Pre-report

Metal **O**rganic **C**hemical **V**apor **D**eposition **(MOCVD)**

Name:
Student number:
Due date:
Class: Compound semiconductor process

1. Introduction

Metal **O**rganic **C**hemical **V**apor **D**eposition **(MOCVD)** or Metal-Organic Vapor Phase Epitaxy (MOVPE) is a widely used method for preparing epitaxial structures by depositing atoms on a wafer substrate. It is utilized for a broad variety of applications in industry and research. The principle of MOCVD is quite simple. Atoms are deposited by decomposing organic molecules (precursors) while they are passing over the hot substrate. The undesired remnants are removed or deposited on the walls of the reactor. III-V semiconductors of high purity and structural order are prepared via MOCVD.

Preparation of epitaxial thin films of III-V compound semiconductors (notably GaAs) for applications in advanced electronic devices became a realistic technology through the development of metal organic chemical vapor deposition (MOCVD) processes and techniques. The processes mainly involve the thermal decomposition of metal alkyls and/or metal hydrides.

In 1968 Manasevit at the Rockwell Corporation was the first to publish on MOCVD for the epitaxial growth of GaAs. This followed his pioneering work in 1963 with the epitaxial growth of silicon on sapphire. The first publication used triethylgallium [$Ga(CH_2CH_3)_3$] and arsine (AsH_3) in an open tube with hydrogen as the carrier gas. Manasevit actually coined the phrase MOCVD and since this seminal work there have been numerous attempts to improve and expand MOCVD for the fabrication of GaAs.

2. Principle of MOCVD process

Conventionally, the metal organic chemical vapor deposition (MOCVD) growth of GaAs involves the pyrolysis of a vapor phase mixture of arsine and, most commonly, trimethylgallium [$Ga(CH_3)_3$, TMG] and triethylgallium [$Ga(CH_2CH_3)_3$, TEG]. Traditionally, growth is carried out in a cold-wall quartz reactor in flowing H_2 at atmospheric or low pressure. The substrate is heated to temperatures 400 - 800 °C, typically by RF heating of a graphite susceptor. Transport of the metal-organics to the growth zone is achieved by bubbling a carrier gas (e.g., H_2) through the liquid sources that are in held temperature-controlled bubblers.

