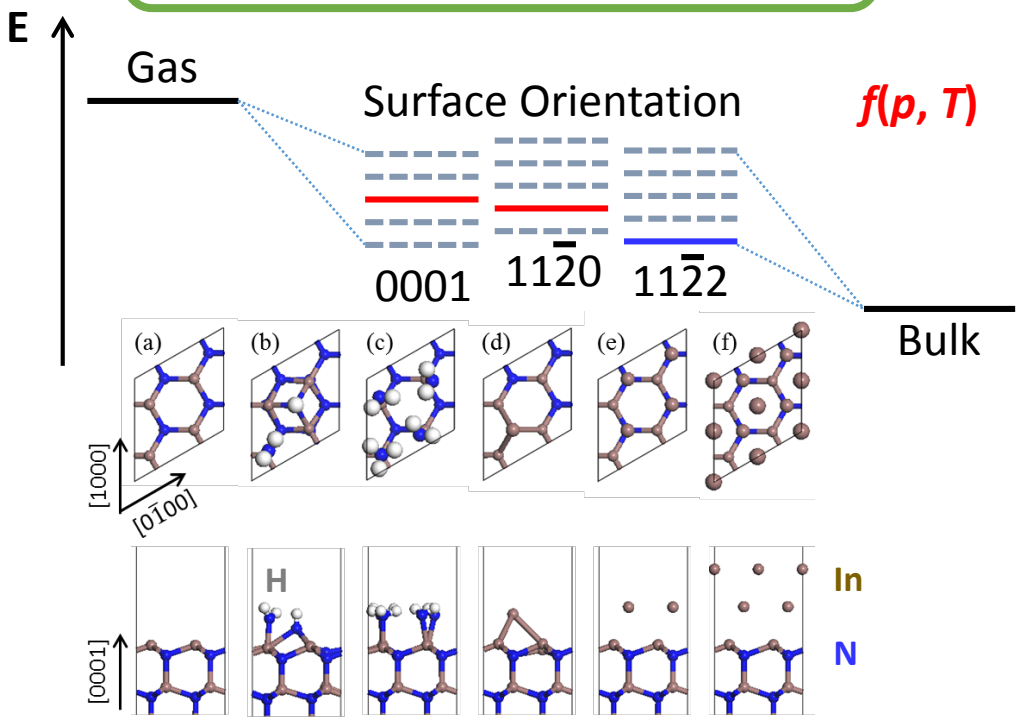




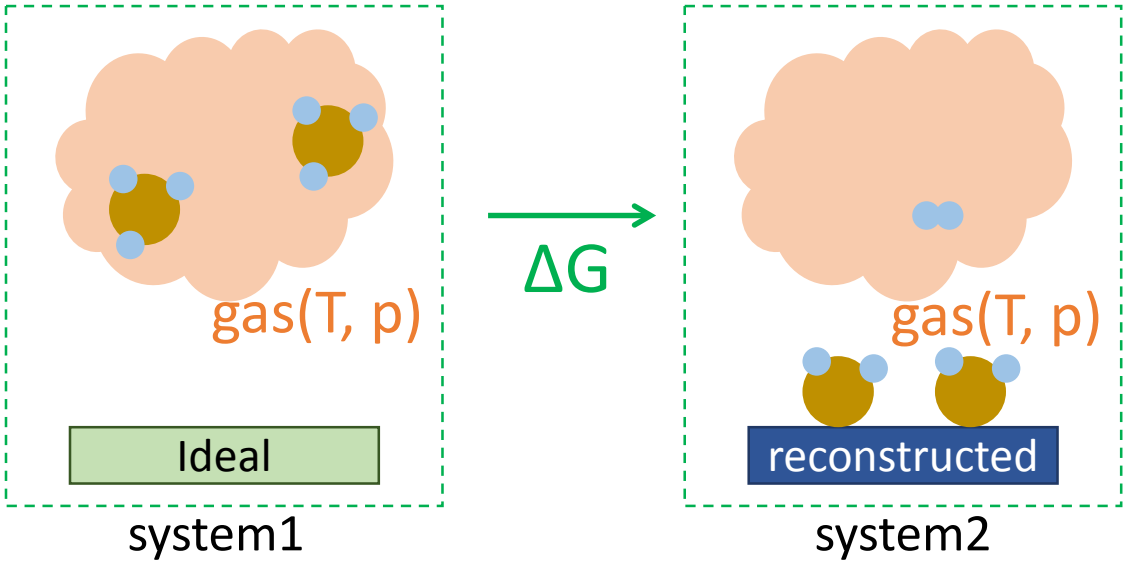
Influence of surface reconstruction on the impurity incorporation in GaN MOVPE

Yoshihiro Kangawa (Kyushu University/Nagoya University)

Influence of growth orientation on InGaN composition

The reconstructed surface which has minimum ΔG appears.

Ab initio



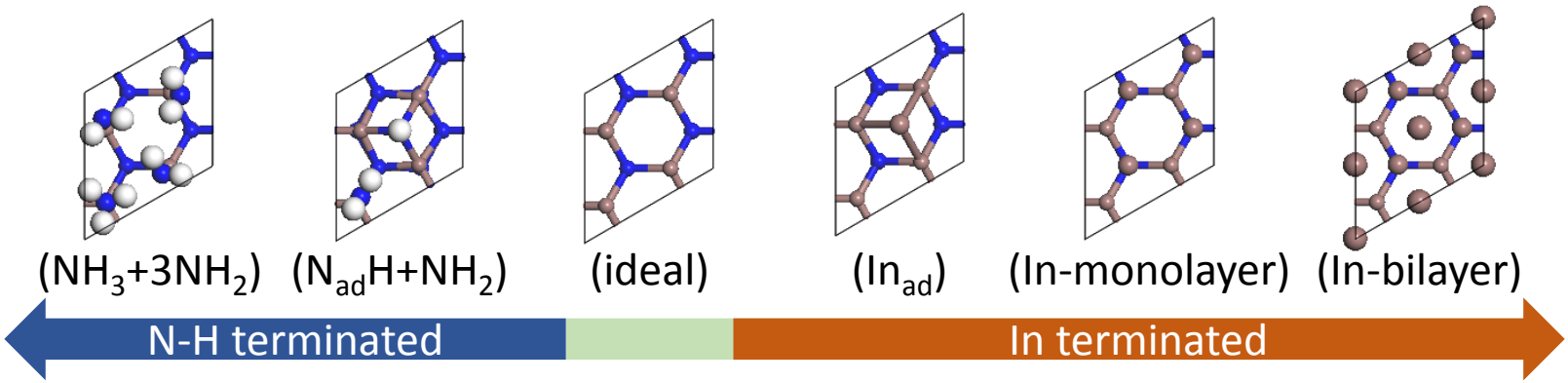
(Gas molecule)

- DFT calculation
  - ✓ Total energy
  - ✓ Frequency
- Statistical mechanics
  - ✓ entropy

(Surface)

