# COMSOL Multiphysicsと実験を併用した薄膜製造プロセスの解析

DESIGN
OF
FOR
WITH
MATERIALS

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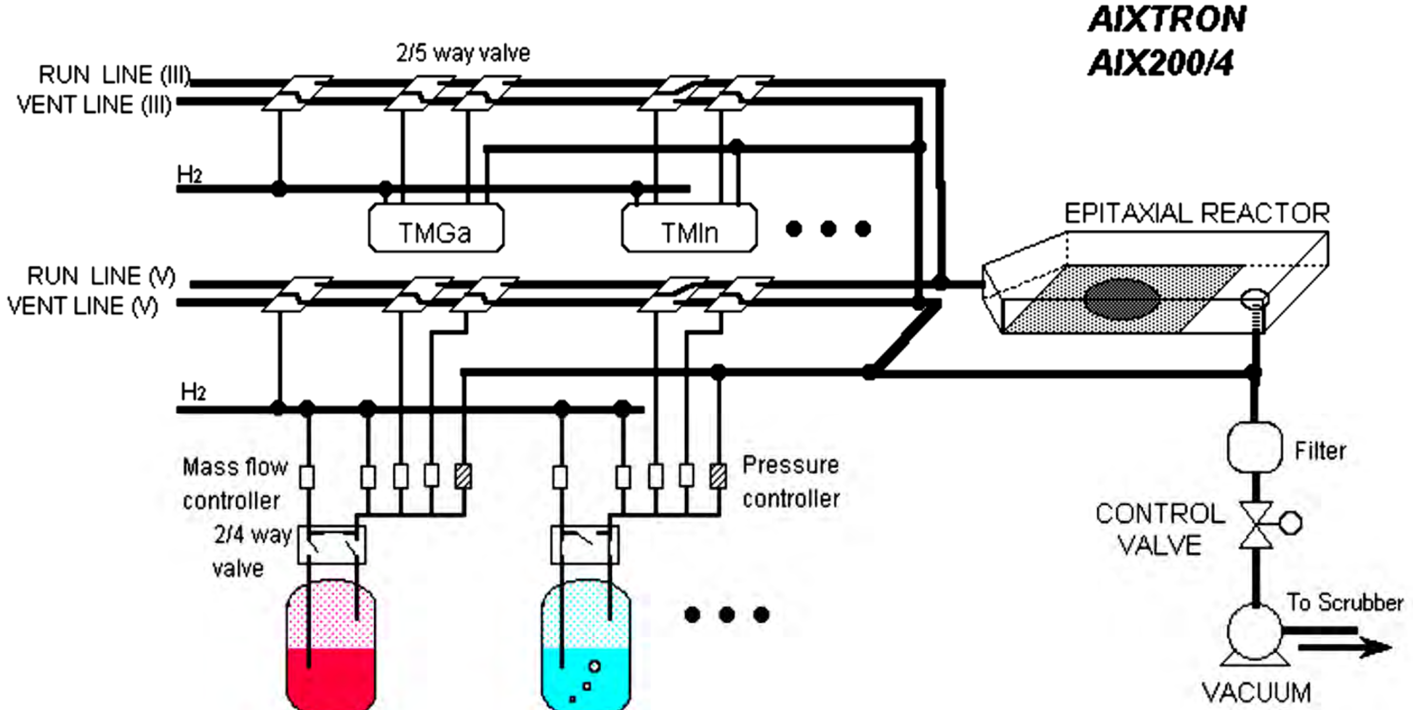
# Outline

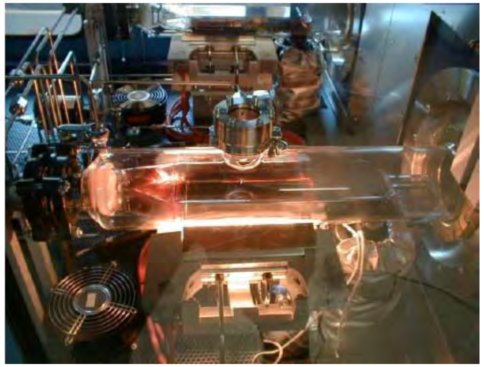
- Introduction
    - Mechanism of Metal Organic Chemical Vapor Deposition
    - Selective Area Growth (SAG)
- GaAs-SAG
    - Linear kinetic analysis
    - Non-Linear kinetic analysis
    - Doping Effects
- InP, InAs, InAsP, GaAsP, InGaAsP
    - Kinetics of InP/InAs and InAsP/GaAsP SAG
    - Estimation of InGaAsP PL wavelength distribution
- Conclusion

# III-V compound semiconductor
# MOCVD Process

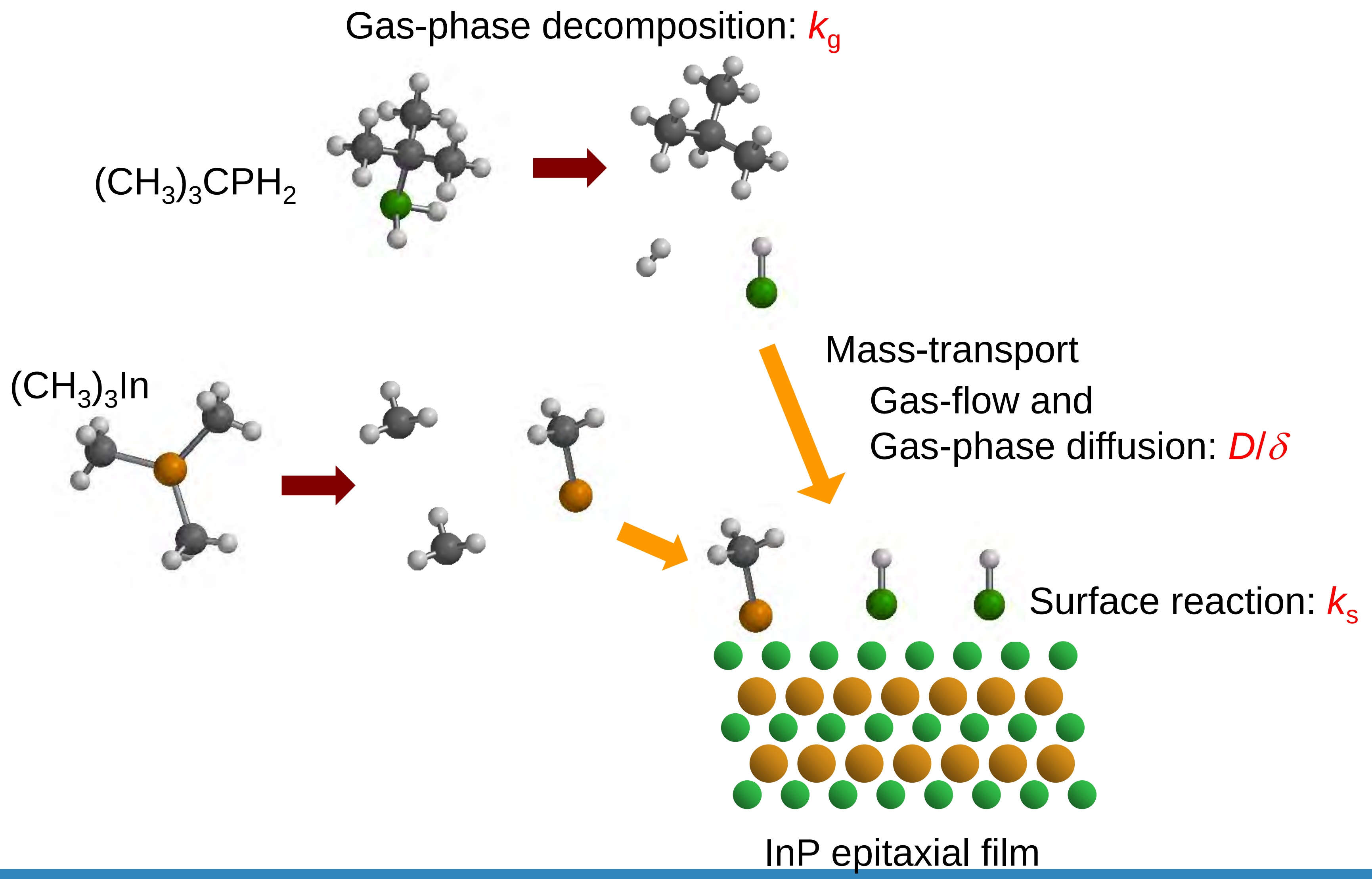


Precursors:
Tertiarybutylarsenide (TBAs)
Tertiarybutylphosphide(TBP)
Trimethylgallium (TMGa)
TrimethylIndium (TMIn)