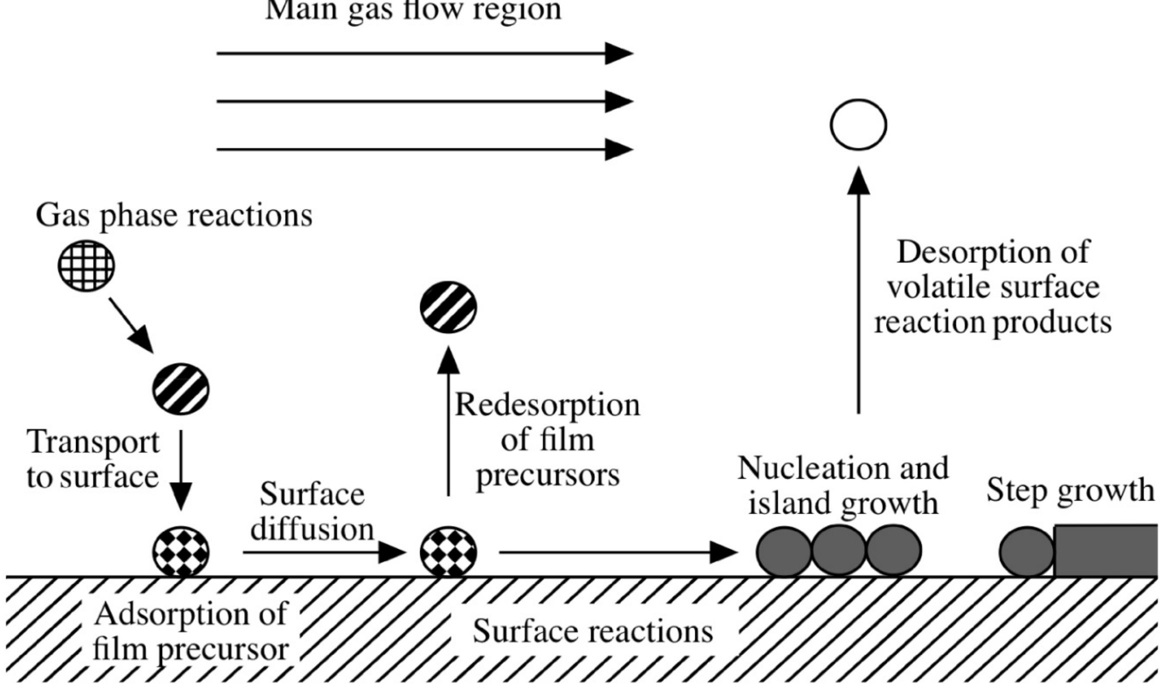


Figure 1. Schematic representation of the fundamental transport and reaction steps underlying MOCVD. Adapted from K. F. Jensen and W. Kern, in Thin Film Processes II, Eds. J. L. Vossen and W. Kern, Academic Press, New York (1991).

① Laminar flow of carrier gas (H_2 or N_2) and of the precursor molecules (metal-organic compounds) over the substrate (wafer) placed on a graphite susceptor inside a reaction vessel (reactor)

② Supply of thermal energy (usually between 400°C and 700°C) for decomposing the molecules,

③ Deposition of the material, evaporation of the molecular fragments into the gas phase.

3. Reaction mechanism

I will explain in GaAs case. While the overall reaction (where R = CH_3 or CH_2CH_3) can be described by Equation (1).

$$R_3Ga + AsH_3 \rightarrow GaAs + 3\,RH \tag{1}$$

The nature of the reaction is much more complex. From early studies it was thought that free Ga atoms are formed by pyrolysis of TMG and As_4 molecules are formed by pyrolysis of AsH_3 and these species recombine on the substrate surface in an irreversible reaction to form GaAs.
Although a Lewis acid-base complex formed between TMG and AsH_3 is possible, it is now known that if there is any intermediate reaction between the TMG and AsH_3, the product is unstable. However, early work indicated that free GaAs molecules resulted from the decomposition of a TMG.AsH_3 intermediate and that the heated surface contributed to the reaction. It was subsequently suggested that the reaction occurs by separate pyrolysis of the reactants and a combination of individual Ga and As atoms at the surface or just above it. Finally, evidence has also been found for TMG pyrolysis followed by diffusion through a boundary layer and for AsH_3 pyrolysis catalyzed by the GaAs surface.
There are several different kinds of potential reactions occuring in the CVD reaction chamber, namely, ligand dissociation, ligand association, , reductive elimination, oxidative addition, β-hydride elimination, etc. Some of them are listed in the following equations:

$$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3 \qquad \text{(ligand dissociation)} \tag{2}$$

$$Ga(CH_3)_2 \rightarrow Ga + CH_3\text{-}CH_3 \qquad \text{(reductive elimination)} \tag{3}$$

$$Ga(CH_3)_3 \rightarrow Ga(CH_3) + CH_3\text{-}CH_3 \qquad \text{(reductive elimination)} \tag{4}$$

$$CH_3 + H \rightarrow CH_4 \qquad \text{(radical recombination)} \tag{5}$$

$$Ga\text{-}CH_2\text{-}CH_3 \rightarrow Ga\text{-}H + H_2C{=}CH_2 \qquad \text{(}\beta\text{-hydride elimination)} \tag{6}$$

$$Ga(CH_3)_3 + AsR_3 \rightarrow (CH_3)_3Ga\text{-}AsR_3 \qquad \text{(ligand association)} \tag{7}$$

Several ideas

① Gas phase reaction

② Adsorption and surface reactions

③ Overall reaction pathway

4. Reactor components

A reactor is a chamber made of a material that does not react with the chemicals being used. It must also withstand high temperatures. This chamber is composed by reactor walls, liner, a susceptor, gas injection units, and temperature control units. Usually, the reactor walls are made from stainless steel or quartz. To prevent over heating, cooling water must be flowing through the channels within the reactor walls. Ceramic or special glasses, such as quartz, are often used as the liner in the reactor chamber between the reactor wall and the susceptor. A substrate sits on a *susceptor* which is at a controlled temperature. The susceptor is made from a material resistant to the metalorganic compounds used; graphite is sometimes used. For growing nitrides and related materials, a special coating on the graphite susceptor is necessary to prevent corrosion by ammonia (NH_3) gas.

