Semiconductor Optical Communication Components and Devices

Lecture 9: Epitaxial growth - II (MOVPE/MOCVD Techniques)

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In MOVPE the precursorgases, such as Trimethyl Gallium (TMG), Trimethyl indium (TMI), Triethyl Aluminium (TEA), Arsine (AsH₃), Phosphene (PH₃), Tertiarybutyl Arsene (TBA), etc. flow over a heated substrate and decompose to supply atoms for epitaxy. These gas molecules decompose on the hot substrate, the resulting organic molecules (CH₄, etc) evaporate, leaving the Ga and As atoms for incorporation into the crystal. At typical Growth Temperatures ~ 600-800°C, growth rate can vary from 1 monolayer/sec to 1µm/hr. This slow growth rate allows the gases to be switched at a very fast rate to give very abrupt interfaces such that quantum wells (~10nm thick) can also be deposited. As the Si-industry is familiar with CVD, the more popular name for this process is Metal-Organic CVD or MOCVD. Another name is OMVPE.
Metalo-Organic Vapor Phase Epitaxy (MOVPE) or more popularly called Metal-Organic Chemical Vapor Deposition (MOCVD) Reactions.

Ga(CH₃)₃ + AsH₃ → GaAs + 3CH₄

Quartz Tube

TMGa → AsH₃ → H₂

Transport to the substrate

Thermal cracking of molecules → Growth

Substrate Susceptor

Heating (-700°C)

T₀ = 300K, v₀

TMGa → AsH₃ → H₂

Temperature

Gas velocity
Trimethyldindium (TMIn) molecules react on the surface, depositing TMIn subspecies.

Incorporation is at the lattice step edge.

Phosphine ($\text{Ph}_3$) molecules leaving phosphorous to react with TMIn subspecies, forming InP and CH₄.

Reaction by-products ($\text{CH}_3$) leave the reactor.

Reactants and products undergo vapor reactions, diffusion, adsorption, and desorption processes.
Horizontal MOCVD (MOVPE) REACTOR

Load lock System

Gas Handling Manifold

Exhaust System

Could be Atmospheric or Low Pressure

Reactor Tube
MOCVD Epitaxy Bubbler System (left), showing the Exhaust system (right) and the cracking furnace (top) Filters (bottom rear) and the schematic.

Two types of MO-Bubbler.

MO-Bubbler CHILLERS.
Metal-Organc Precursors

- DMZn
- Silane
- Arsin

Graph showing vapor pressure vs. temperature for various precursors:
- JBP
- TBAa
- TMGa
- TMAI
- TMLn
- TEGa
- DADI
- TElIn
GaAs handling manifold in a vertical MOCVD system.

Flow path lines of precursors and carrier gas for a vertical MOCVD system.

Multiple substrate wafers for epitaxial deposition in a vertical MOCVD system.
Plumbing Schematic of a Horizontal MOCVD System, Reactor, Load lock chamber (top), Scrubber & exhaust (top right), Evacuation port (bottom).
MOCVD Group III mole-fraction and Group V partial pressures

Group III Mole fraction in Solid as a function
Mole fraction in Vapor

Group V Mole fraction in Solid as a function of Partial Pressure

\[
\frac{P_{PH_3}}{P_{PH_3} + P_{AsH_3}}
\]
Growth rate and composition varies in a MOCVD growth system due to differences in the incorporation rates of different species and due to the difference in the partial pressures of different precursor gases.

**Growth rate versus distance along the substrate (left)**

**and compositional variation along the substrate (bottom).**
MOCVD Growth

AlGaAs growth rate distribution along the wafer in an AIX 200 horizontal reactor

Carrier Flow rate ‘F’ ltr/min

Growth Rate ‘G’ μm/min

\[ G = K(\text{Mol. Frac.}_{\text{III}}), \quad K \approx 350-400 \]

GaAs growth rate - vertical reactor

Mol. Frac.\(_{\text{III}}\) = \[\frac{\text{Gr. III Flow Rate (FL\(_{\text{III}}\))}}{\text{Carrier Flow rate (FL\(_{\text{H}_2}\))}}\]

\[ (\text{FL\(_{\text{III}}\))_{\text{actual}}} = (\text{FL\(_{\text{III}}\))} \cdot \frac{P_{\text{H}_2}[1600\text{torr}]}{V_{\text{III}}[64.7\text{torr} \text{ TMG at 0 C}]}) \]

\[ \text{Al}_x\text{Ga}_{1-x}\text{As}, \quad \text{Mol. F}_{\text{Al}} = (x/D)(\text{Mol. F}_{\text{III}}) \]

\[ D = 2 \text{ for Al, } D = 1 \text{ for Ga, In} \]

\[ \text{Mol. F}_{\text{Ga}} = \text{Mol. F}_{\text{III}} - \text{Mol. F}_{\text{Al}} \]

\[ \text{FL}_{\text{Al}} = (\text{Mol. F}_{\text{Al}}) \cdot F \cdot P_{\text{H}_2}/V_{\text{Al}}[7.3\text{ torr TMA at 0 C}] \]

\[ (V/\text{III}) \approx 20 \text{ (As)} \]

\[ \text{FL}_V = \text{Mol. F}_{\text{III}} \cdot (V/\text{III}) \cdot F, \]

\[ (P/\text{As}) = 200-400 \text{ for P}_y\text{As}_{1-y} \]
Reflection Anisotropy Spectroscopy (RAS) or using Polarized light one can do Reflection Difference Spectroscopy (RDS) in 250 - 850 nm

Information obtained may be like
- composition
- Bragg mirror properties
- wafer temperature
- doping

There is usually deposit on the (cold wall) quartz wall of unwanted reactant species which does not leave the viewport complete transparent thus leading to errors, if not cleaned quite often.
In Atomic Layer Epitaxy, the substrate moves alternatively under Group III and Group V flow with intermediate swiping of the remnants under H₂ flow.

Role of Growth Interruption
Growth Interruption for smooth surface and composition uniformity on the wafer in MOCVD Growth.
1. A graded $\text{Al}_{0.36}\text{Ga}_{0.64}\text{As}$ is to be grown on GaAs for a thickness of 1$\mu$m at a growth rate of 1$\mu$m/hr. in an MOCVD system using TMG, TEG, and AsH$_3$. Find the flow rates of TMG, TEG, and AsH$_3$ with time if growth is done at 750$^\circ$C. The carrier gas (H$_2$) flow rate is 10 SLM (Standard Litres per minute).

2. An $\text{In}_x\text{Ga}_{(1-x)}\text{As}_y\text{P}_{(1-y)}$ is to be grown lattice matched to InP at a band gap of 0.8eV. Find the flow rates of TMG, TMI, AsH$_3$, and PH$_3$, if growth is to be done at 700$^\circ$C. The carrier gas (H$_2$) flow rate is 15 SLM.