V/III >> 1



# MOCVD Reaction Mechanism



Gas-phase decomposition: $k_g$

$(CH_3)_3CPH_2$

$(CH_3)_3In$

Mass-transport

Gas-flow and

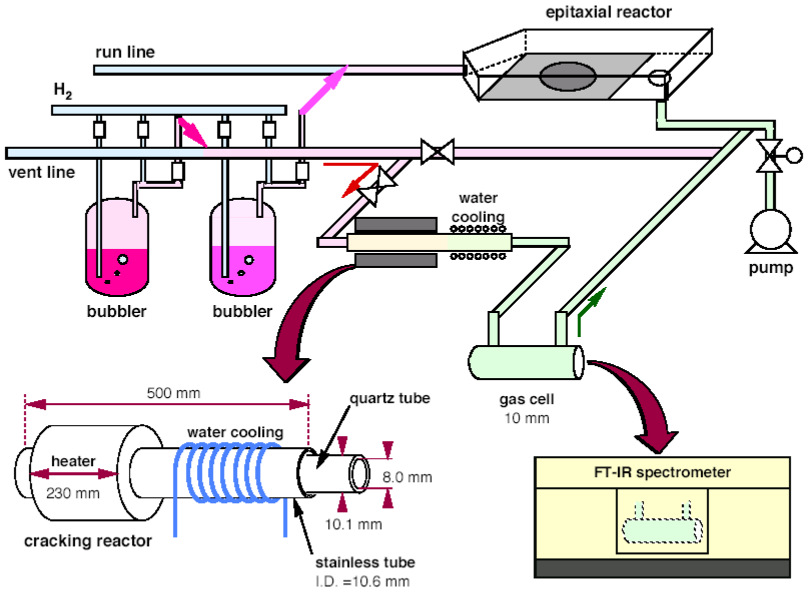
Gas-phase diffusion: $D/\delta$

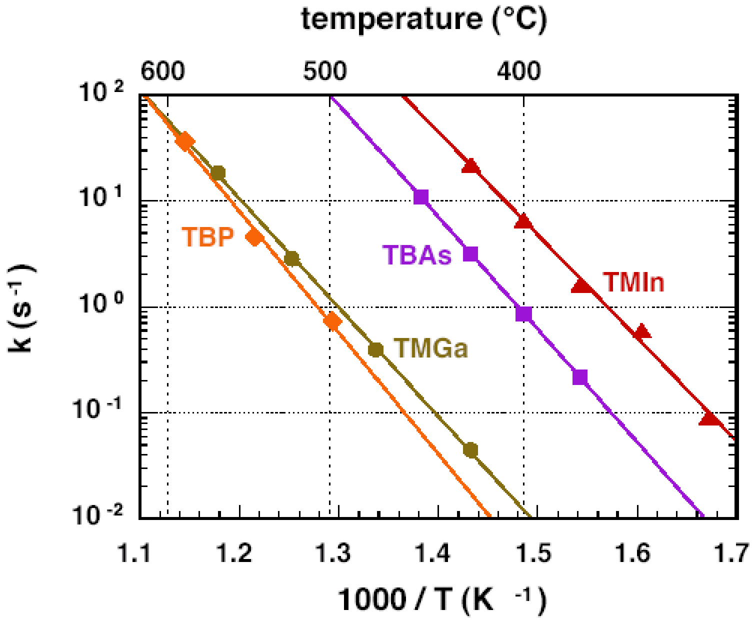
Surface reaction: $k_s$

InP epitaxial film

# Gas-Phase reaction rate constant

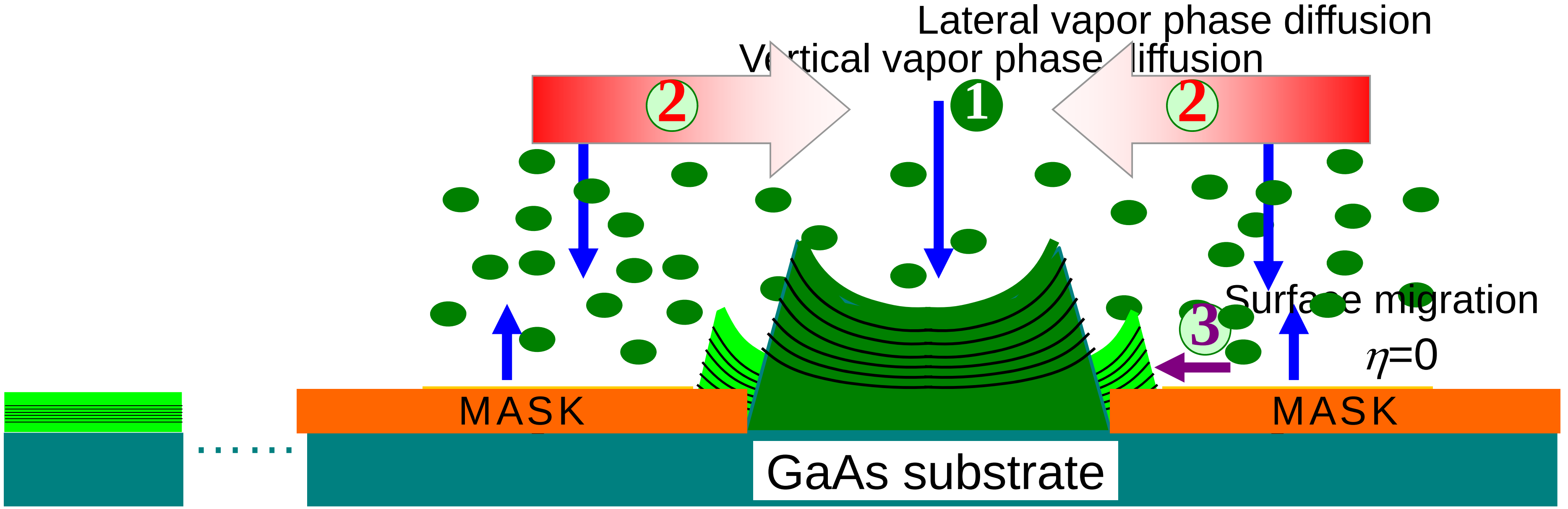
## Flow cracking reactor and FT-IR gas analysis





Arrhenius plot of
decomposition rate constants

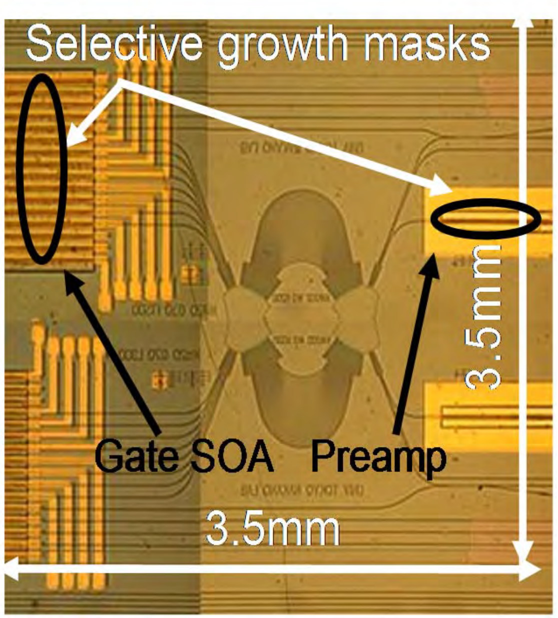
# Selective area growth (SAG) MOCVD



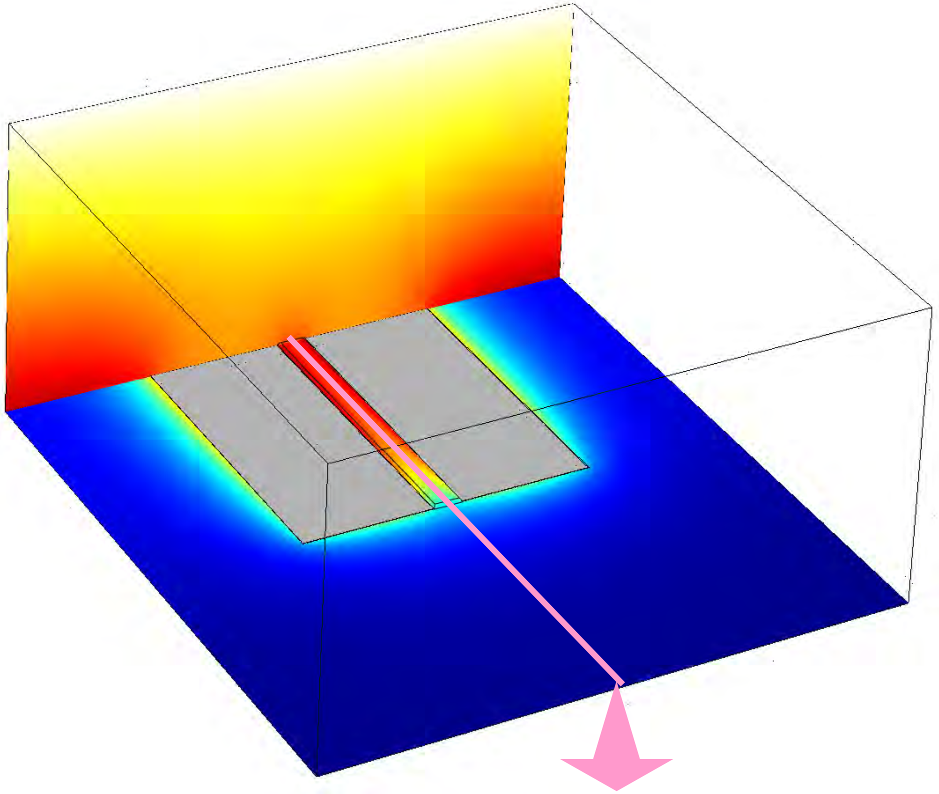
Film thickness & composition can be locally controlled by mask.

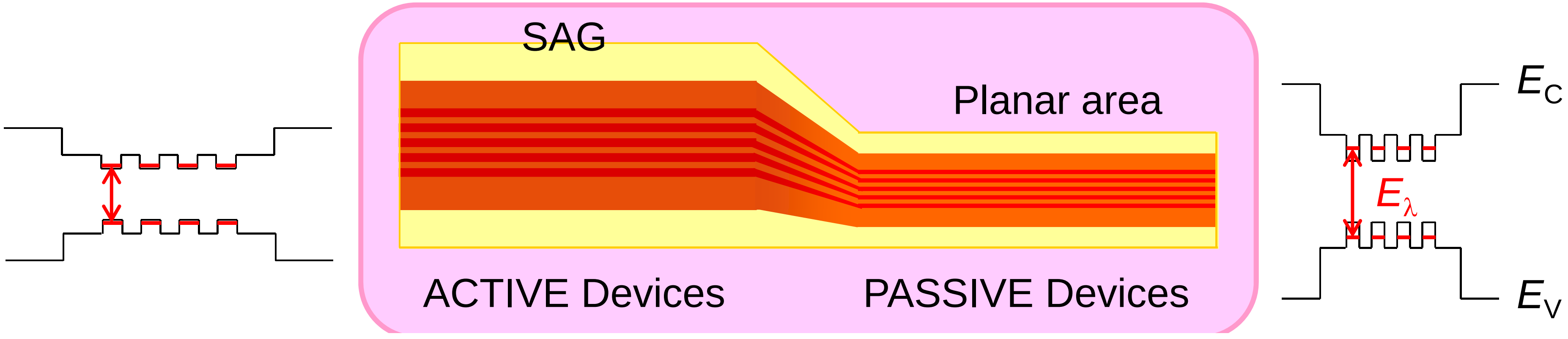
SAG

- ◆ For monolithic integration of OEICs (one step fabrication)
- ◆ Analysis of surface reaction kinetics (wide stripe SAG)