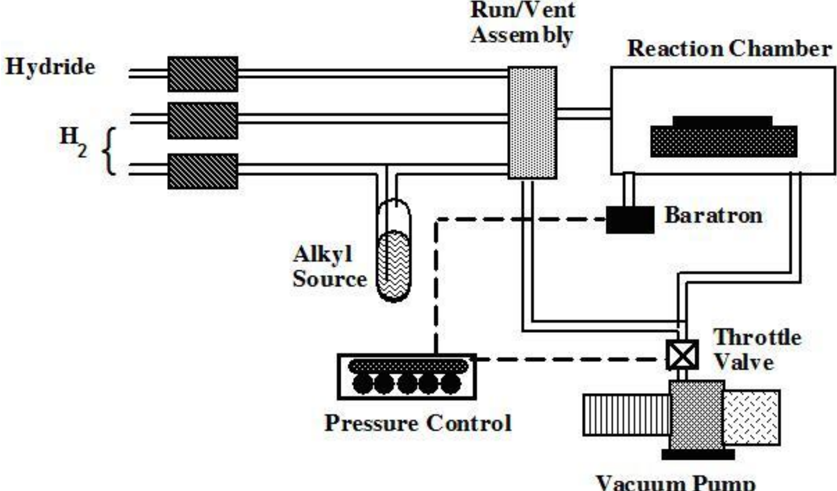


Figure 2. Reactor component [http://www.ask.com/wiki/MOCVD]

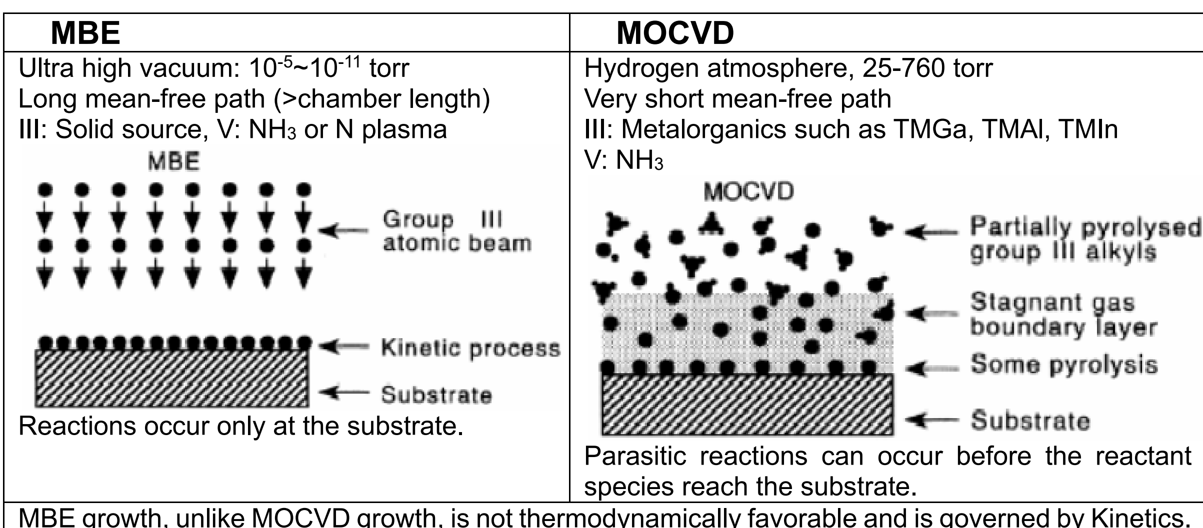
Gas inlet and switching system, Gas is introduced via devices known as 'bubblers'. In a bubbler, a carrier gas (usually nitrogen or hydrogen) is bubbled through the metalorganic liquid, which picks up some metalorganic vapour and transports it to the reactor. The amount of metalorganic vapour transported depends on the rate of carrier gas flow and the bubbler temperature, and is usually controlled automatically and most accurately by using a Piezocon type vapour control system. Allowance must be made for saturated vapours.