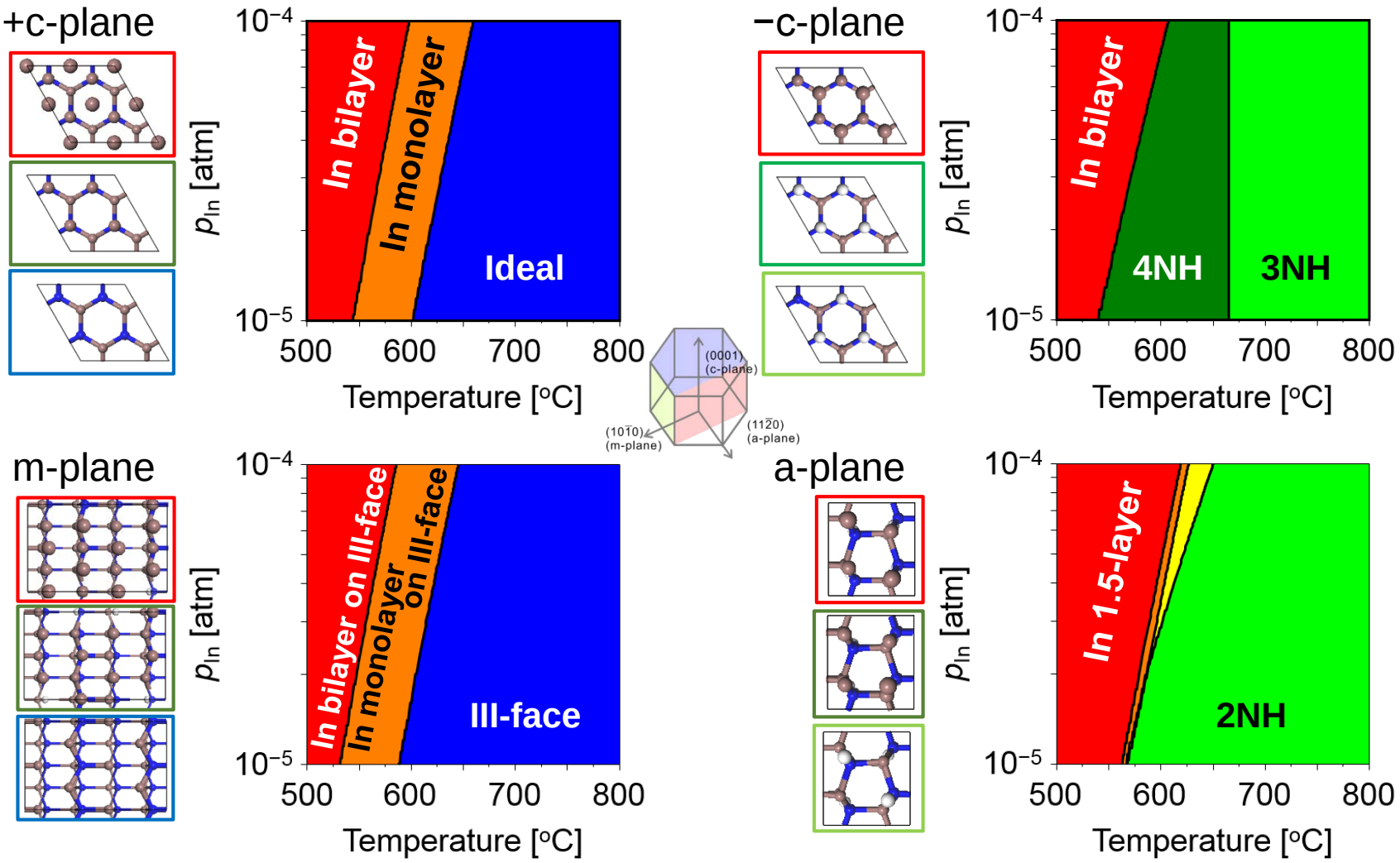
- DFT calculation
  - ✓ Total energy

Candidates for surface reconstruction

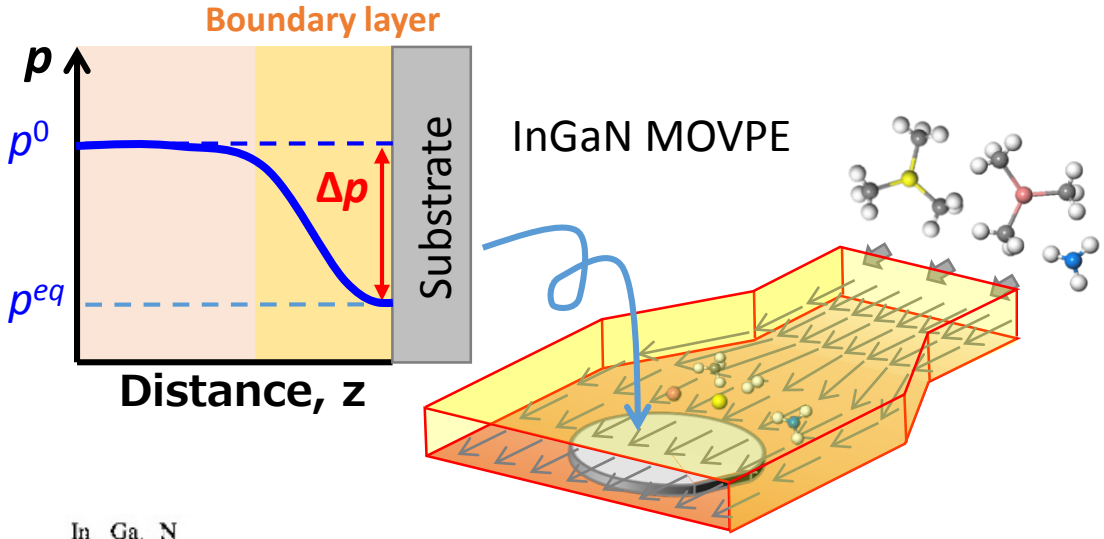


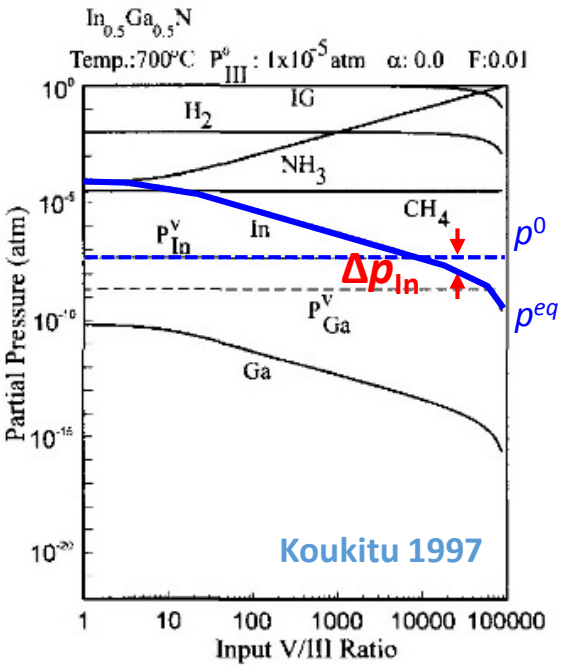
Influence of growth orientation on InGaN composition

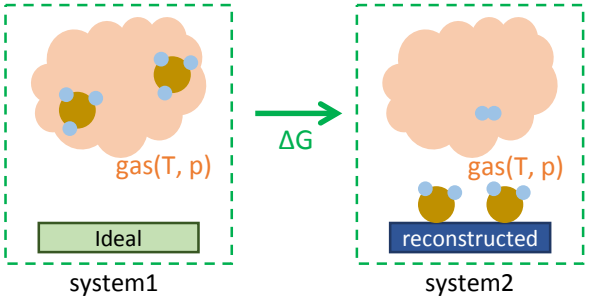
Surface phase diagram (p_{tot} = 1 atm, p_{NH3} = 0.2 atm, F = 0, α = 0.25)



Influence of growth orientation on InGaN composition







Thermodynamic analysis

Vapor-solid interface

$TMI(g)+3/2\ H_2(g) = In(g)+3CH_3H(g)$

Substrate surface

$In(g)+NH_3(g) = InN(s)+3/2\ H_2(g)$

Conservation constraints

$$\Sigma P_i = P_{In}+P_{NH3}+P_{H2}+P_{CH4}+P_{IG}$$

Parameters; *F* and α

$$F=P_{H2}{}^0/(P_{H2}{}^0+P_{IG}{}^0)$$

$$NH_3(g)\rightarrow(1-\alpha)NH_3(g)+\alpha/2\ N_2(g)+3\alpha/2\ H_2(g)$$

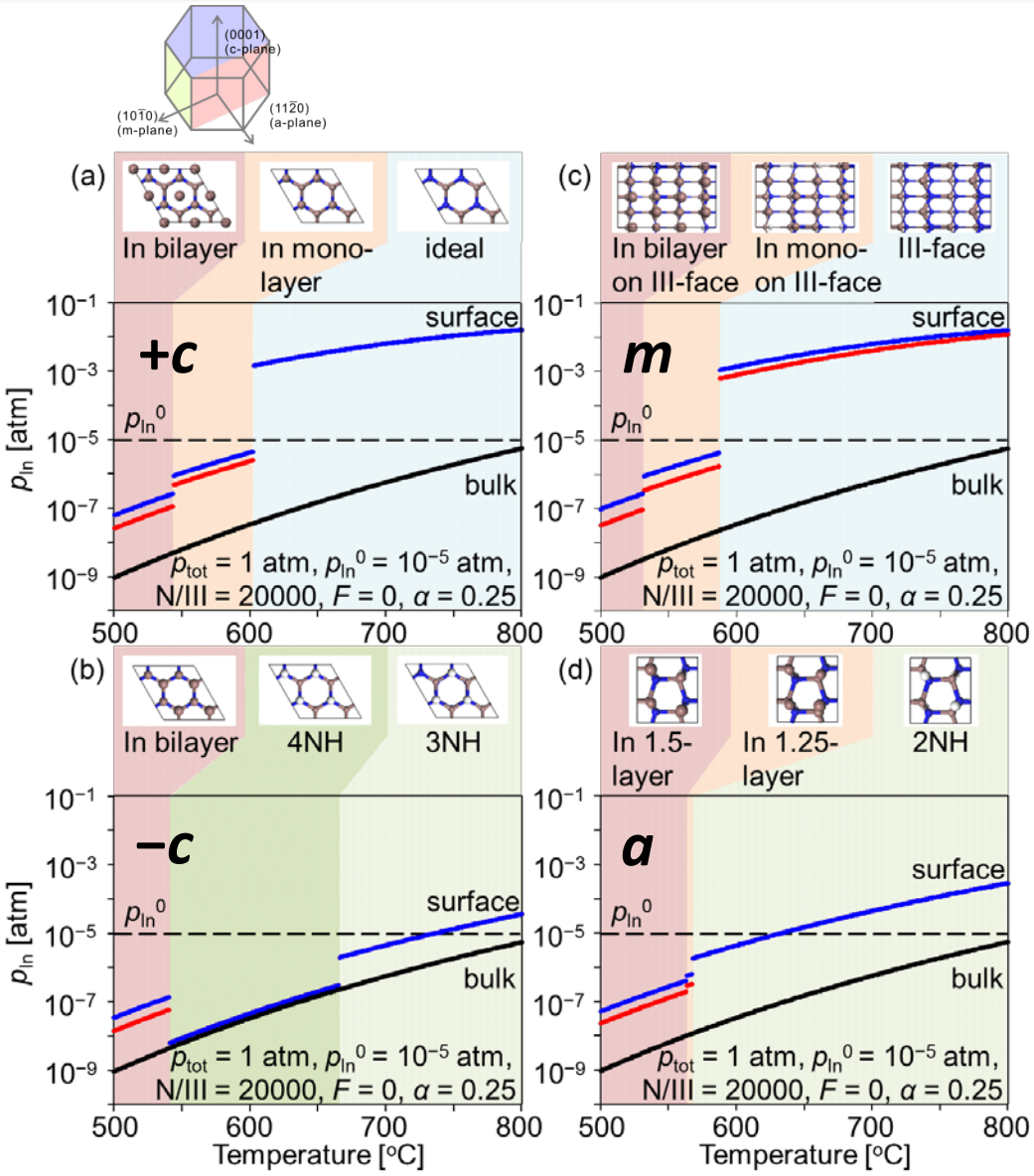
Equilibrium equation for reaction

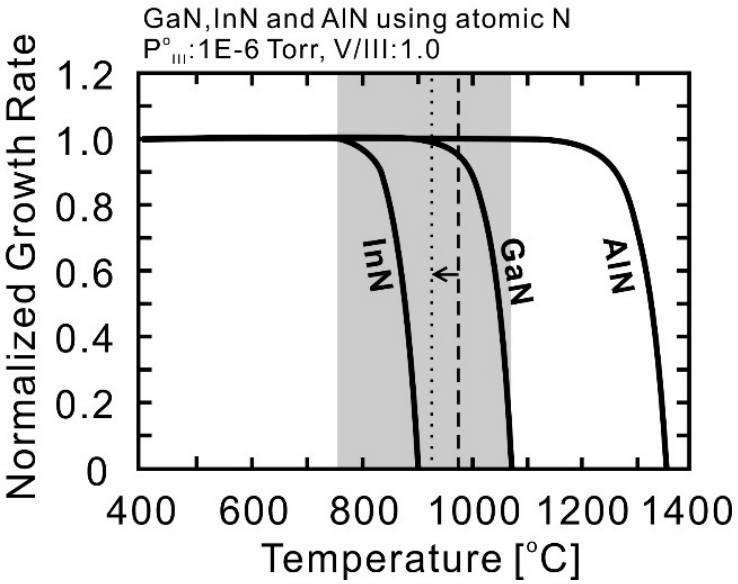
$$K_1=\frac{a_{InN}P_{H2}{}^{3/2}}{P_{In}\cdot P_{NH3}}$$

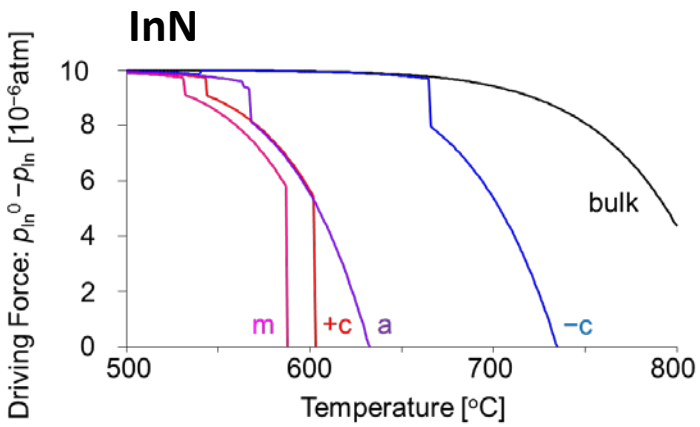
K: Equilibrium constant,
a: Activity

$$K_i = \exp\left(\frac{-\Delta G_i^{surf\_form}}{RT}\right)$$

Influence of growth orientation on InGaN composition







Influence of growth orientation on InGaN composition

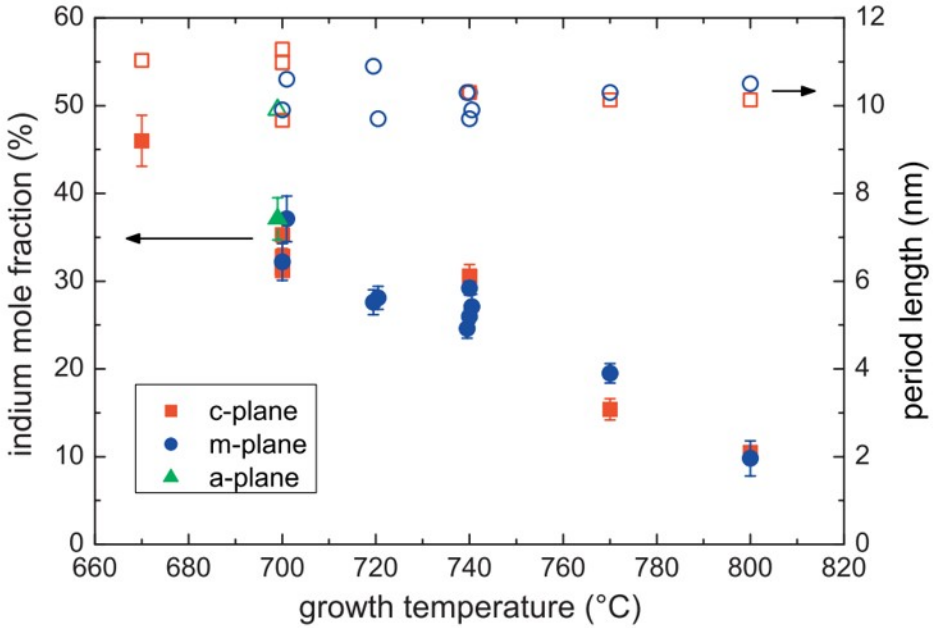


Figure 2 (online color at: www.pss-b.com) Results of XRD measurements: In contents (filled symbols) and period lengths (open symbols) of *c*-plane, *a*-plane, and *m*-plane 5 × GaInN/GaN QW structures as a function of growth temperature.