# Monolithic integration of multiple Eg Multi-Quantum Wells by SAG





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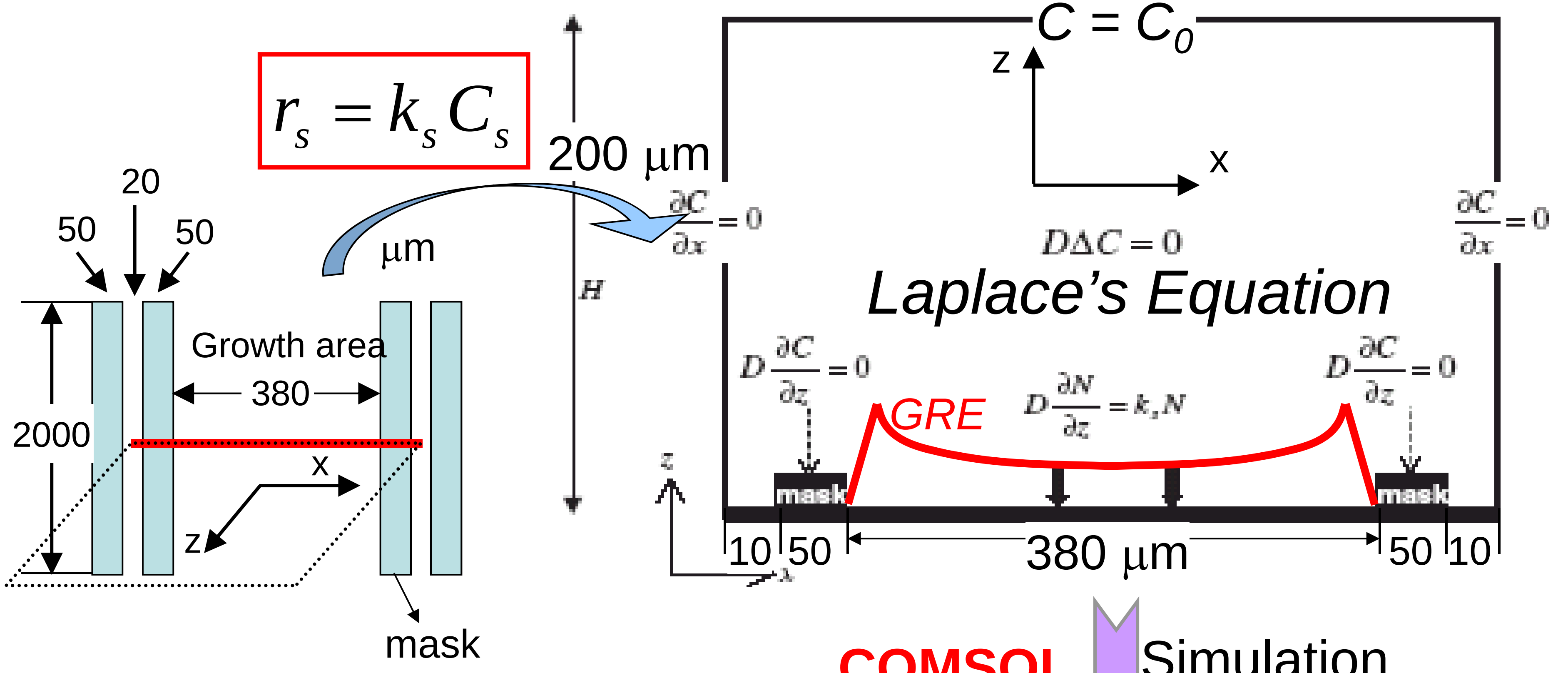
# SAG Analysis method by Simulation



**Growth-Rate-Enhancement**

$$G.R.E. = \frac{R_{SAG}}{R_{Planar}}$$

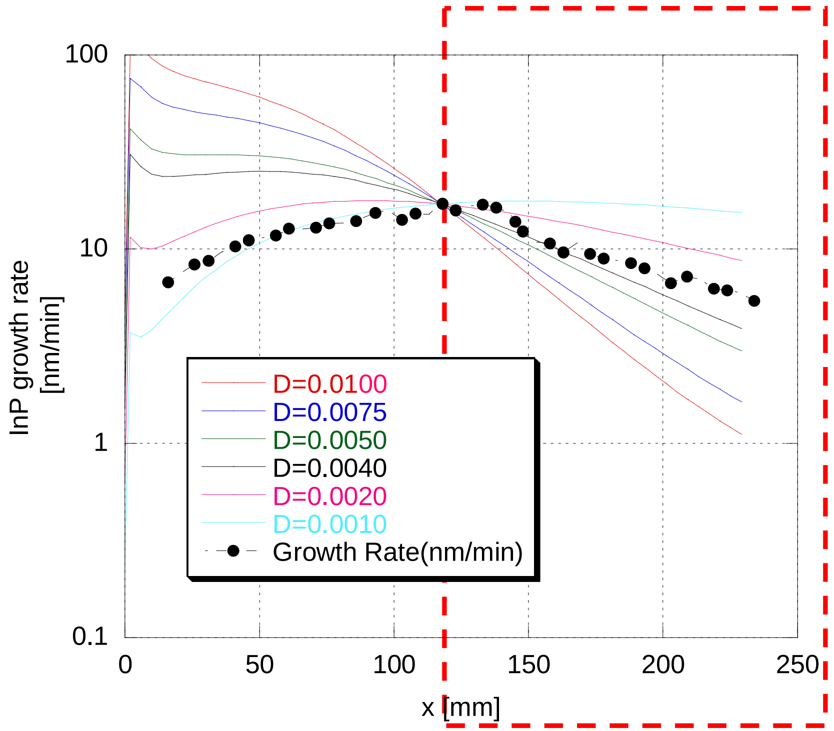
**COMSOL**

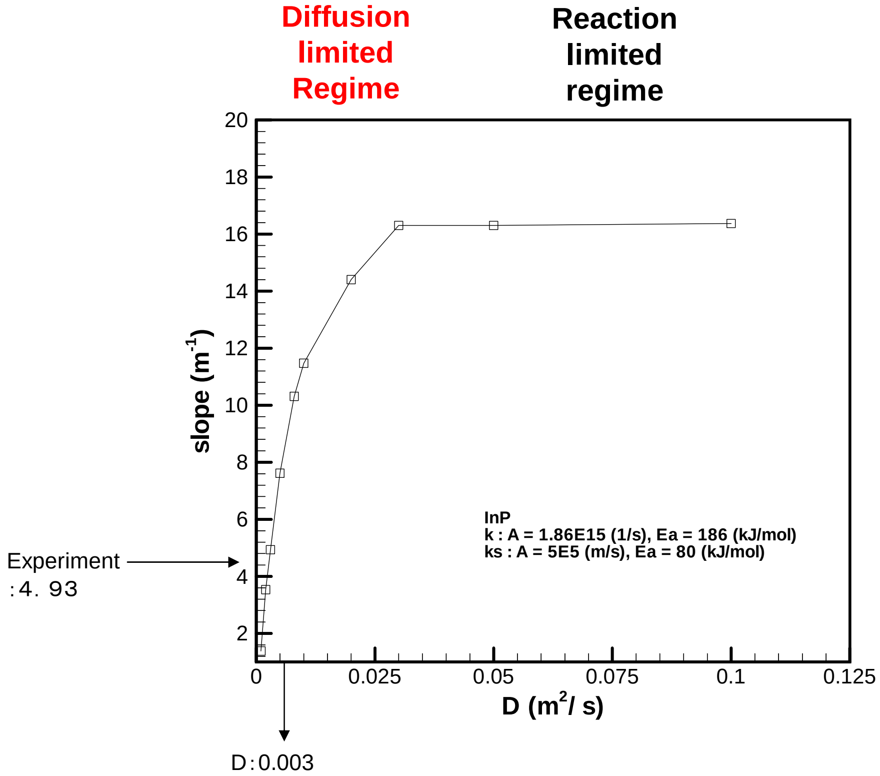
Simulation & Fitting

$k_s$: surface reaction rate constant

***$D/k_s$***

# Estimation of Diffusion Coefficient





- Diffusion coefficient can be estimated from the slope of the growth rate profile.
- We can also use Chapman-Enskog equation to estimate the diffusion coefficient.

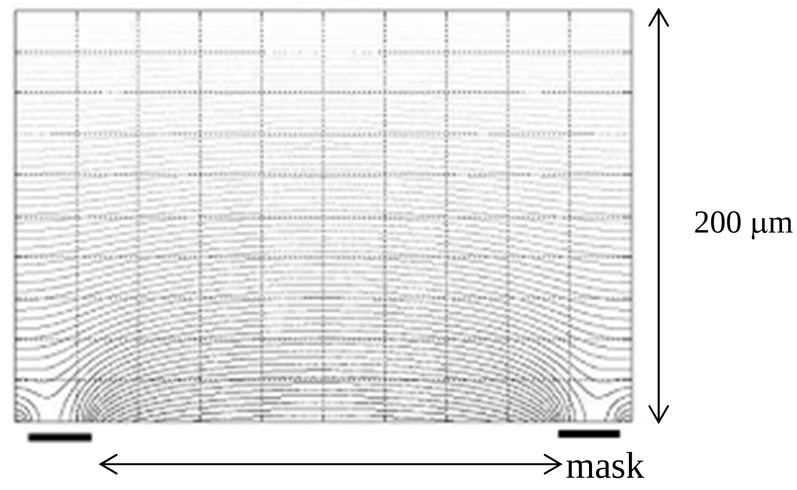
# Estimation of Surface Reaction Rate Constant, $k_s$ by SAG

