Chapter 2 Theoretical Background

2.1 MOCVD Technique

Metalorganic Chemical Vapor Deposition (MOCVD) is a nonequilibrium growth technique which relies on vapor transport of the precursors and subsequent reactions of group III alkyls and group V hydrides in a heated zone. The MOCVD technique originated from the early research of Manasevit (1968) [1] who demonstrated that triethylgallium (TEGa) and arsine deposited single crystal GaAs pyrolytically in an open tube cold-water reactor. Manasevit and Simpson (1969) [2]；Manasevit and Hess (1979) subsequently expanded the use of this technique for growth of $GaAs_{1-y}P_y$, $GaAs_{1-y}Sb_y$, and Al containing compounds. Composition and growth rate are controlled by precisely controlling mass flow rate and dilution of various components of the gas stream. Organometallic group III sources are either liquids, such as trimethylgallium (TMGa) and trimethylaluminum (TMAl), or solids such as trimethylindium (TMIn). The Organometallic sources are stored in bubblers through which carrier gas (typically hydrogen) flows. The bubbler temperature is to precisely control the vapor pressure over source material. Carrier gas will saturate with vapor from the source and transport vapor to the heated substrate. Group V sources are most commonly gaseous hydrides, for example, ammonia (NH_3) for nitride growth. Dopant materials can be metal organic precursors (Bis-cyclopentadienylmagnesium Cp_2Mg) or hydrides (silane SiH_4 or disilane Si_2H_6). The substrate usually rests on a block of graphite called a susceptor that can be heated by a radio frequency (RF) coil, resistance heated, or radiantly by a strip heater.

In the past few years, MOCVD has become the major production tools for

producing III-V compound semiconductor materials [3-5]. It has overwhelmed other growth technique by its versatility and the capability for large-scale production. This technique has been used for producing high LED, LD and HBT devices etc [6,7].

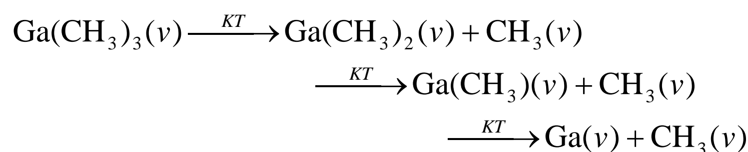
2.2 MOCVD Growth Process

As shown in Fig 2.1, the TMGa and NH_3 are introduced into the reactor as group-III and group-V precursors. According the boundary layer model, the precursors are depleted near the substrate interface, and abundantly supplied at the top of the boundary layer. In the boundary layer, these precursors are driven toward the substrate by diffusion due to the concentration gradient.

The chemical reactions involved in MOCVD are usually very complex. In high temperature reaction, the GaN deposition process can be written

$$Ga(CH_3)_{3(v)} + NH_3 \xrightarrow{kT} GaN_{(s)} + 3CH_{4(v)}$$

where v = vapor and s = solid. This balanced expression ignores the specific reaction path and most reactive species because the details of the reaction are not completely known and the intermediate reactions are rather complicated. A likely reaction pathways leading to the growth of GaN epilayers involves homogeneous decomposition of TMGa as reported by Nishizawa *et al.* [8] and DenBaars *et al.* [9]

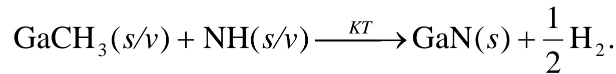


$$\begin{aligned} Ga(CH_3)_3(v) &\xrightarrow{KT} Ga(CH_3)_2(v) + CH_3(v) \\ &\xrightarrow{KT} Ga(CH_3)(v) + CH_3(v) \\ &\xrightarrow{KT} Ga(v) + CH_3(v) \end{aligned}$$

The group-V hydride source is thought to decompose heterogeneously on the GaN surface or reactor walls to yield atomic nitrogen or a nitrogen containing radical at high growth temperatures. Abstraction of the first hydrogen bond is thought to be the rate-limiting step in decomposition of ammonia.