H. Jönen et al., physica status solidi (b), 248, 600-604 (2011).

OUTLINE

Introduction

- ✓ *Background* *~ Roles of crystal growth simulations ~*

Methodology

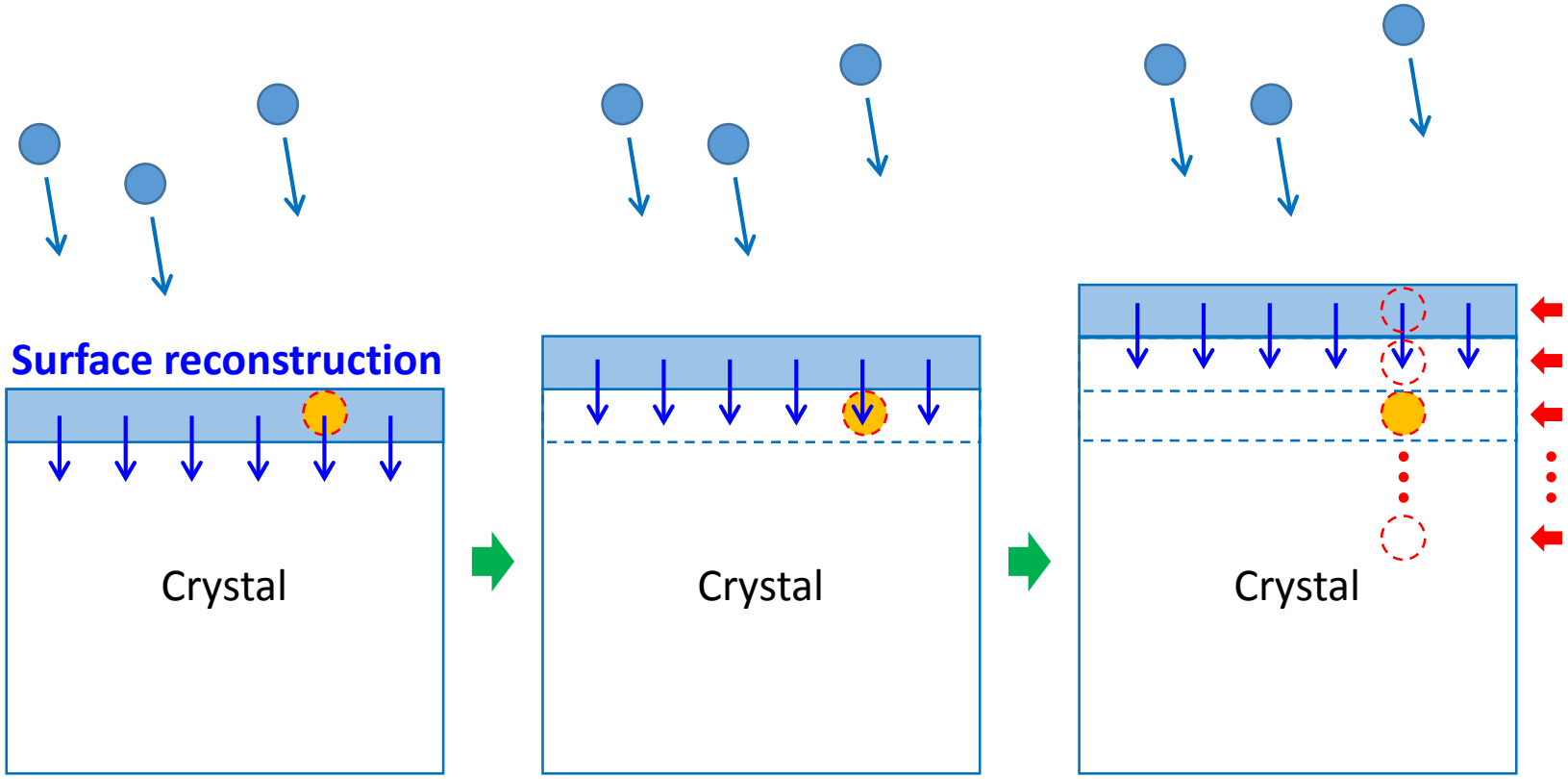
- ✓ *Ab initio based−approach*

Results

- ✓ *Influence of growth orientation on InGaN composition*
- ✓ *Incorporation mechanism of C & O in GaN MOVPE*

Summary

Incorporation mechanism of C & O in GaN MOVPE

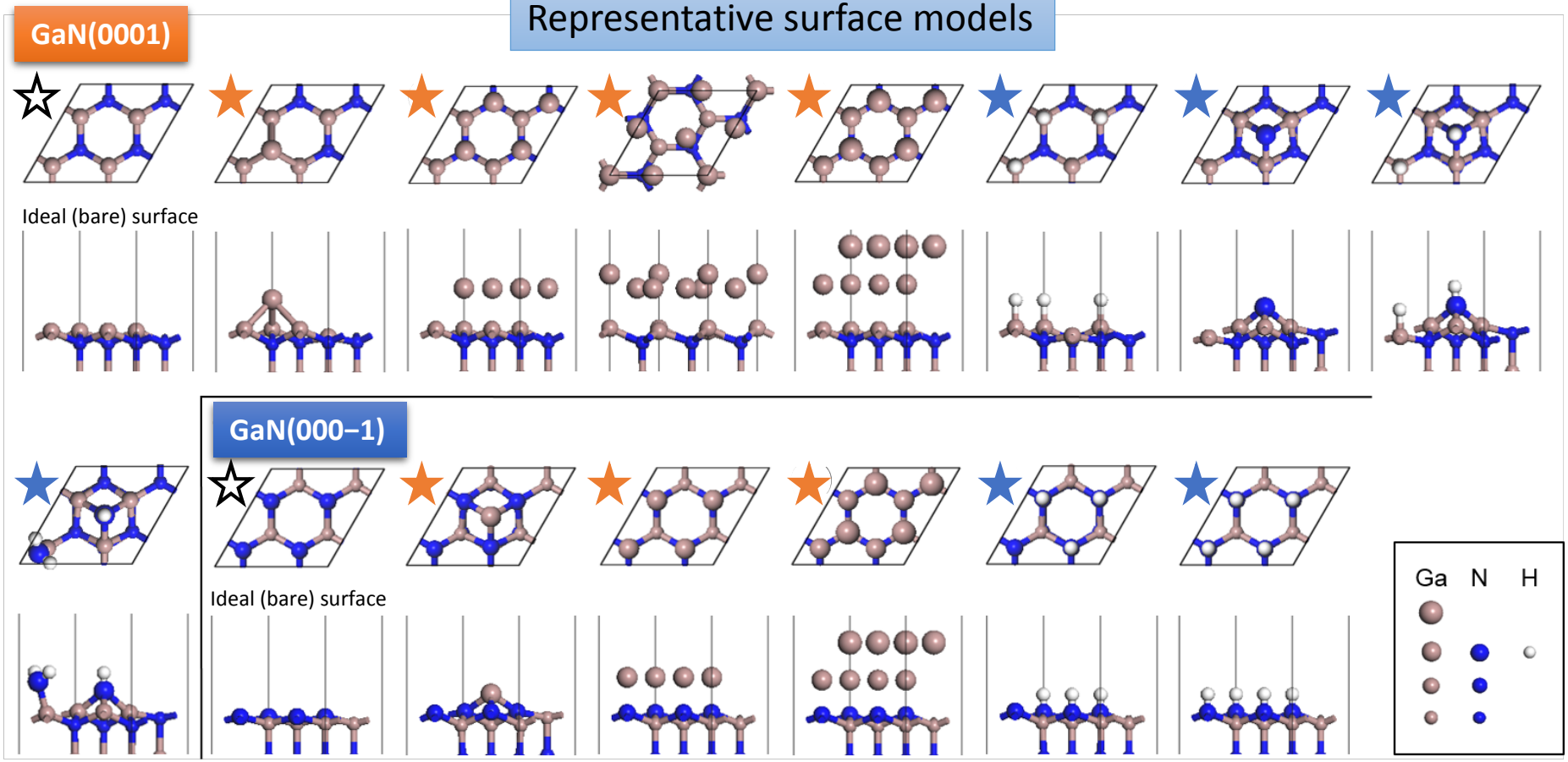


Matter for investigation

- Reconstructed structure on the growth surface (*p*–*T* surface phase diagram).
- Formation energy of a substitutional impurity in each layer.

Incorporation mechanism of C & O in GaN MOVPE

Representative surface models



Evaluation criteria of stable surface reconstruction under a certain growth condition

$$G = E_{\mathrm{slab}}^{\mathrm{recon}} - \left[E_{\mathrm{slab}}^{\mathrm{ideal}} + n_{\mathrm{Ga}}^{\mathrm{ad}}\mu_{\mathrm{Ga}}^{gas} + \frac{1}{2}n_{\mathrm{N}}^{\mathrm{ad}}\mu_{\mathrm{N2}}^{gas} + \frac{1}{2}n_{\mathrm{H}}^{ad}\mu_{\mathrm{H2}}^{gas}\right].$$