## Growth Rate distribution analysis

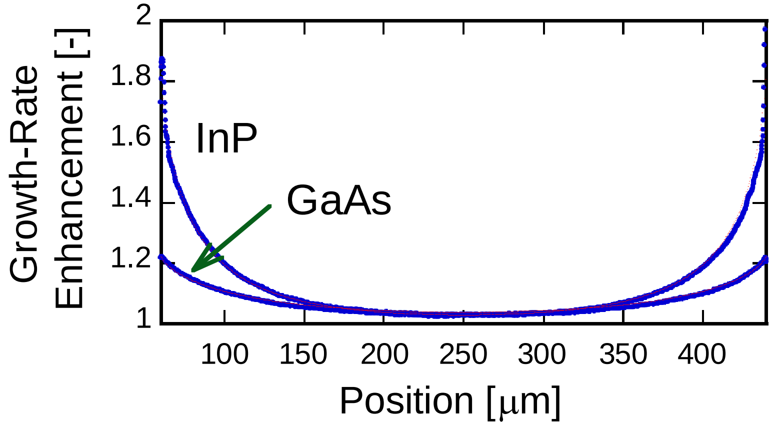
$$D\Delta C = 0$$

On masks $-\left(D\nabla C\right)\bullet\vec{n} = 0$

On films $-\left(D\nabla C\right)\bullet\vec{n} = k_s C_s$



growth area 380 μm

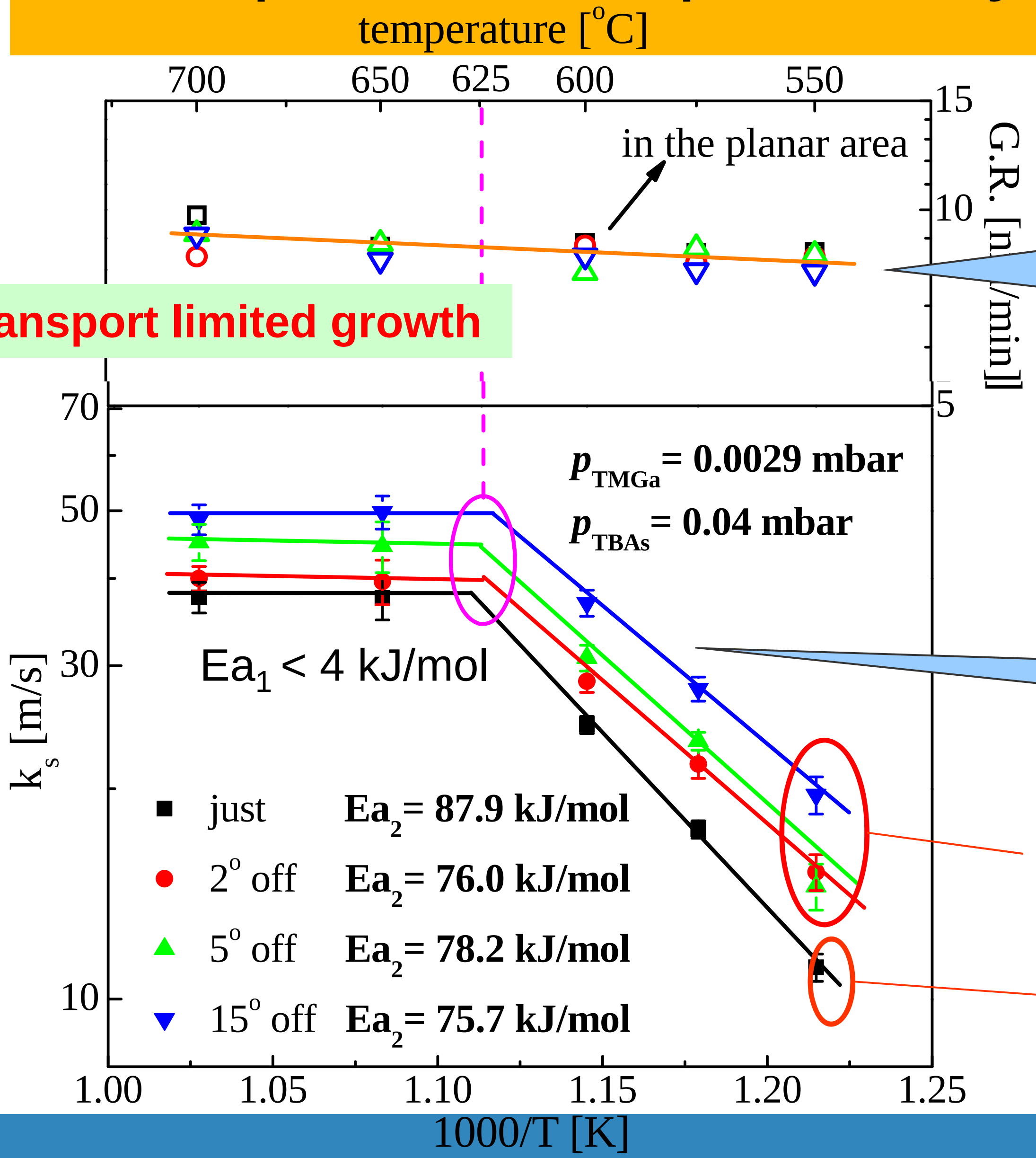


Fitting → *D*/*k*$_s$ is determined

*D* can be estimated

*k*$_s$ is obtained!