$$NH_3(s/v) \xrightarrow{KT} NH_{3\text{-}x}(s/v) + xH(s/v)$$

Therefore, one possible growth mechanism of GaN that occur at the solid vapor interface can be expressed as follows,



$$GaCH_3(s/v) + NH(s/v) \xrightarrow{KT} GaN(s) + \frac{1}{2}H_2.$$

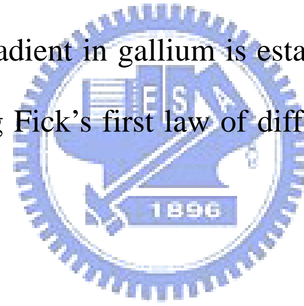
The foregoing GaN growth process is just a simple description. More fully description requires the understanding of process kinematics and growth mechanisms occurring at the vapor/solid interface during the MOVPE growth. Figure 2-1 illustrates several possible reaction pathways that may occur in a MOVPE reactor. Pyrolysis and diffusion of group-III source through boundary layer is the main pathway controlling growth rate. Nevertheless, parasitic side reactions such as solid adduct formation between TMGa and NH_3 will decrease growth rate by limiting flux of group-III sources to the growing interface.

Optimization of MOVPE growth is typically done by empirical studies of external parameters such as growth temperature, V/III ratio, substrate orientation, and mass flow rates of the reactants. These studies have identified three regions of growth: mass transport limited, desorption limited, and surface kinetically limited regimes. Conventional GaN MOVPE is usually performed in mass transport limited regime

that occurs over a wide temperature range from 600°C to 1,100°C. In this temperature region, growth is limited by mass transport of the group-III reactants to the growing interface. Because the diffusion process is slightly temperature dependent, the growth rate increases also slightly in this temperature range. From Fick's first law of diffusion [10], the flux (J) of group-III elements toward the substrate can be described as

$$J = D\,(\partial C / \partial X)$$

where D is the growth species' diffusion coefficient and C is concentration in the gas phase. The space gradient of concentration ($\partial C/\partial X$) is along the epitaxial growth direction, *i.e.* the normal of the substrate. For flow over a horizontal plate as shown in Fig. 2-2, the concentration gradient in gallium is established across a boundary layer of thickness $dX = \delta b$. Solving Fick's first law of diffusion and rewritting in terms of input partial pressures yield:



$$J_{Ga} = D_{Ga}(P^{o}_{Ga} - P_{Ga}) / \delta_b RT$$

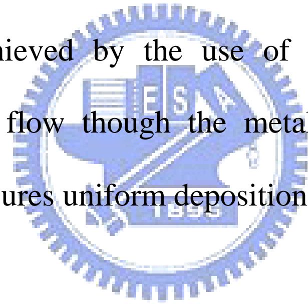
where P^{o} is the input gas stream partial pressure and P is the partial pressure at the gas/solid interface. δ_b is the thickness of boundary layer. For temperatures above 600 °C, metal alkyl pyrolysis efficiency is unity. One can assume $P^{o}_{Ga} \approx P_{TMGa}$. At the interface the Ga partial pressure is small in comparison to input partial pressure of TMGa (*i.e.* $P_{TMGa} >> P_{Ga}$), so that the group-III source flux at the interface can be reduced to

$$J_{Ga} = D_{Ga}\, P_{TMGa} / \delta_b RT.$$

Under common growth conditions for hydride MOVPE system, the ratio of group-V to group-III partial pressures is >> 1. This is because high thermal stability of NH_3 and high active nitrogen pressure are required to stabilize the GaN surface at high growth temperatures. The growth rate can then be calculated by

$$\text{growth rate} = J_{Ga} MW_{Ga} / \rho ,$$

where MW_{Ga} is the molar weight of Ga and ρ is the GaN density. Under these conditions, growth rate will be controlled by the diffusion of Ga species toward the substrate surface. The growth rate is obtained by controlling partial pressure of metal alkyls injected into the reactor from the above equation. Therefore, precise control of the growth rate is then achieved by the use of accurate electronic mass flow controllers that regulate the flow though the metal alkyl bubbler. In addition, a uniform boundary layer δ_b ensures uniform deposition.



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