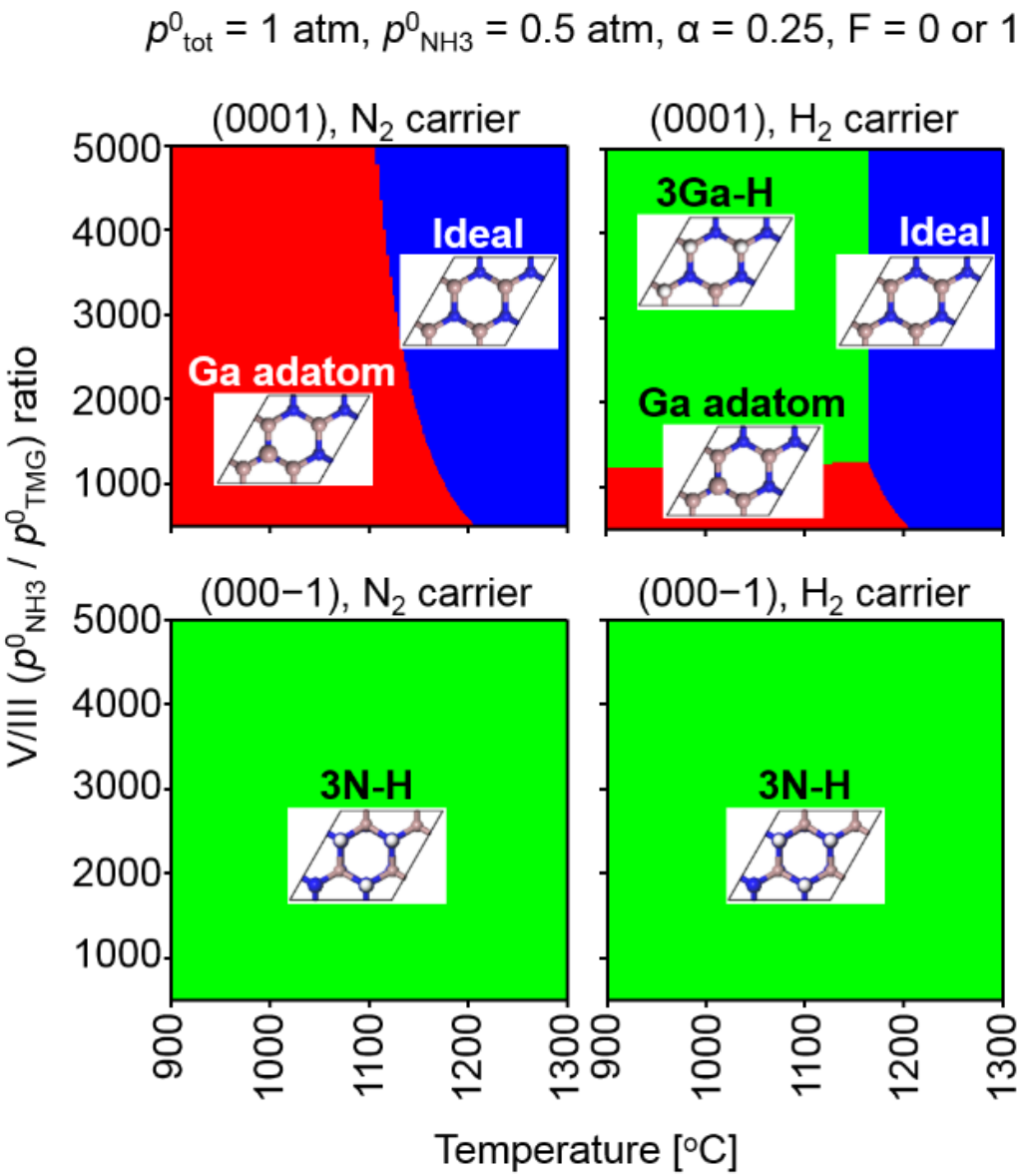
G: Gibbs free energy, ***n***: number of adatoms, ***μ***: chemical potential
(***μ*** is functions of ***p*** and ***T***)

★ Ga-rich surface model

★ N−H-rich surface model

A. Kusaba et al., JJAP **56** (2017) 070304

Incorporation mechanism of C & O in GaN MOVPE



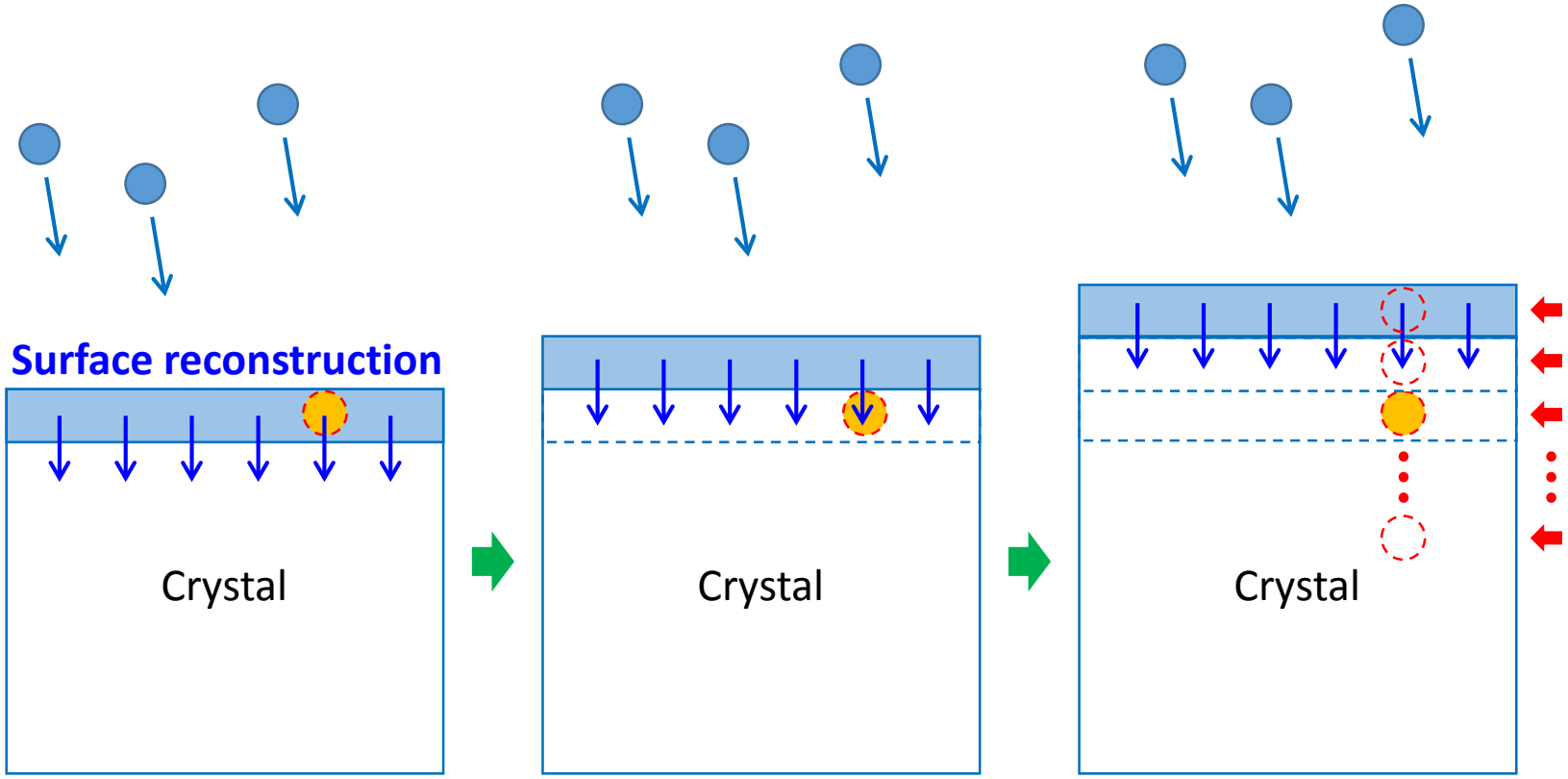
GaN(0001)

- ✓ Ga_{ad} surface is stable under N_2 carrier gas condition.
- ✓ 3Ga-H surface is stable under H_2 carrier gas condition.

GaN(000−1)

- ✓ 3N-H surface is stable under typical growth condition.

Incorporation mechanism of C & O in GaN MOVPE



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Incorporation mechanism of C & O in GaN MOVPE

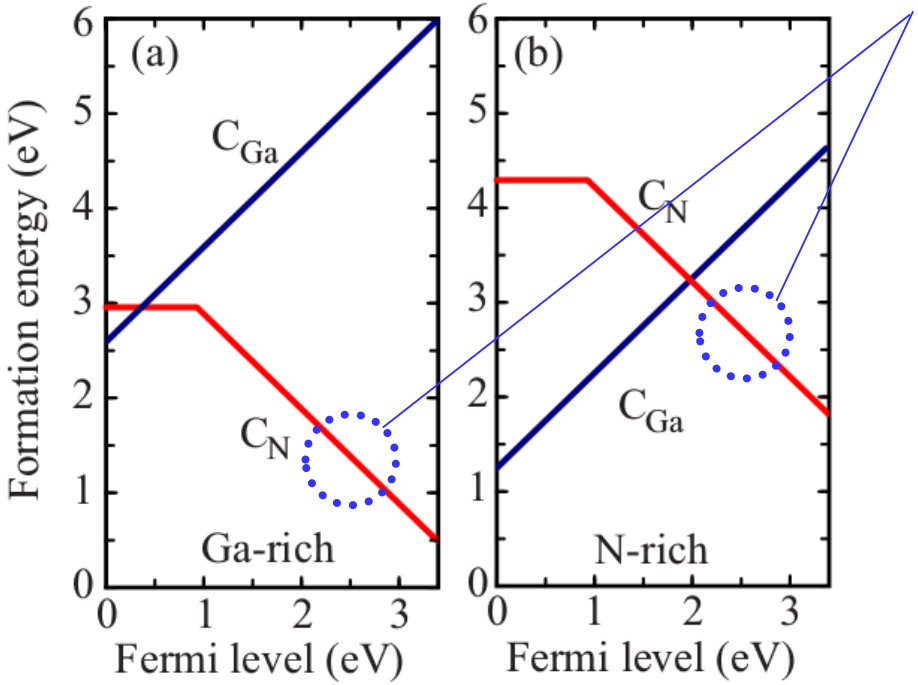
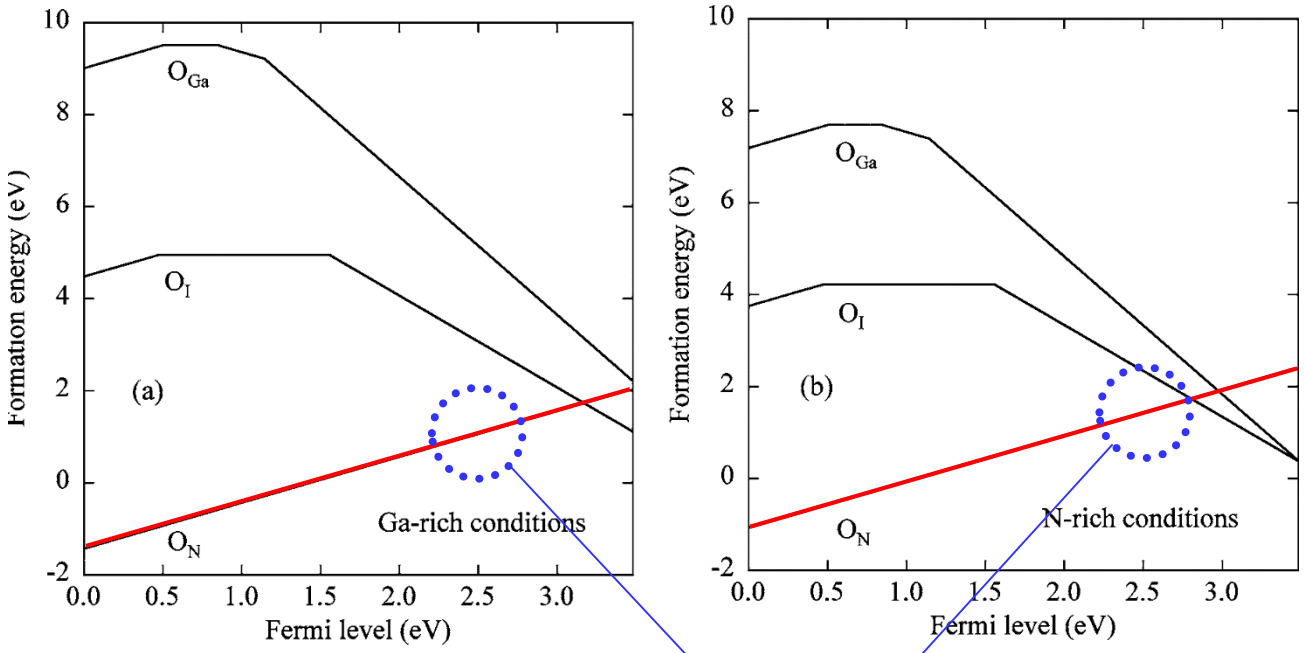


FIG. 1. (Color online) Formation energy vs Fermi level for C_{Ga} and C_N in GaN. Ga-rich conditions are shown in (a) and N-rich conditions in (b).

$$E^f(C_N^q) = E_{tot}(C_N^q) - E_{tot}(GaN) - \mu_C + \mu_N + q(E_F + \epsilon_v + \Delta V),$$

C_N (carbon substituting nitrogen) is stable in n-type GaN.