# Temperature Dependency of GR and $k_s$



**mass transport limited growth**

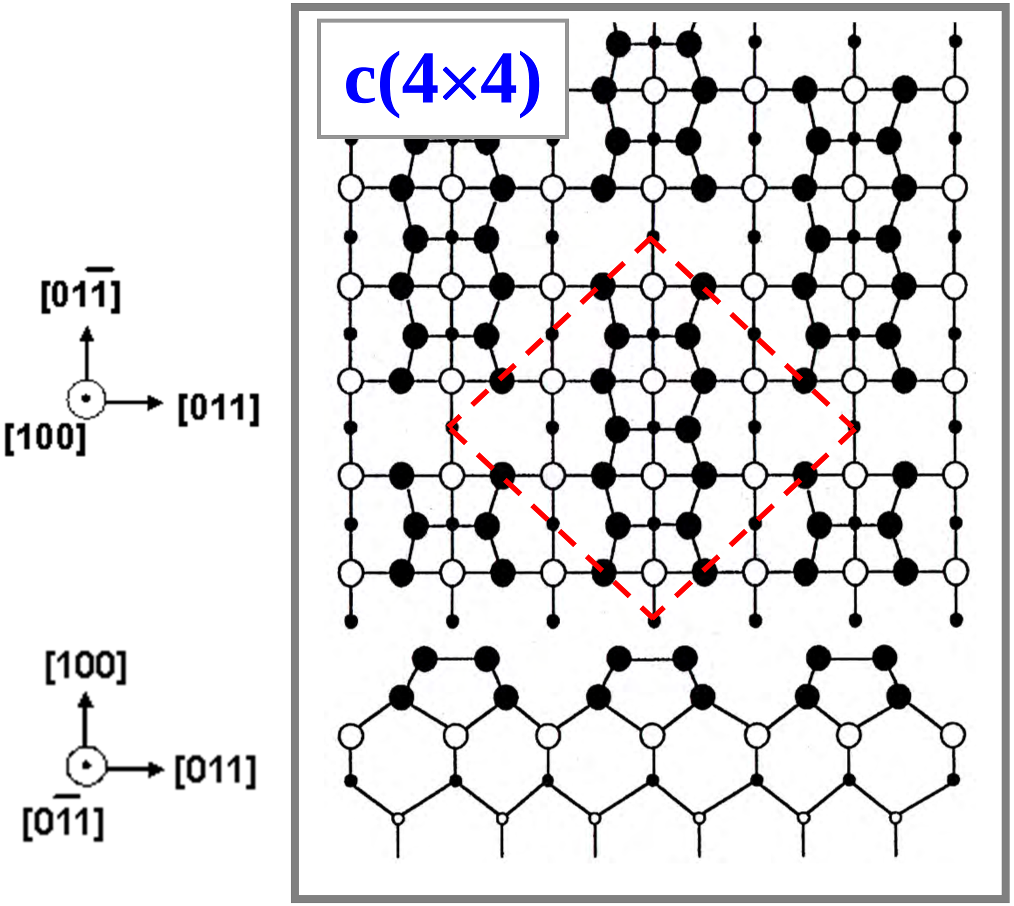
Growth rate in planar area

$k_{s\text{-}GaAs}$

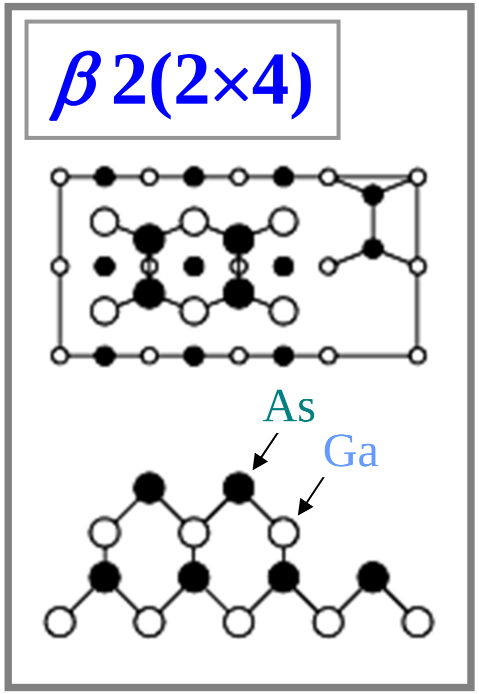
Step flow growth mode

2D nucleation dominated

# GaAs Surface Structure



*Ref. Q.Fu, JCG* ***225*** *(2001) 405*

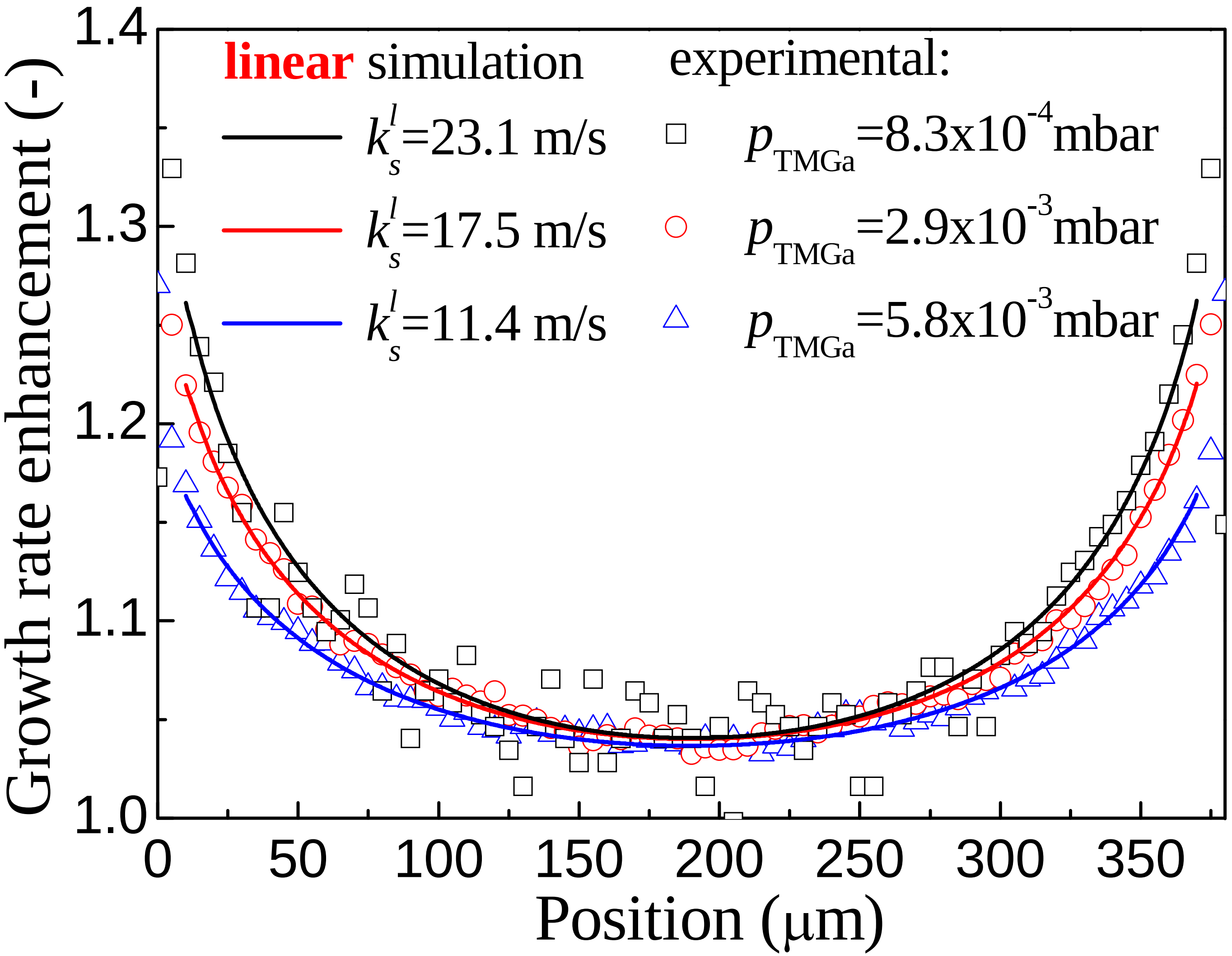


As surface coverage : 1.0 ML 0.75 ML

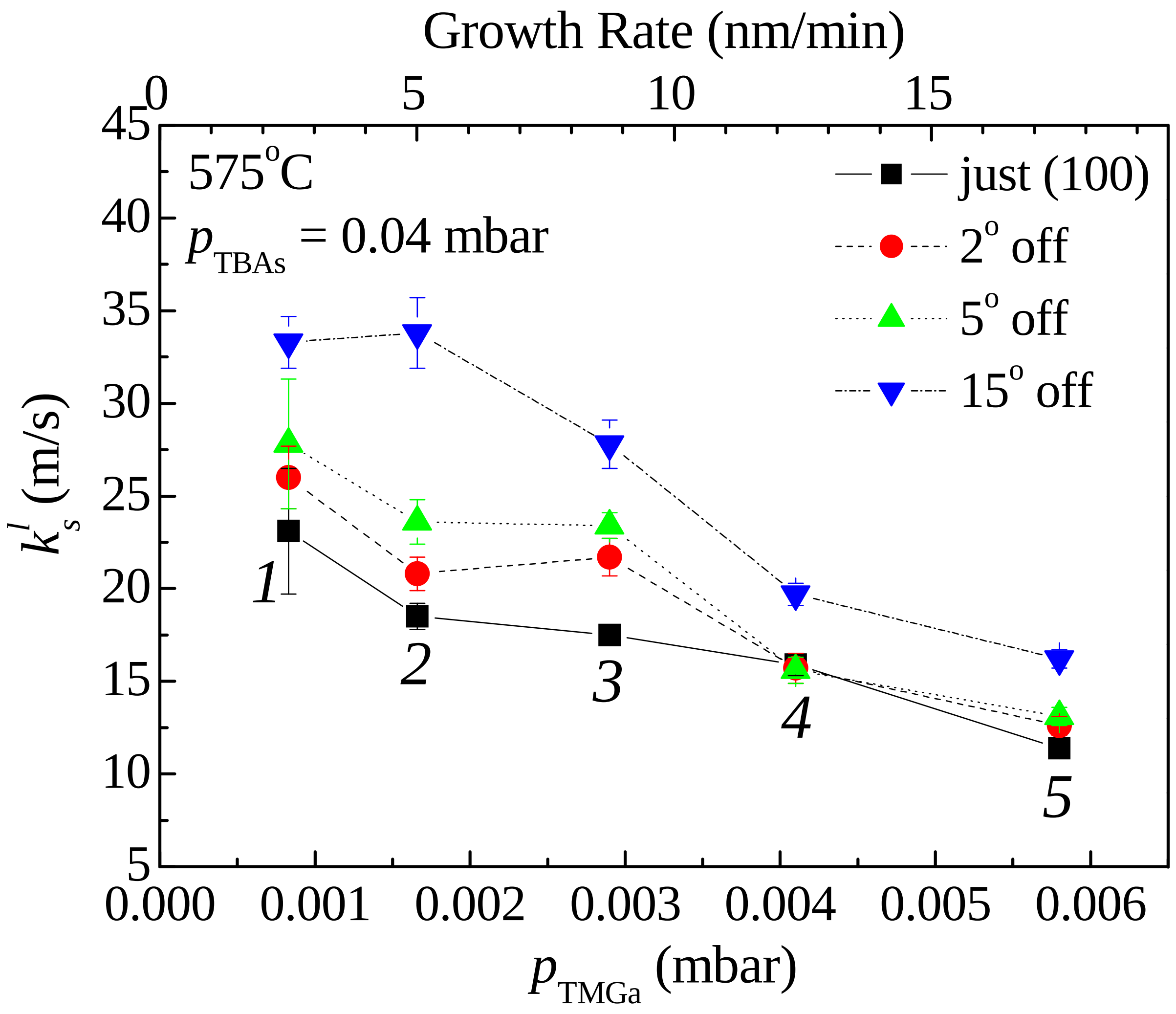
Low Temperature High Temperature

# Effect of $P_{TMGa}$ on SAG Profile

@575ºC



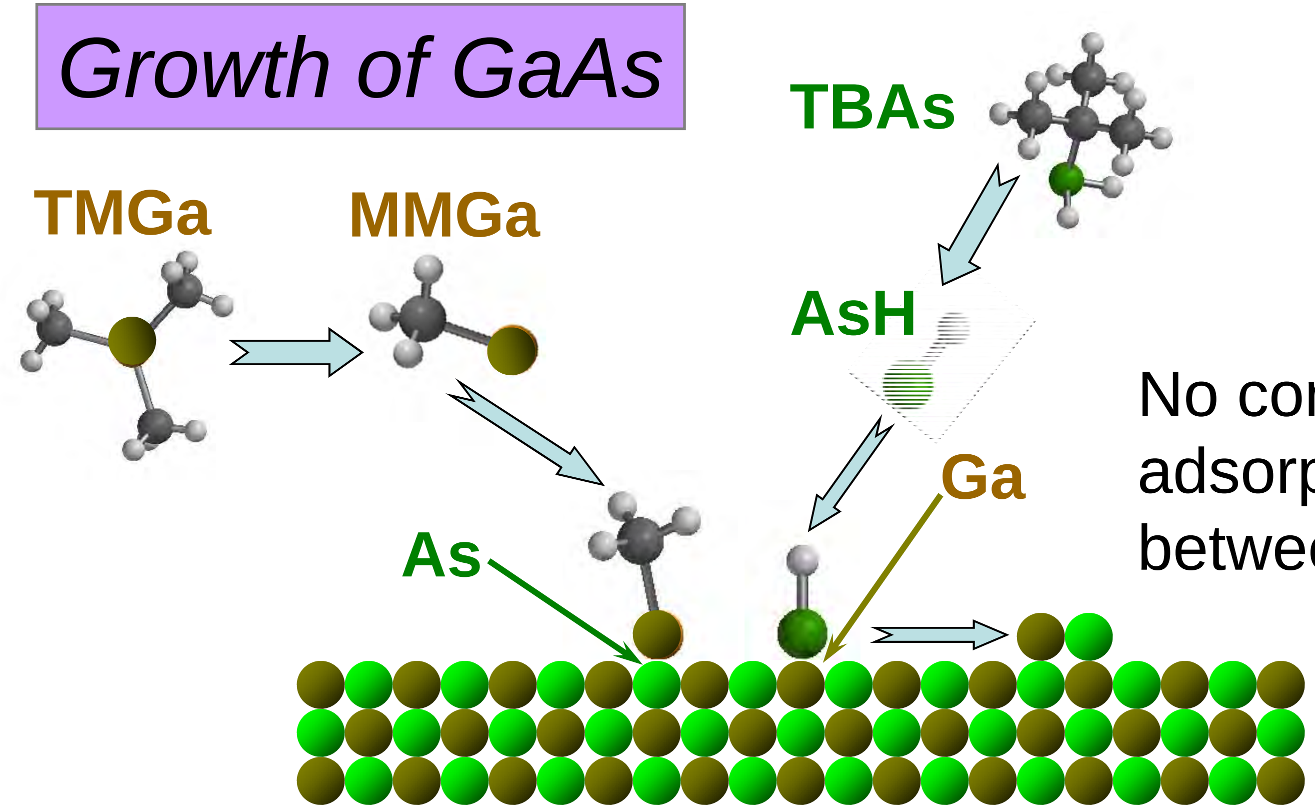
# $P_{TMGa}$ Dependency of $k_s$



@575ºC

$$r_s = k_s C_s \,?$$

# *Growth of GaAs*



No competition for the adsorption processes between Ga and As.

