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

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

V/III >> 1
MOCVD Reaction Mechanism

Gas-phase decomposition: $k_g$

$(\text{CH}_3)_3\text{CPH}_2$ $\rightarrow$ $(\text{CH}_3)_3\text{In}$

Gas-flow and Gas-phase diffusion: $D/\delta$

Mass-transport

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.

- 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

\[ r_s = k_s C_s \]

Growth area

\[ \frac{\partial C}{\partial x} = 0 \]

\[ D \Delta C = 0 \]

Laplace’s Equation

\[ D \frac{\partial C}{\partial z} = k_s N \]

GRE

COMSOL Simulation & Fitting

\[ k_s : \text{surface reaction rate constant} \]

\[ D/k_s \]

Growth-Rate-Enhancement

\[ G.R.E. = \frac{R_{SAG}}{R_{Planar}} \]
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 $- (D \nabla C) \cdot \vec{n} = 0$

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

$D \Delta C = 0$

Growth area 380 \( \mu \text{m} \)

Fitting $\rightarrow \frac{D}{k_s}$ is determined

$D$ can be estimated

$k_s$ is obtained!
Temperature Dependency of GR and $k_s$

**Temperature [°C]**

Growth rate in planar area

mass transport limited growth

$Ea_1 < 4 \text{ kJ/mol}$

$p_{\text{TMGa}} = 0.0029 \text{ mbar}$

$p_{\text{TBAs}} = 0.04 \text{ mbar}$

$k_s$-GaAs

Step flow growth mode

2D nucleation dominated

- just $Ea_2 = 87.9 \text{ kJ/mol}$
- $2^\circ$ off $Ea_2 = 76.0 \text{ kJ/mol}$
- $5^\circ$ off $Ea_2 = 78.2 \text{ kJ/mol}$
- $15^\circ$ off $Ea_2 = 75.7 \text{ kJ/mol}$
GaAs Surface Structure

As surface coverage:

- **c(4×4)**: 1.0 ML, Low Temperature
- **β 2(2×4)**: 0.75 ML, High Temperature

Ref: Q. Fu, *JCG* 225 (2001) 405
Effect of $P_{\text{TMGa}}$ on SAG Profile

@575°C

linear simulation

- $k^l_s = 23.1$ m/s
- $k^l_s = 17.5$ m/s
- $k^l_s = 11.4$ m/s

experimental:

- $p_{\text{TMGa}} = 8.3 \times 10^{-4}$ mbar
- $p_{\text{TMGa}} = 2.9 \times 10^{-3}$ mbar
- $p_{\text{TMGa}} = 5.8 \times 10^{-3}$ mbar
$P_{\text{TMGa}}$ Dependency of $k_s$

Growth Rate (nm/min)

$575^\circ C$

$p_{\text{TBAs}} = 0.04$ mbar

$r_s = k_s C_s$ ?

@575$^\circ$C
**Growth of GaAs**

\[ \text{MMGa} + \text{AsH} \rightarrow \text{GaAs} + \text{by-products} \]

No competition for the adsorption processes between Ga and As.

\[
r = k_s^n \theta_{Ga} \theta_{As} \quad \text{V/III} \gg 1
\]

\[
\theta_{Ga} = \frac{KC_{Ga}}{1 + KC_{Ga}}
\]

**Langmuir-Hinshelwood adsorption isotherm**

\[
r = \frac{k_s^n KC_{Ga}}{1 + KC_{Ga}}
\]
Non-Linear Simulation

\[ C = C_0 = \frac{H r_{sp}}{D} + \frac{r_{sp}}{k_s^n K - K r_{sp}} \]

Laplace's equation:
\[ D \nabla^2 C = 0 \]

\[ \frac{\partial C}{\partial x} = 0 \]
\[ \frac{\partial C}{\partial z} = 0 \]

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

\[ J_{\text{planar}} = D \left( C_0 - C_{sp} \right) = \frac{r_{sp}}{H} = \frac{k_s^n K C_{sp}}{1 + K C_{sp}} \]

\[ \text{GRE} = \frac{r_s}{r_{sp}} = \frac{k_s^n K C_s}{1 + K C_s} \]

\[ C_s : \text{COMSOL} \]
\[ r_{sp} : \text{experiment} \]

\[ k_s^n, K \]
Non-Linear Simulation Results

At 575 °C

Just (100) non-linear simulation

\[ k_s^n = 3.6 \times 10^{-5} \text{ mol/m}^2/\text{s} \]

\[ K = 6.9 \times 10^5 \text{ m}^3/\text{mol} \]

experimental:

- \( p_{\text{TMGa}} = 8.3 \times 10^{-4} \text{ mbar} \)
- \( p_{\text{TMGa}} = 2.9 \times 10^{-3} \text{ mbar} \)
- \( p_{\text{TMGa}} = 5.8 \times 10^{-3} \text{ mbar} \)
just $k_s = 3.6 \times 10^{-5} \text{mol/m}^2/\text{s}$, $K = 6.9 \times 10^5 \text{m}^3/\text{mol}$

$\rho_{TMGa}$
$k_s^n$ reactivity of Ga-species with As-species on the surface

Lifetime (on GaAs (100)) : 0.30 sec

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

$k_a$: independent of $d$.

$k_d$: $\sim d$

$d \uparrow \Rightarrow$ 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

\[
\theta_{Ga} = \frac{KC_{Ga}}{1 + KC_{Ga}}
\]

@575°C

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<th>( p_{TMGa} ) (10^{-3} mbar)</th>
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Estimation of PL Wavelength of InGaAsP

(G) GRE of In and Ga precursors

\[ G = (1-x_0)G_{\text{In}} + x_0 G_{\text{Ga}} \]

\[ x = x_0 \frac{G_{\text{Ga}}}{(1-x_0)G_{\text{In}} + x_0 G_{\text{Ga}}} \]

\[ \text{In}_{(1-x)}\text{Ga}_x\text{As}_y\text{P}_{(1-y)} \quad (x) \]
1.55 μm PL Wavelength Estimation

Measured and simulated photoluminescence (PL) peak wavelength
Mask design for transition region

![Graph showing PL peak wavelength vs position with marks for conventional and taper designs, along with calculated and experimental data points.]

- $D/k_s(Ga) = 180 \mu m$
- $D/k_s(In) = 30 \mu m$

Transition region:
- $5 \mu m$
- $20 \mu m$
- $50 \mu m$
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 600°C, 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.