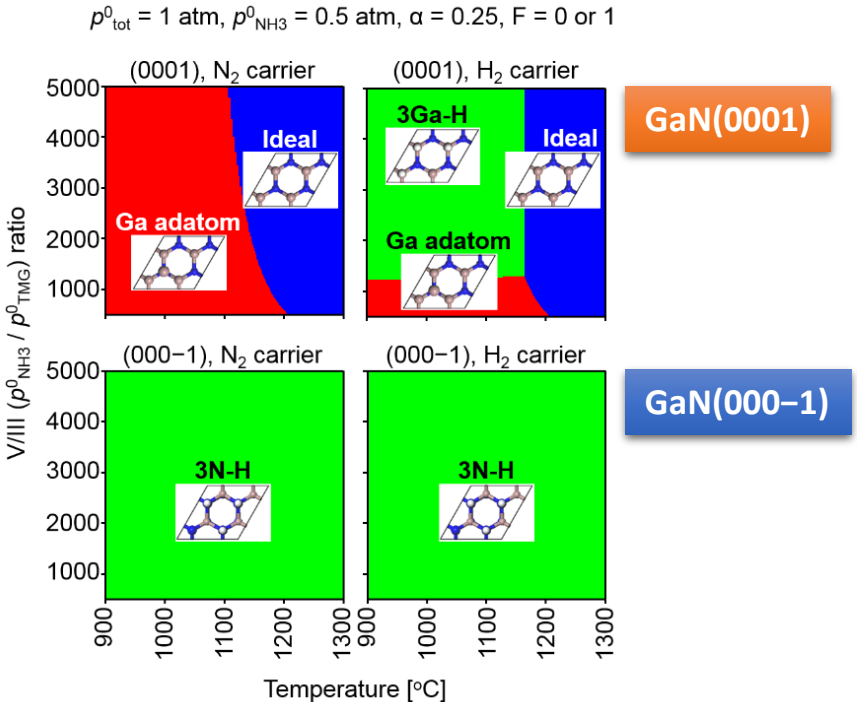
Incorporation mechanism of C & O in GaN MOVPE

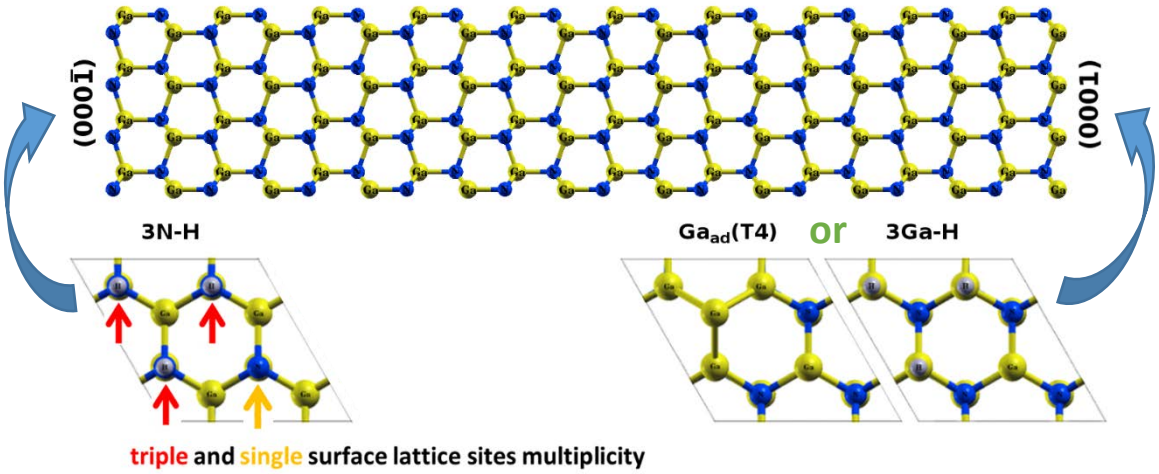


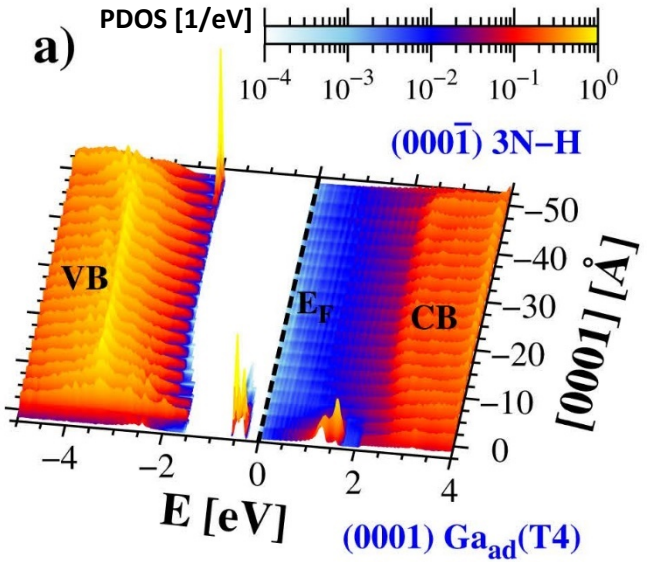
O_N (oxygen substituting nitrogen) is stable in n-type GaN.

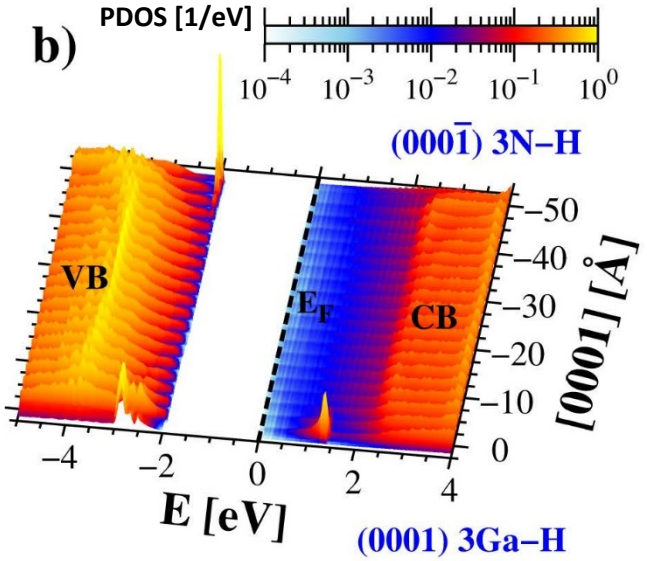
A. F. Wright et al., JAP **98** (2005) 103531

Incorporation mechanism of C & O in GaN MOVPE



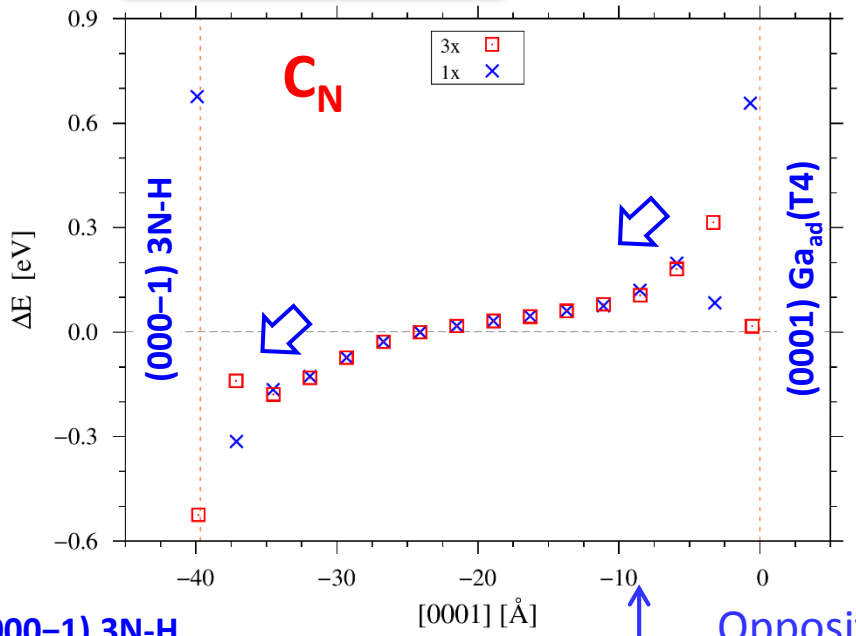




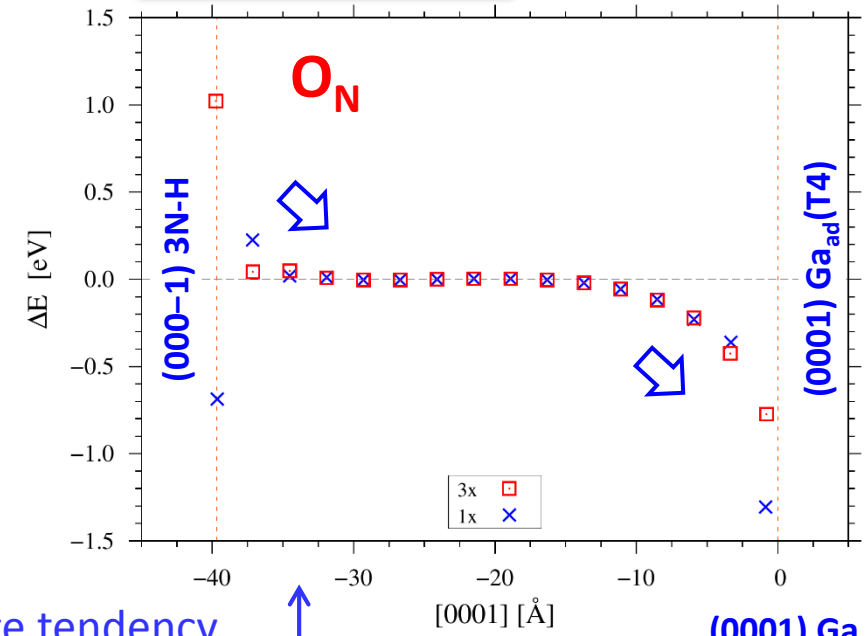


Incorporation mechanism of C & O in GaN MOVPE

C_N in n-type GaN



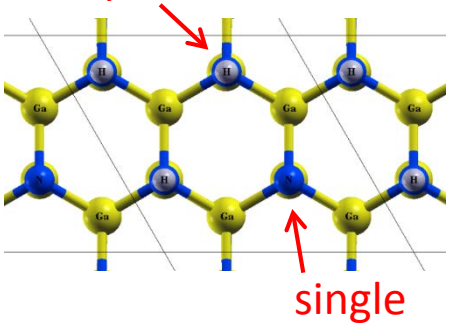
O_N in n-type GaN



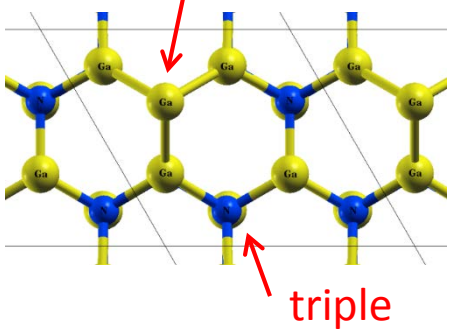
Opposite tendency

C_N in n-GaN has **negative** charge.
O_N in n-GaN has **positive** charge.