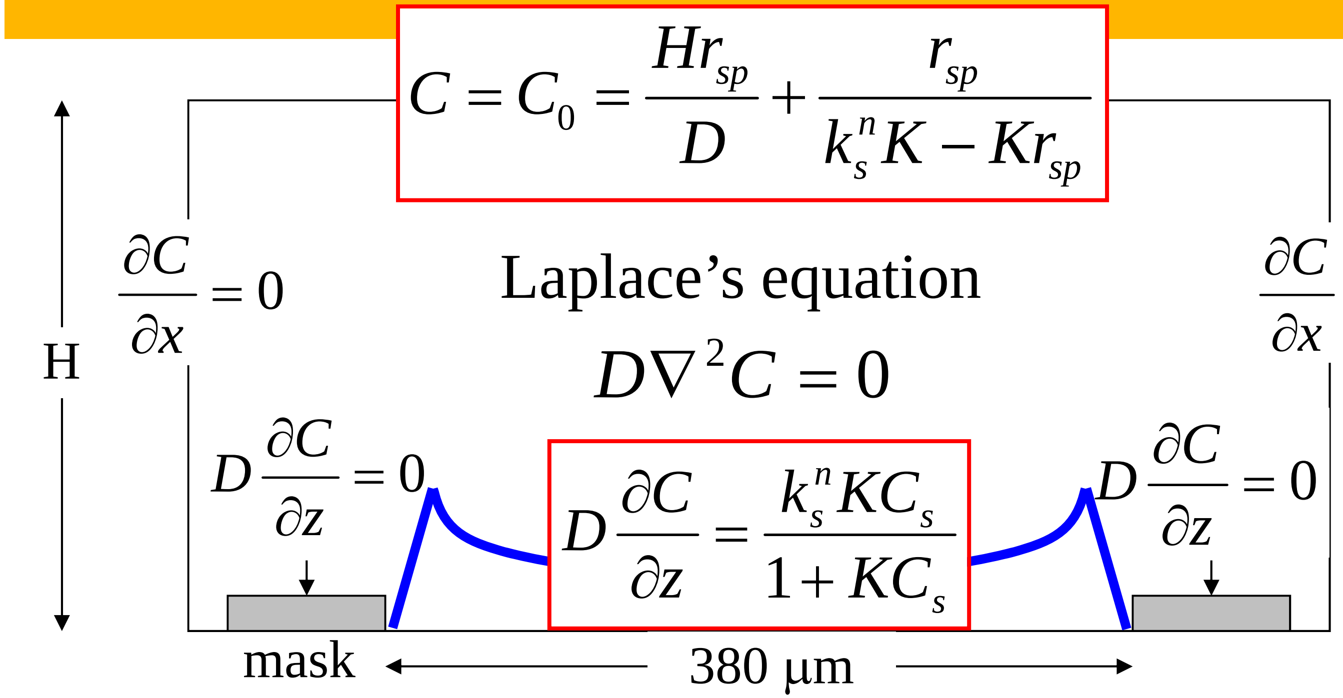
**MMGa + AsH → GaAs + by-products**

$$r = k_s^n \theta_{Ga} \theta_{As} \left\{ \begin{array}{l} \text{V/III} >> 1 \\ \theta_{Ga} = \dfrac{KC_{Ga}}{1 + KC_{Ga}} \end{array} \right. \Rightarrow$$

Langmuir-Hinshelwood adsorption isotherm

$$\boxed{r = \frac{k_s^n KC_{Ga}}{1 + KC_{Ga}}}$$

# Non-Linear Simulation



$$C = C_0 = \frac{Hr_{sp}}{D} + \frac{r_{sp}}{k_s^n K - Kr_{sp}}$$

$$\frac{\partial C}{\partial x} = 0$$

Laplace’s equation

$$D\nabla^2 C = 0$$

$$\frac{\partial C}{\partial x} = 0$$

$$D\frac{\partial C}{\partial z} = 0$$

$$D\frac{\partial C}{\partial z} = \frac{k_s^n K C_s}{1 + KC_s}$$

$$D\frac{\partial C}{\partial z} = 0$$

$$J_{planar} = D\frac{C_0 - C_{sp}}{H} = r_{sp} = \frac{k_s^n K C_{sp}}{1 + KC_{sp}}$$

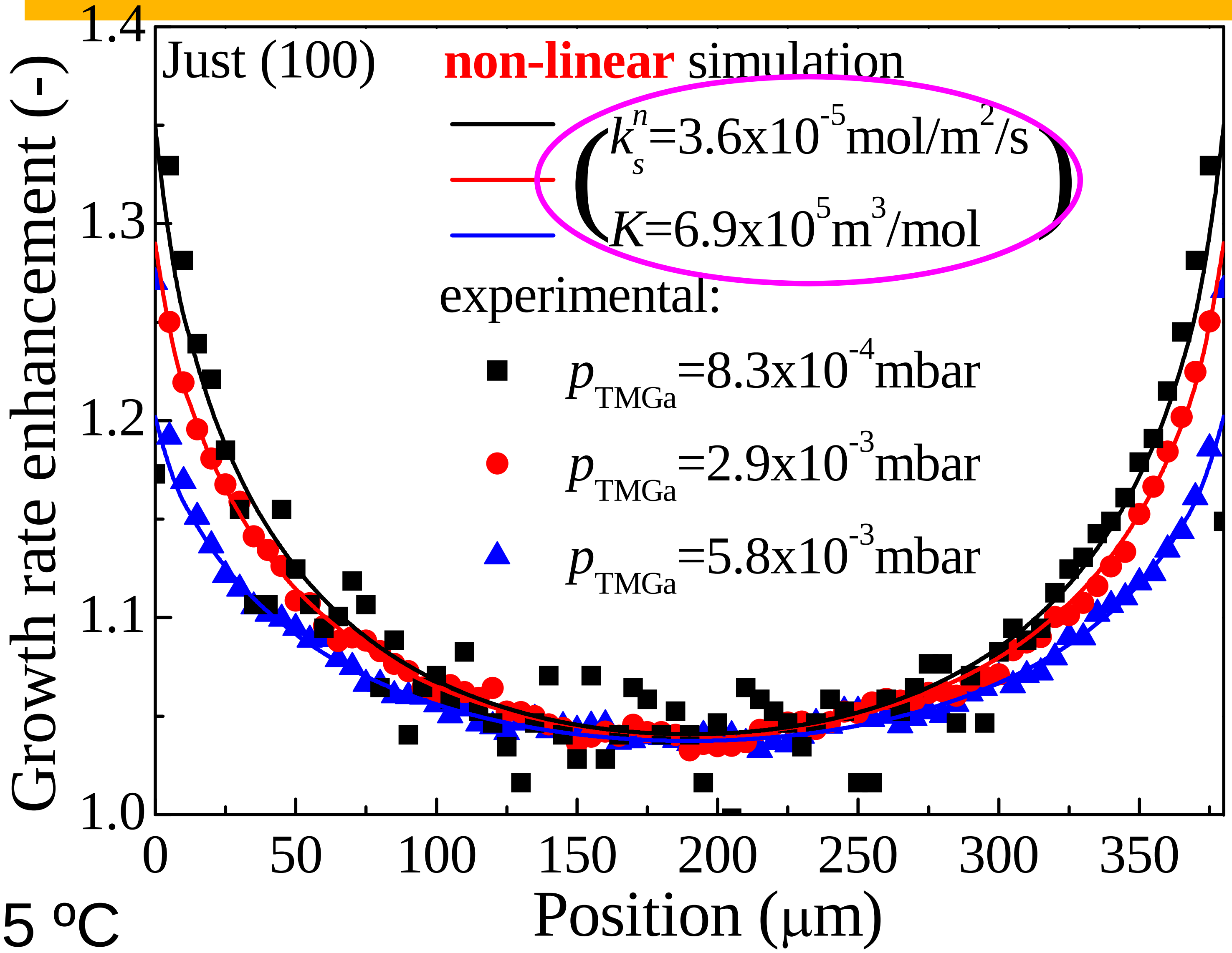
$$GRE = \frac{r_s}{r_{sp}} = \frac{\dfrac{k_s^n K C_s}{1 + KC_s}}{r_{sp}}$$