Pressure maintenance system

Gas Exhaust and cleaning System. Toxic waste products must be converted to liquid or solid wastes for recycling (preferably) or disposal. Ideally, processes will be designed to minimize the production of waste products.

5. Comparison with molecular beam epitaxy (MBE)

Mean free path $\lambda = \frac{kT}{1.414P\sigma} \approx \frac{5\text{x}10^{-4}}{P}\ (m)\ at\ 1000℃$ where σ is the collision cross-section



MBE	MOCVD
Ultra high vacuum: 10^{-5}~10^{-11} torr Long mean-free path (>chamber length) III: Solid source, V: NH_3 or N plasma Reactions occur only at the substrate.	Hydrogen atmosphere, 25-760 torr Very short mean-free path III: Metalorganics such as TMGa, TMAl, TMIn V: NH_3 Parasitic reactions can occur before the reactant species reach the substrate.
MBE growth, unlike MOCVD growth, is not thermodynamically favorable and is governed by Kinetics.	

6. Advantages and disadvantages

① Advantages

i. Faster growth than MBE, can be a few microns per hour; multi-wafer capability easily achievable

ii. Higher temperature growth; growth process is thermodynamically favorable

iii. Quality of layers is high

② Disadvantages

i. Difficult to monitor growth rate exactly (no Rheed possible due to higher pressure)
ii. Not as abrupt a process as MBE due to gas flow issues and memory effects
iii. Toxic gases are to be handled

7. Summary

Metal-Organic Chemical Vapor Deposition (MO-CVD) belongs to the class of chemical thin film deposition methods and is quite similar to other techniques, such as spray pyrolysis, where the vaporization method and the precursors may vary.

It is in principle a simple “non-vacuum” technique, which allows the fast deposition of various film materials without using high vacuum pumps.

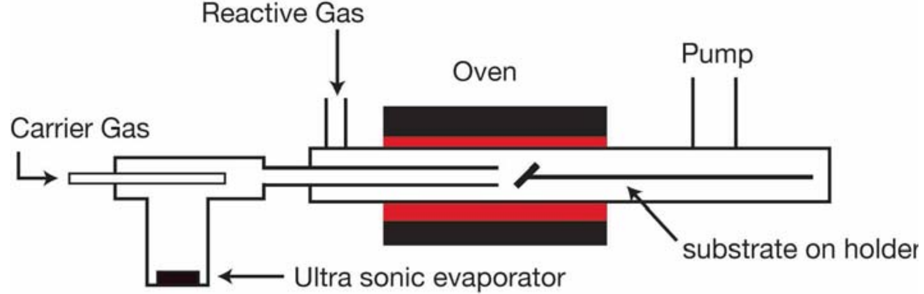


Figure 3. MOCVD Summary [http://materials.web.psi.ch/Research/Thin_Films/Methods/MOCVD.htm]

8. References

① Reaction mechanism [http://en.wikipedia.org/wiki/Reaction_mechanism]

② Susceptor [http://en.wikipedia.org/wiki/Susceptor]

③ MOCVD [http://www.ee.sc.edu/personal/faculty/simin/ELCT871/05%20MOCVD.pdf]

④ MOCVD [http://cnx.org/content/m25614/latest/]

⑤ MOCVD [http://www.helmholtz-berlin.de/forschung/enma/materialforschung-pv/se4/arbeitsgebiete/solarzellenstrukturen/mocvd_en.html]

⑥ MOCVD [http://www.ask.com/wiki/MOCVD#Organometallic_precursors]

⑦ MOCVD [http://materials.web.psi.ch/Research/Thin_Films/Methods/MOCVD.htm]

⑧ MOCVD [http://www.dt.co.kr/contents.html?article_no=2009120902011832614001]

⑨ MOCVD [http://mylv.net/know/view.asp?no=114&page=1&txtsearch2=&sltsearch=§ion=2]