(000−1) 3N-H



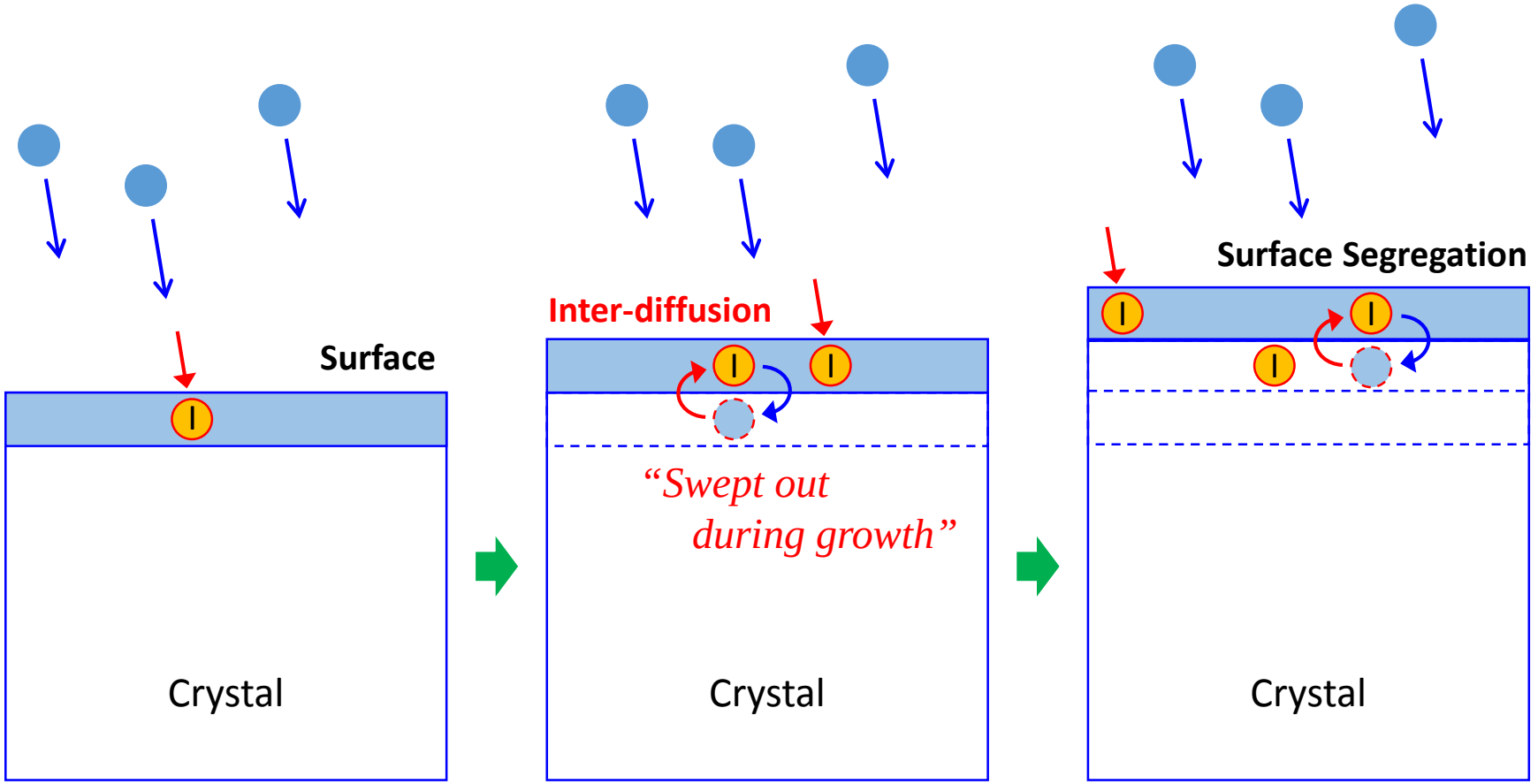
(0001) Ga_{ad}(T4)



Trend	(0001)+c	(000−1)−c
C concentration	High	Low
O concentration	Low	High

Incorporation mechanism of C & O in GaN MOVPE

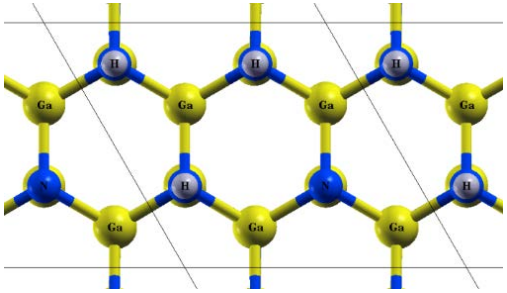
Surface segregation process

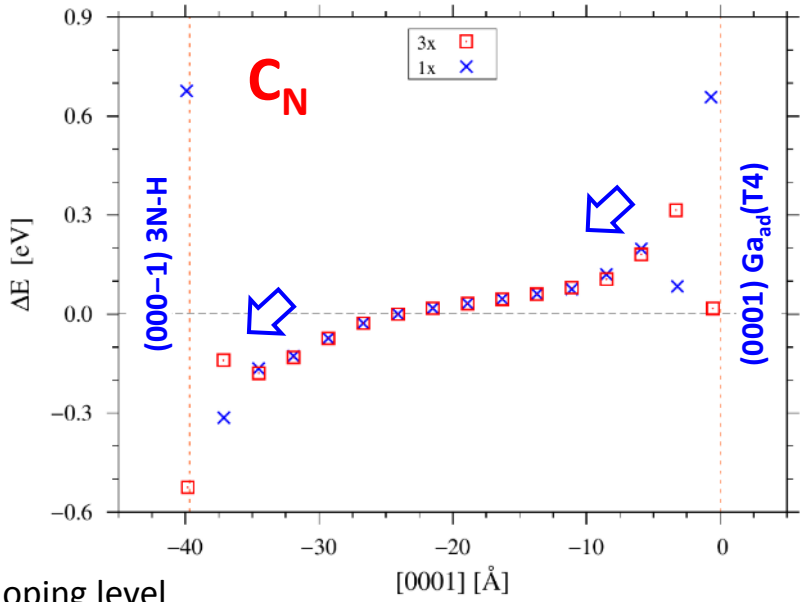


Incorporation mechanism of C & O in GaN MOVPE

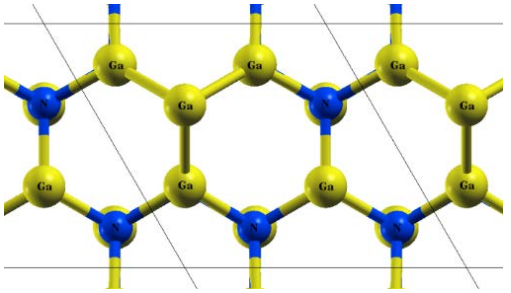
MC simulation

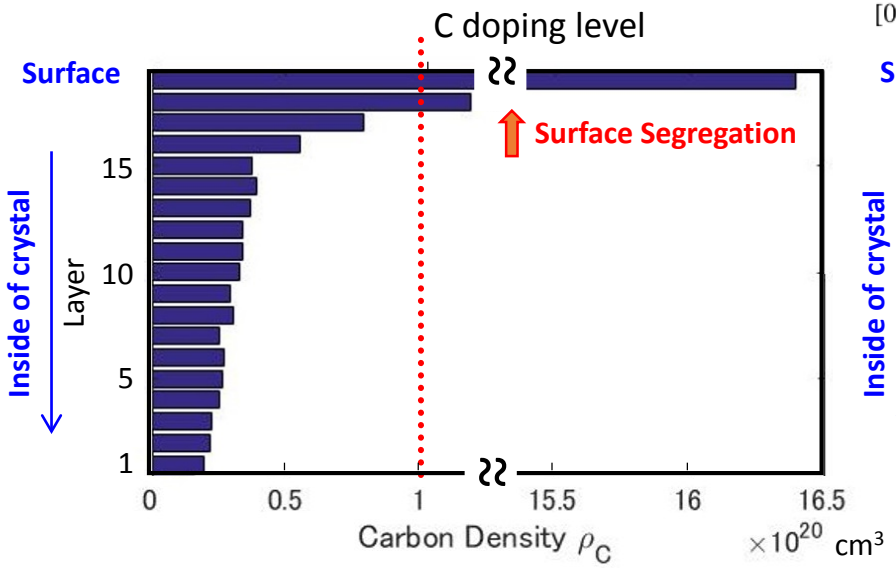
(000−1) 3N-H

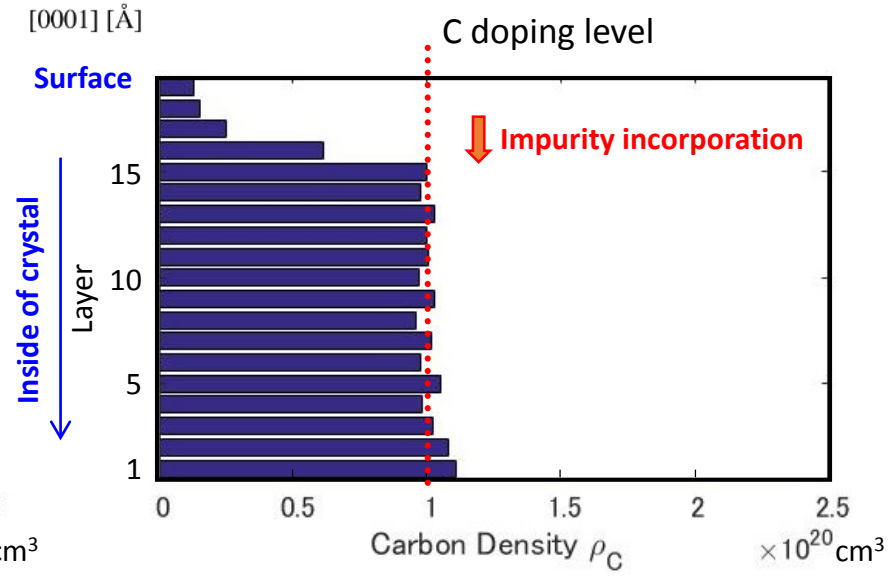




(0001) Ga_ad(T4)