$C_s$ : COMSOL

$r_{sp}$: experiment

→ $k_s^n$, $K$

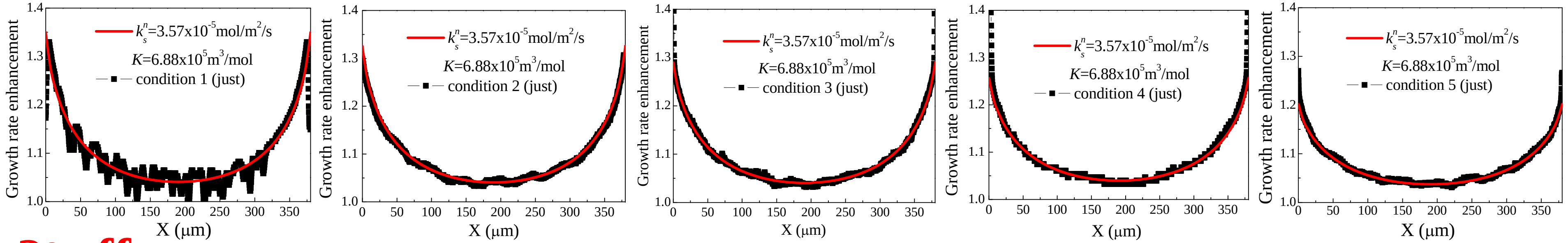
# Non-Linear Simulation Results



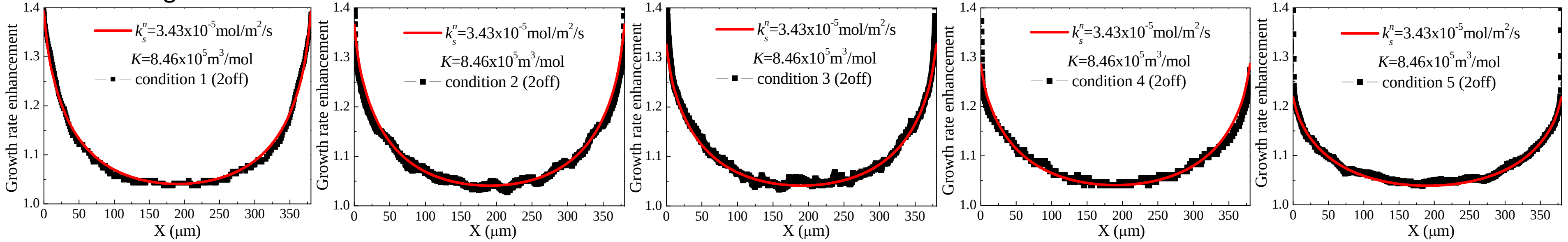
At 575 ºC

$p_{TMGa}$

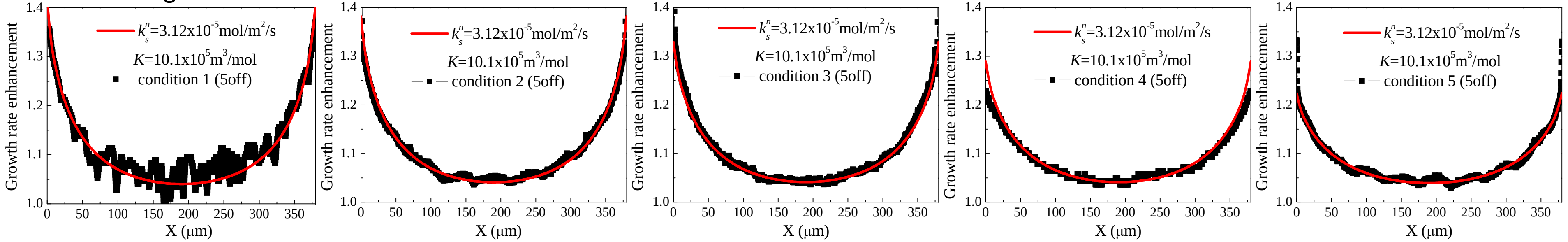
**just** $k_s^n$=3.6x10$^{-5}$mol/m$^2$/s, $K$=6.9x10$^5$m$^3$/mol



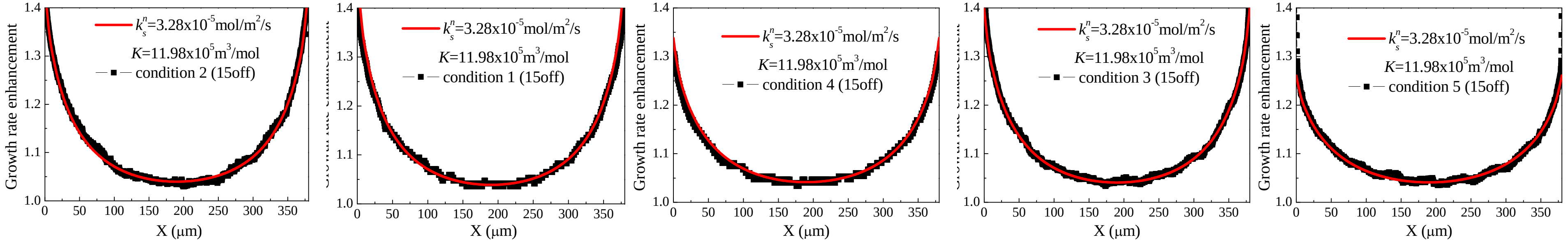
**2° off** $k_s^n$=3.4x10$^{-5}$mol/m$^2$/s, $K$=8.5x10$^5$m$^3$/mol



**5° off** $k_s^n$=3.1x10$^{-5}$mol/m$^2$/s, $K$=10x10$^5$m$^3$/mol



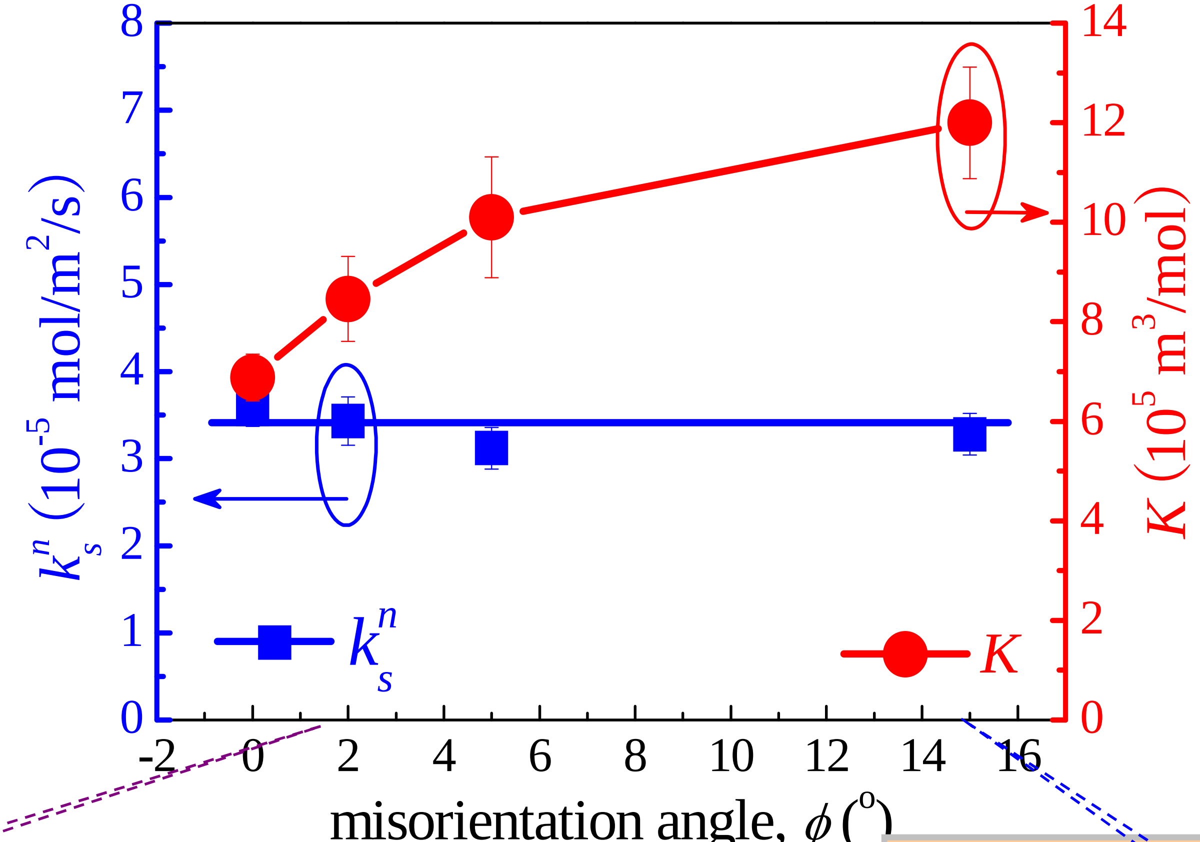
**15° off** $k_s^n$=3.3x10$^{-5}$mol/m$^2$/s, $K$=12x10$^5$m$^3$/mol

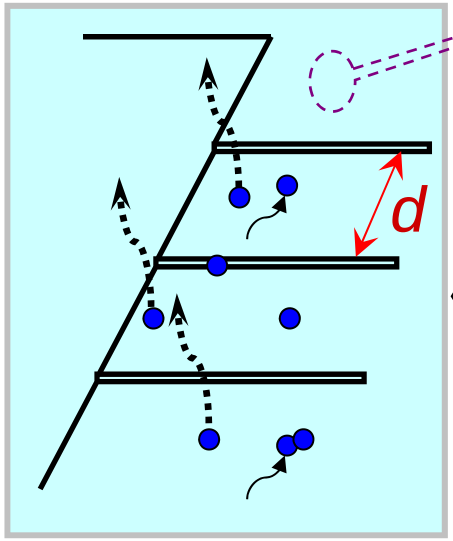


## $k_s^n$

reactivity of
Ga-species with
As-species on
the surface

Lifetime (on GaAs (100)) : 0.30 sec





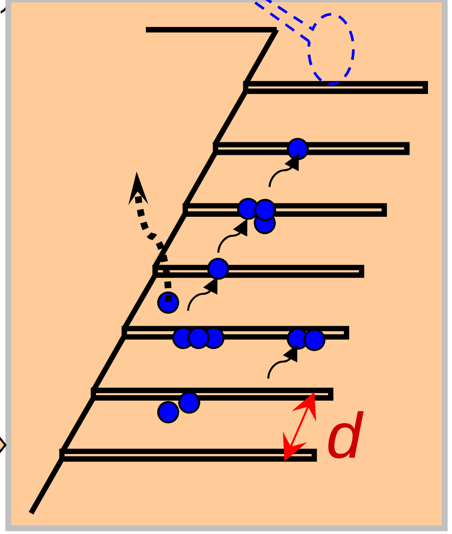
$$\boxed{K = \frac{k_a}{k_d}}$$

$k_a$: independent of *d*.

$k_d$: ~ *d*

$d\uparrow \Rightarrow$ easily desorbed $\Rightarrow k_d \uparrow \Rightarrow K \downarrow$

$d\downarrow \Rightarrow$ easily move to step edge $\Rightarrow k_d \downarrow \Rightarrow K \uparrow$



# Estimation of Surface Coverage

*Surface coverage*

$$\theta_{Ga} = \frac{KC_{Ga}}{1+KC_{Ga}}$$

@575ºC

| | surface coverage ($\theta_{Ga}$ ) | | | | |
|---|---|---|---|---|---|
| $p_{\text{TMGa}}$ ($10^{-3}$ mbar) | 0.83 | 1.7 | 2.9 | 4.1 | 5.8 |
| Just | 0.08 | 0.15 | 0.23 | 0.34 | 0.45 |
| $2^{o}$ off | 0.10 | 0.18 | 0.26 | 0.39 | 0.51 |
| $5^{o}$ off | 0.12 | 0.21 | 0.30 | 0.43 | 0.55 |
| $15^{o}$ off | 0.13 | 0.24 | 0.34 | 0.47 | 0.59 |