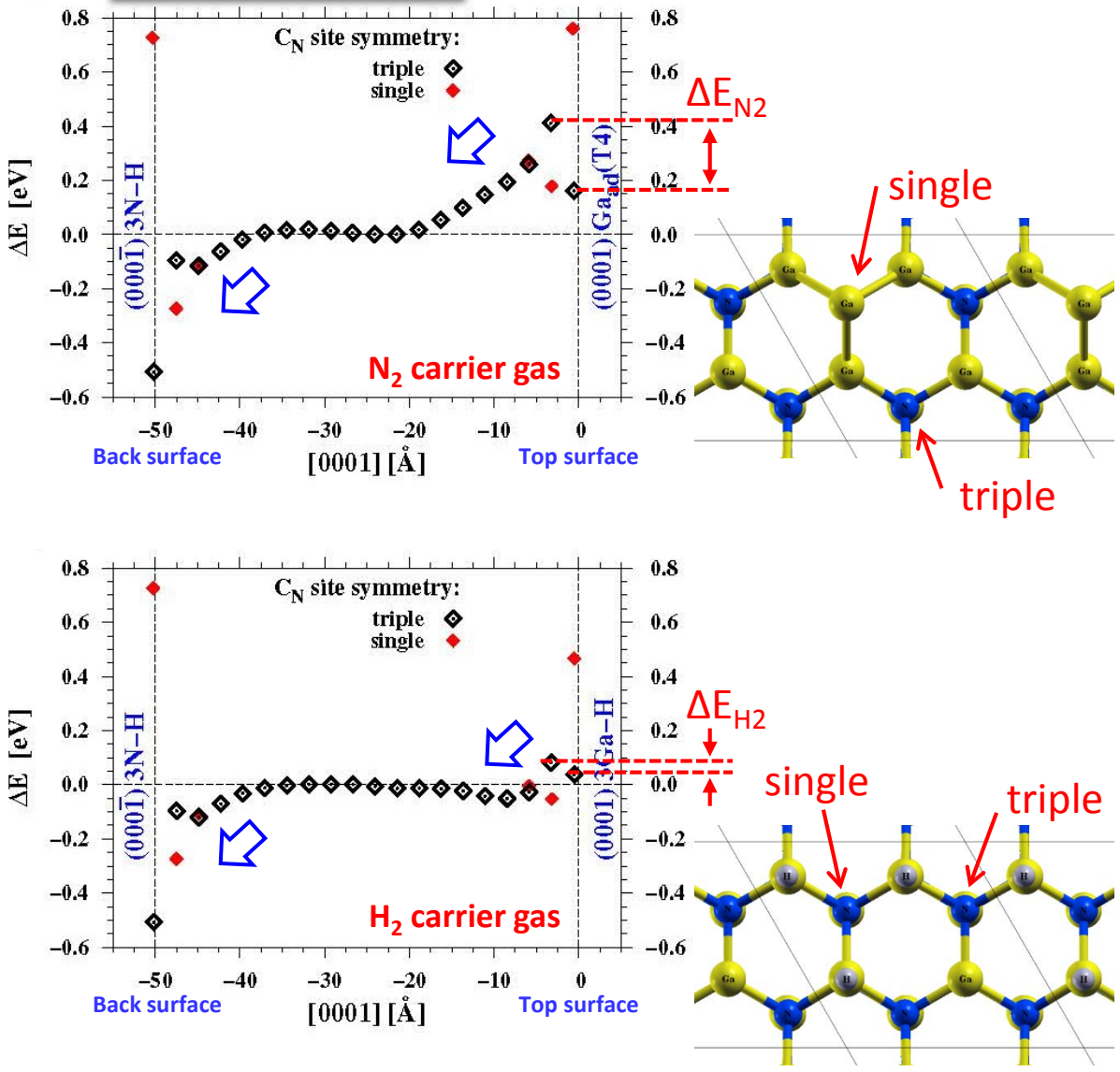


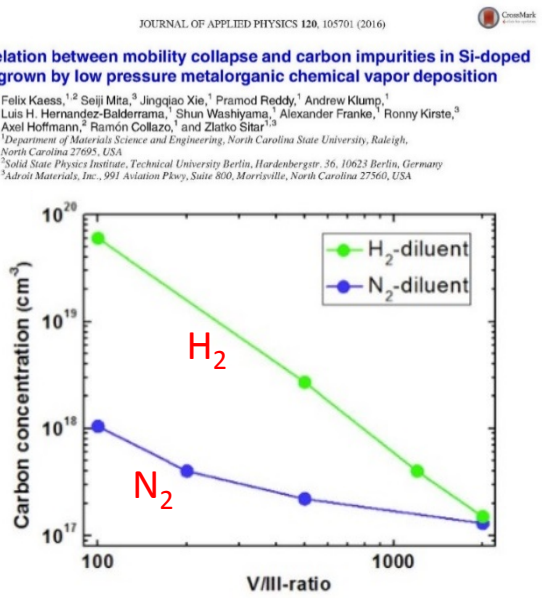
Incorporation mechanism of C & O in GaN MOVPE

C_N in n-type GaN

Energy barrier between surface and sub-surface is **0.14–0.15 eV** for $Al_{0.17}Ga_{0.83}N$/GaN

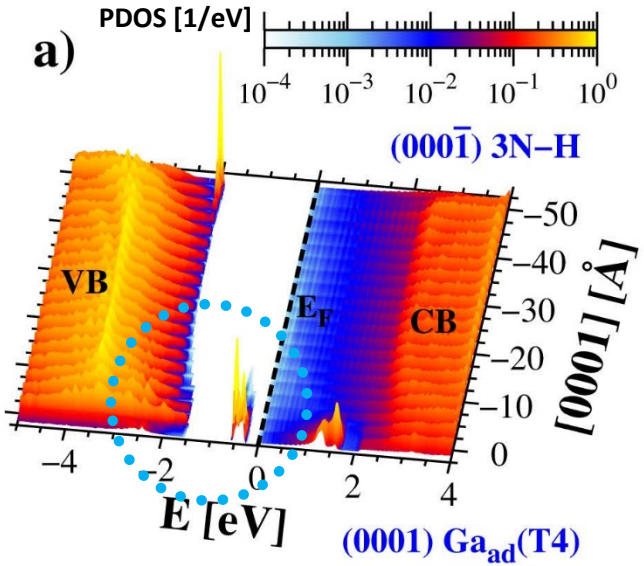
T. Walter et al., J. Mater. Sci. **48** (2013) 1883

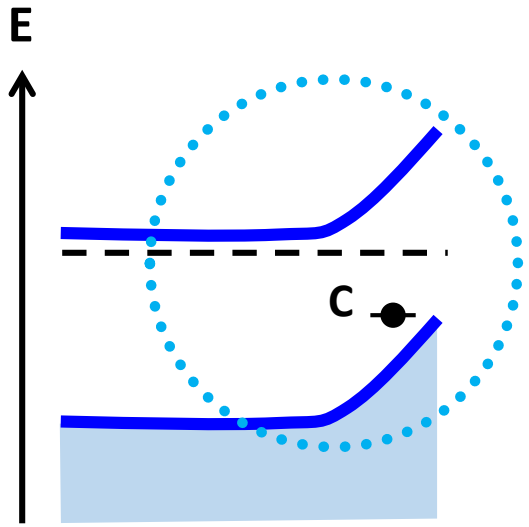


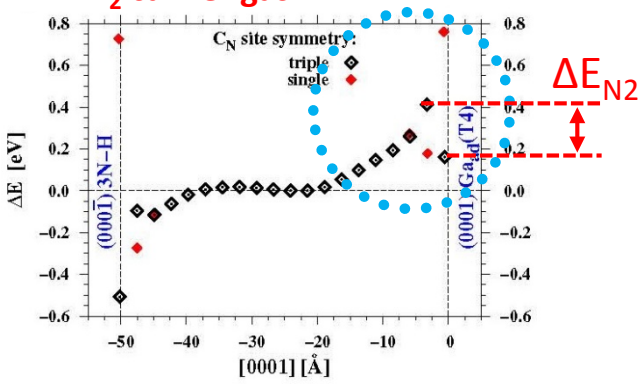


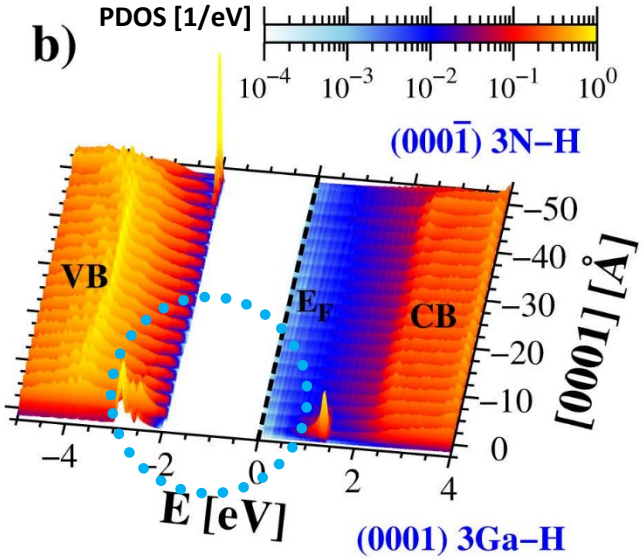
Trend	$N_{2(0001)+c}$	$H_{2(0001)+c}$
C concentration	Low	High

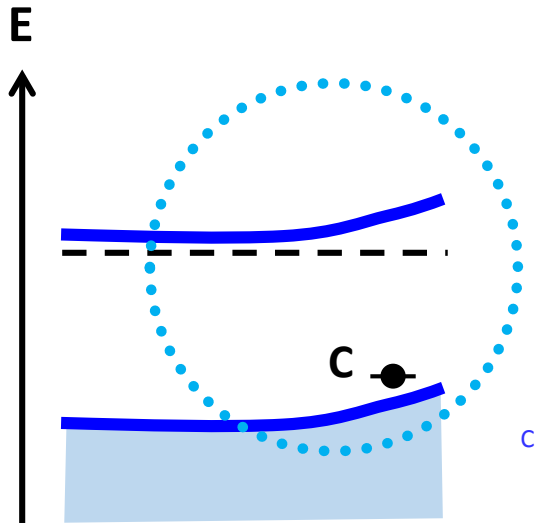
Incorporation mechanism of C & O in GaN MOVPE

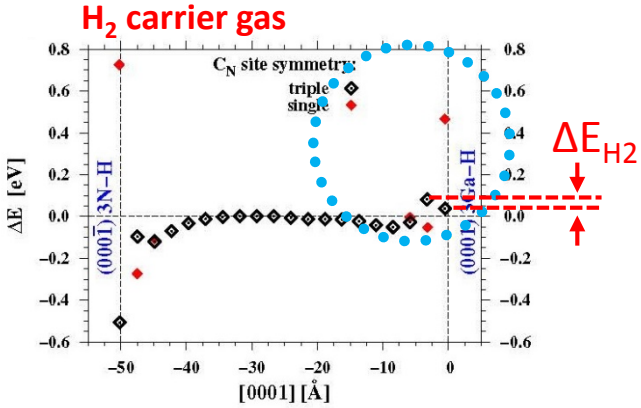












C incorporation ratio depends on surface band bending

OUTLINE

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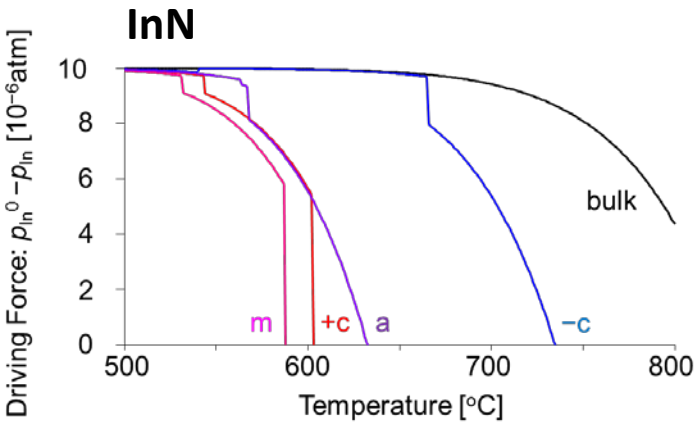
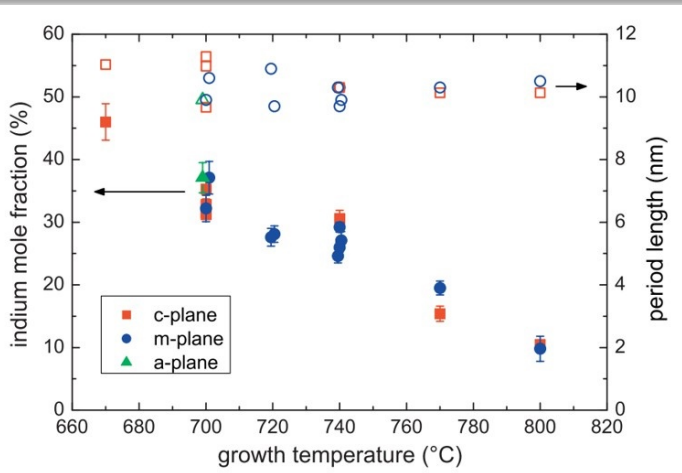
Summary

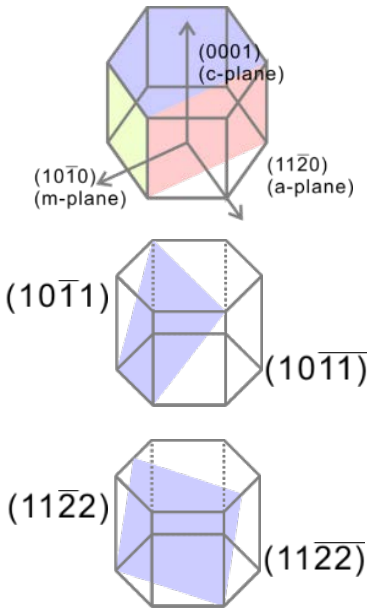
Summary I

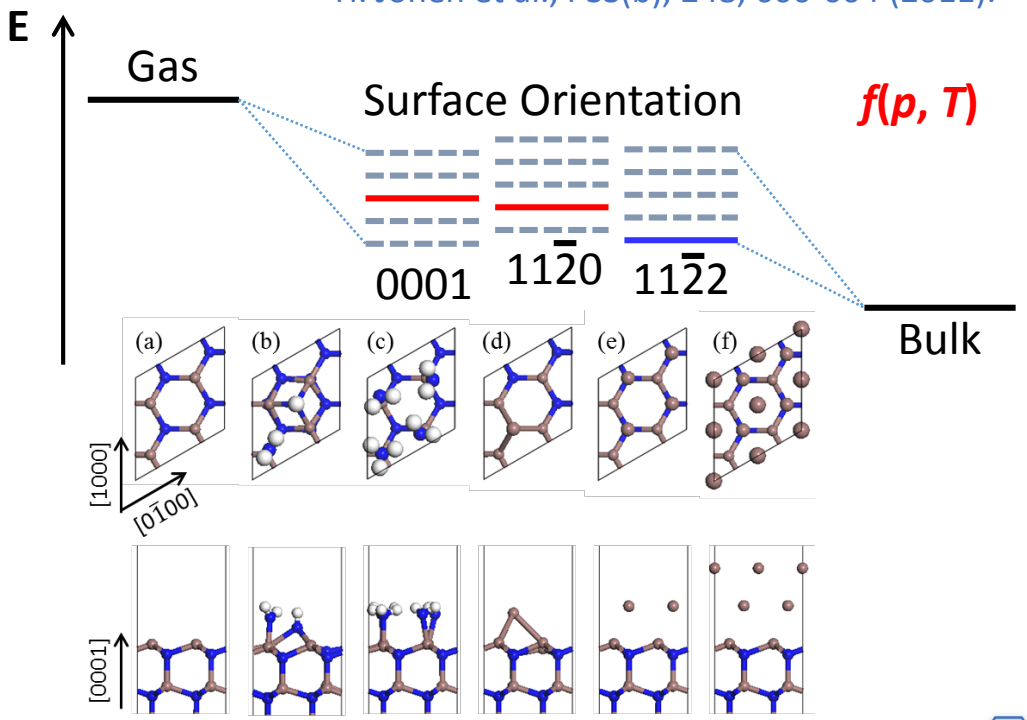




H. Jönen et al., PSS(b), 248, 600-604 (2011).

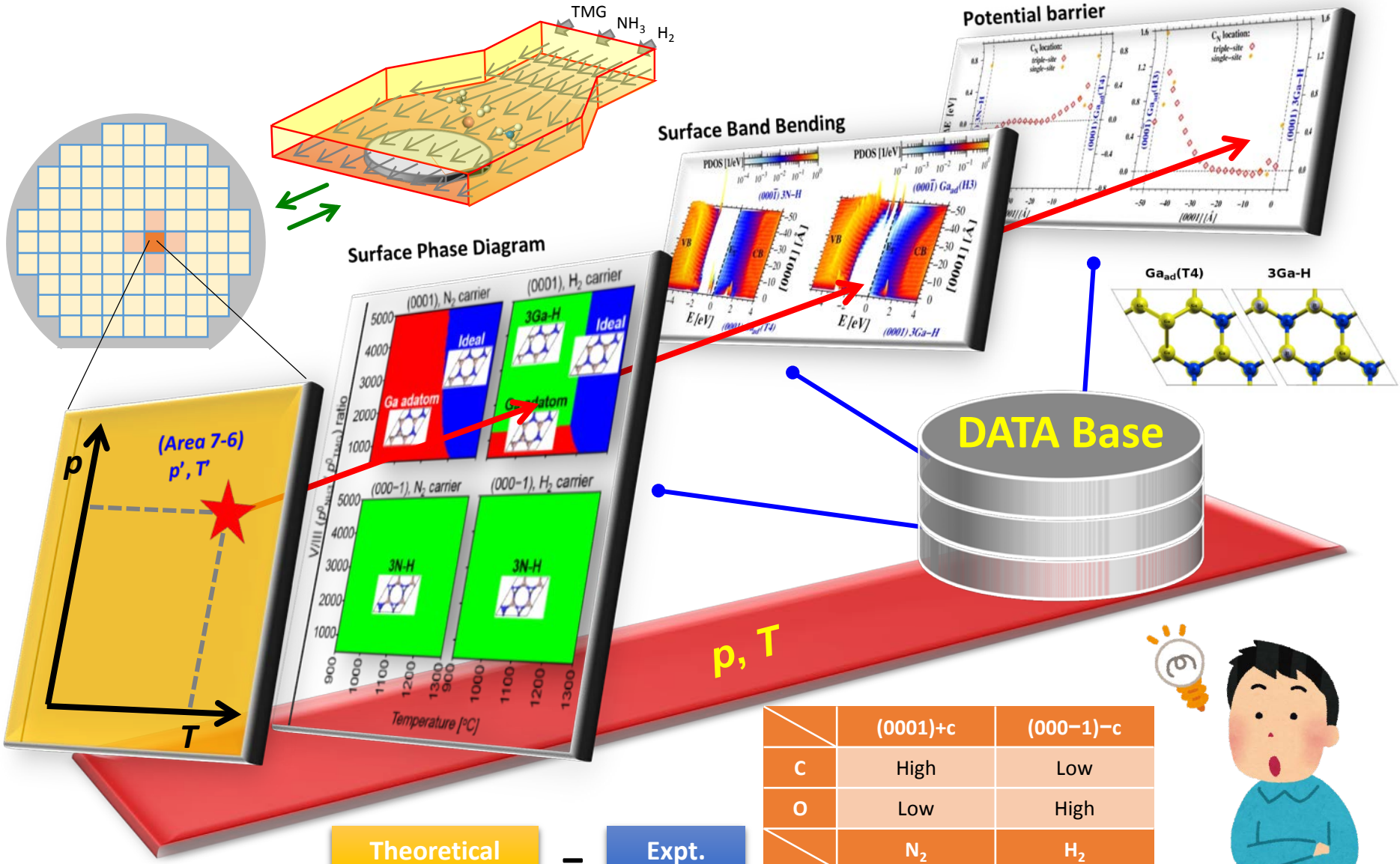
Growth orientation





Influence of surface reconstruction on the impurity incorporation in GaN MOVPE
Yoshihiro Kangawa (Kyushu University/Nagoya University)

Summary II



	(0001)+c	(000−1)−c
C	High	Low
O	Low	High
	N_2	H_2
C	Low	High

Theoretical results ≡ **Expt. results**

Influence of surface reconstruction on the impurity incorporation in GaN MOVPE

Yoshihiro Kangawa (Kyushu University/Nagoya University)

Research Institute for Applied Mechanics, Kyushu University

RIAM 九州大学応用力学研究所

Thank you for your kind attention :)

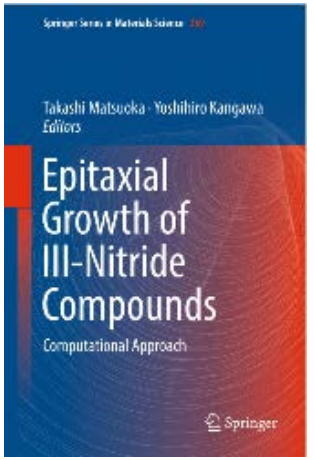
T. Akiyama, T. Ito, Y. Kangawa, T. Nakayama, and K. Shiraishi

"Epitaxial Growth of III-Nitride Compounds: Computational Approach"

T. Matsuoka, Y. Kangawa (Eds.)

Springer Series in Materials Science, vol. 269, 2018

[DOI: 10.1007/978-3-319-76641-6]



Appendix

$$\Delta E_{\text{surface-bulk}} = \left\{\left[E_{\text{slab}} + n_{\text{N}}^{\text{ad}}\mu_{\text{In}}^{\text{InN(bulk)}} + n_{\text{In}}^{\text{ad}}\mu_{\text{N}}^{\text{InN(bulk)}}\right] - \left[\left(n_{\text{InN}}^{\text{slab}} + n_{\text{N}}^{\text{ad}} + n_{\text{In}}^{\text{ad}}\right)\mu_{\text{InN}}^{\text{InN(bulk)}} + n_{\text{H}}^{\text{ad}}\left(\mu_{\text{NH3}} - \mu_{\text{N}}^{\text{InN(bulk)}}\right)/3 + A_{\text{slab}}\sigma_{\text{bottom}}\right]\right\} \cdot N_{\text{A}}/\left(n_{\text{InN}}^{\text{top}} + n_{\text{N}}^{\text{ad}} + n_{\text{In}}^{\text{ad}}\right)$$

σ_{bottom}: surface energy of bottom side; E_{slab}: total energy of surface slab model; μ_{NH3}: total energy of an ammonia molecule; $\mu_{In}^{InN(bulk)}$, $\mu_{N}^{InN(bulk)}$, $\mu_{InN}^{InN(bulk)}$: chemical potentials of In, N, InN in InN(bulk); n_{In}^{ad}, n_{N}^{ad}, n_{H}^{ad}: numbers of In, N, and H adatoms; n_{InN}^{slab}: number of InN formula units; n_{InN}^{top}: number of InN formula unit of the topmost layers; N_A is Avogadro's number; A_{slab}: surface area.