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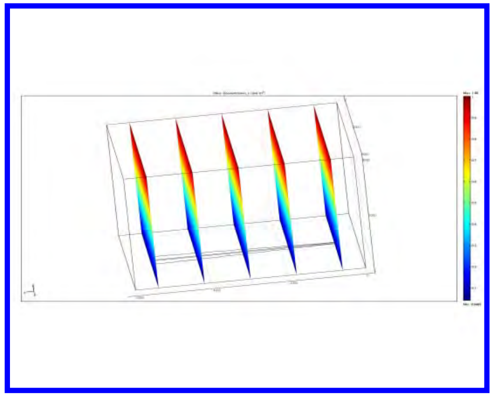
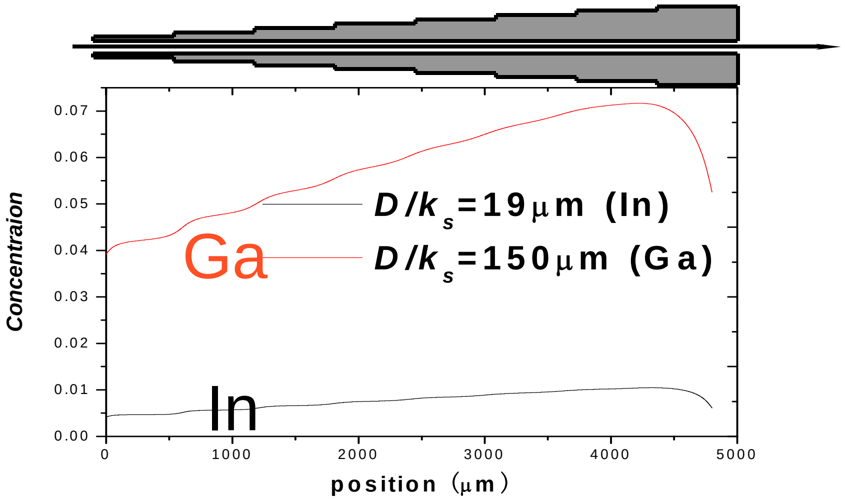
# Estimation of PL Wavelength of InGaAsP

simulation





Concentration close to surface

(G) GRE of In and Ga precursors

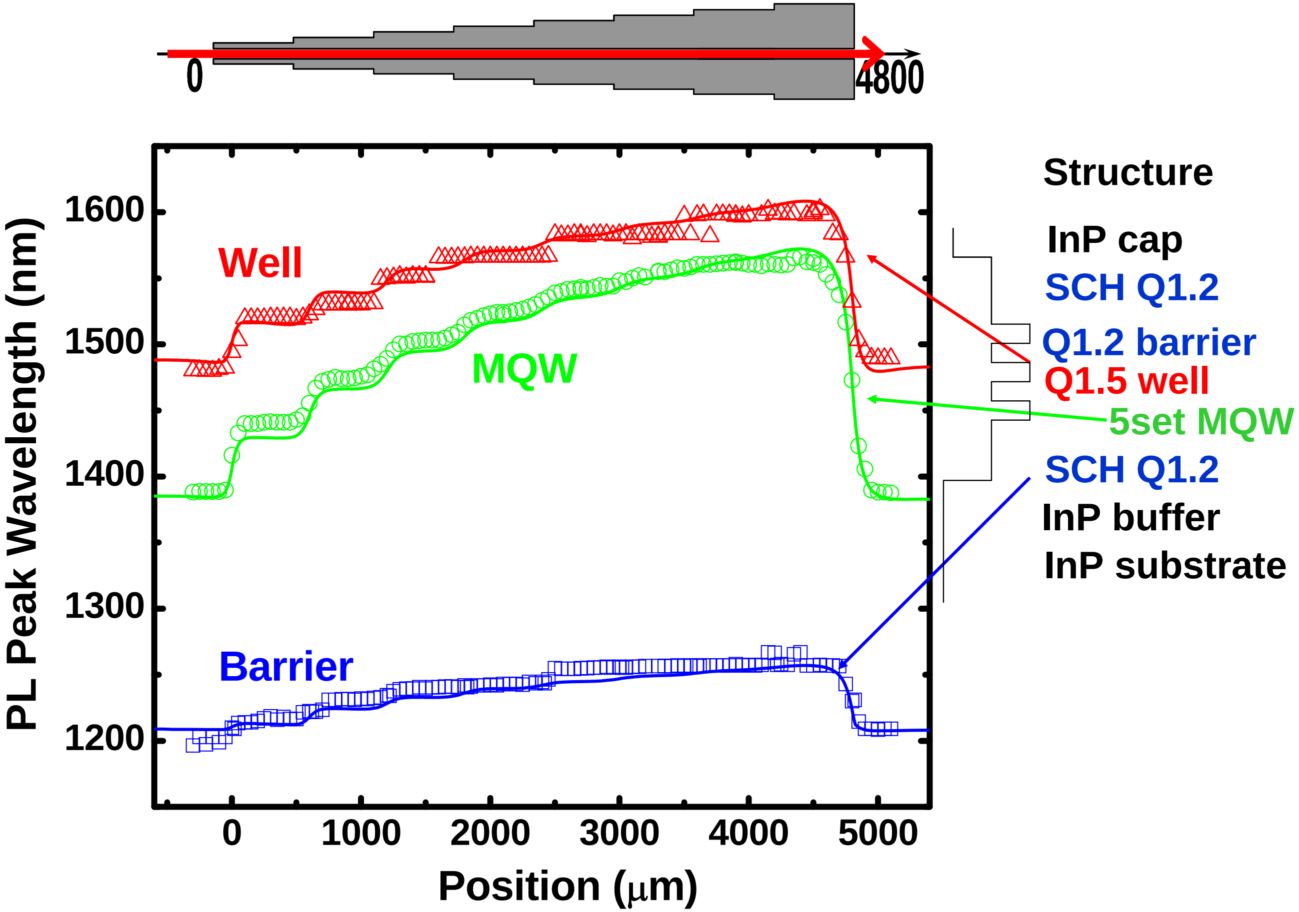
$G = (1-x_0)G_{In} + x_0\, G_{Ga}$

$x = x_0\, G_{Ga} / \{(1-x_0)G_{In} + x_0\, G_{Ga}\}$

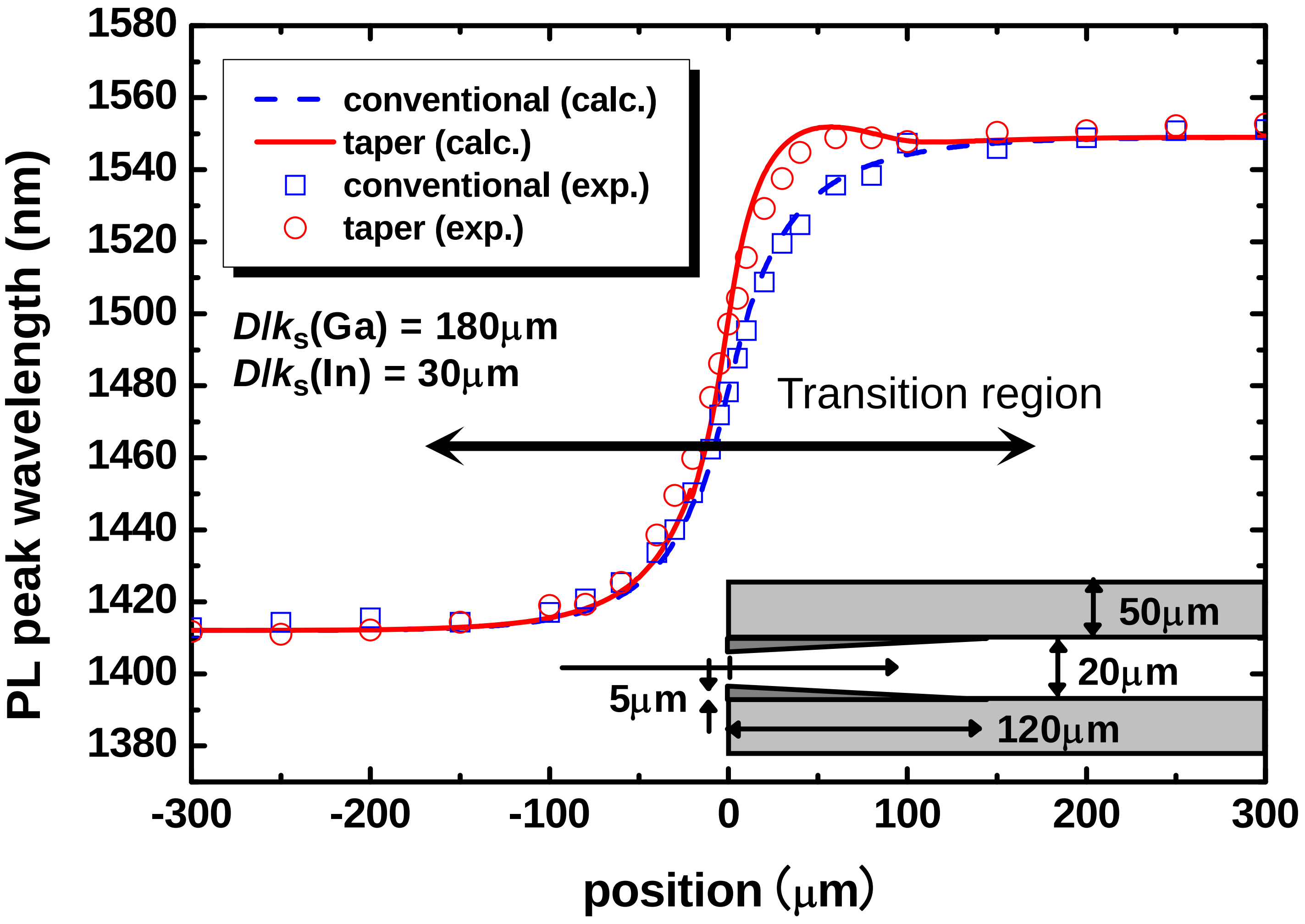
$In_{(1-x)}Ga_xAs_yP_{(1-y)}$ **(x)**

# 1.55μm PL Wavelength Estimation

Measured and simulated photoluminescence (PL) peak wavelength



# Mask design for transition region



# Summary

- SAG-MOCVD is a powerful tool to fabricate OEICs and is also effective to extract true surface kinetics during MOCVD.
- GaAs-MOCVD process was examined by SAG analysis.
  - Below 600ºC, surface kinetics shows non-linear behavior.
  - Surface reaction rate constant of adsorbed species was constant against offset angle, while adsorption equilibrium constant has a offset angle dependency.
  - S/Zn doping shows little or no effect on surface kinetics.
- InGaAsP PL wavelength was well predicted by SAG simulation based on the obtained kinetics.
- Mask design for OEICs is possible based on kinetic data base and kinetic simulation.