Mechanism of the Metal Organic Chemical Vapor Deposition of Gallium Arsenide*

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1 Introduction

Preparation of epitaxial thin films of III-V (13-15) 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(CH₂CH₃)₃] and arsine (AsH₃) 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.

Several processes, partly in series, partly in parallel take place during the growth by CVD. They are presented schematically in Figure 1. The relative importance of each of them depends on the chemical nature of the species involved and the design of the reactor used. The actual growth rate is determined by the slowest process in the series of events needed to come to deposition.

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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(CH₃)₃, TMG] and triethylgallium [Ga(CH₂CH₃)₃, TEG]. Traditionally, growth is carried out in a cold-wall quartz reactor in flowing H₂ 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., H₂) through the liquid sources that are in held temperature-controlled bubblers.

2 Reaction mechanism

While the overall reaction (where R = CH₃ or CH₂CH₃) can be described by (1).

\[ R₃Ga + AsH₃ \rightarrow GaAs + 3RH \]  

(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 As₂ molecules are formed by pyrolysis of AsH₃ 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 AsH₃ is possible, it is now known that if there is any intermediate reaction between the TMG and AsH₃, the product is unstable. However, early work indicated that free GaAs molecules resulted from the decomposition of a TMG·AsH₃ 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 AsH₃ pyrolysis catalyzed by the GaAs surface.

There are several different kinds of potential reactions occurring 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:

\[ Ga(CH₃)₃ \rightarrow Ga(CH₂)₂ + CH₃ \]  

(1)

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2.1 Using ALE studies as insight for MOCVD

Given the stepwise and presumably simplified mechanism for atomic layer epitaxy (ALE) growth of GaAs, a number of mechanistic studies have been undertaken of ALE using TMG and AsH\(_3\) to provide insight into the comparable MOCVD reactions. Nishizawa and Kurabayashi proposed that a CH\(_3\)-terminated GaAs surface inhibits further heterogeneous decomposition of TMG and self-limits the growth rate to one monolayer/cycle. While, X-ray photoelectron spectroscopy (XPS) studies showed that no carbon was observed on a GaAs surface reacted with TMG. Furthermore, the same self-limiting growth was seen in in ALE using a metalorganic molecular beam epitaxy (MOMBE) with TMG and AsH\(_3\). It was reported that a transient surface reconstruction is observable by reflection high-energy electron diffraction (RHEED) during the ALE of GaAs in MOMBE. It was suggested that this structure is caused by CH\(_3\)-termination and the self-limitation of the growth rate is attributed to this structure. However, measurement of the desorption of CH\(_3\) by means of a combination of pulsed molecular beams and time-resolved mass spectrometry, indicates that CH\(_3\) desorption is too fast to attribute the self-limitation to the CH\(_3\)-terminated surface. Subsequently, investigations of the pyrolysis of TMG on a (100)GaAs surface by the surface photo-absorption method (SPA) allowed for the direct observation of CH\(_3\) desorption from a GaAs surface reacted with TMG. From the measured CH\(_3\) desorption kinetics, it was shown that the CH\(_3\)-terminated surfaces causes the self-limitation of the growth rate in ALE because the excess TMG cannot adsorb.

All this research helped people to visualize the real reaction mechanism in the formation of GaAs by MOCVD methods, in which the decomposition, diffusion and surface reaction interact with each other and result in a much more complicated reaction mechanism.

2.2 Gas phase reaction: pyrolysis of TMG and AsH\(_3\)

In the TMG/H\(_2\) system, there is almost no reactions at a temperature below 450 °C, whereas the reaction of TMG with H\(_2\) almost completely changed into CH\(_4\) and Ga at a temperature above 600 °C, (1).

\[
\text{Ga(CH}_3\text{)}_3 + \frac{3}{2}\text{H}_2 \rightarrow \text{Ga} + 3\text{CH}_4
\]  

As for the AsH\(_3\) decomposition, without any deposition of Ga or GaAs in the reactor, the pyrolysis of AsH\(_3\) proceeded barely at a temperature below 600 °C, however, it proceeded nearly completely at a temperature above 750 °C. In the AsH\(_3\)/H\(_2\) system with the TMG introduced previously, the decomposition of AsH\(_3\)
was largely enhanced even at a temperature below 600 °C. The decomposition of AsH$_3$ seems to be affected sensitively by the deposited GaAs or Ga. This phenomenon may be concluded to be caused by the catalytic action by GaAs or Ga. The reaction at a temperature below 600 °C can be described as shown in (1), but at a temperature above 600 °C, pyrolysis of AsH$_3$ can occur even without GaAs or Ga, (1).

\[
\text{GaAs} \\
\text{AsH}_3 \rightarrow \text{As}_{(ad)} + \frac{3}{2} \text{H}_2 \\
\text{AsH}_3 \rightarrow \text{As} + \frac{3}{2} \text{H}_2
\]

(1)

### 2.3 Adsorption and surface reactions

From the temperature dependent measurements of the desorption spectrum from a surface on which TMG was supplied, it was estimated that the surface-adsorbed species was Ga at the high temperature region of $T_{sub} > 500$ °C, GaCH$_3$ at the range of $350$ °C < $T_{sub} < 500$ °C, and Ga(CH$_3$)$_2$ and Ga(CH$_3$)$_3$ at the range of $T_{sub} < 350$ °C. The reactions, where (ad) means the adsorbed state of the molecules, are:

\[
\text{Ga(CH}_3)_3(\text{g}) \rightarrow \text{Ga(CH}_3)_2(\text{ad}) + \text{CH}_3 \quad (T_{sub} < 350 \ ^\circ \text{C})
\]

(1)

\[
\text{Ga(CH}_3)_3(\text{g}) \rightarrow \text{Ga(CH}_3)_3(\text{ad}) \quad (T_{sub} < 350 \ ^\circ \text{C})
\]

(1)

\[
\text{Ga(CH}_3)_3(\text{g}) \rightarrow \text{GaCH}_3(\text{ad}) + 2 \text{CH}_3 \quad (350 \ ^\circ \text{C} < T_{sub} < 500 \ ^\circ \text{C})
\]

(1)

\[
\text{Ga(CH}_3)_3(\text{g}) \rightarrow \text{Ga}_{(ad)} + 3 \text{CH}_3 \quad (T_{sub} > 500 \ ^\circ \text{C})
\]

(1)

When AsH$_3$ is supplied, the reactions with these adsorbates are:

\[
\text{Ga(CH}_3)_2 + \text{AsH}_3 \rightarrow \text{no reaction} \quad (T_{sub} < 350 \ ^\circ \text{C})
\]

(1)

\[
\text{Ga(CH}_3)_3(\text{ad}) + \text{AsH}_3 \rightarrow \text{no reaction} \quad (T_{sub} < 350 \ ^\circ \text{C})
\]

(1)

\[
\text{GaCH}_3(\text{ad}) + \text{AsH}_3 \rightarrow \text{GaAs} + \text{CH}_4 + \text{H}_2 \quad (350 < T_{sub} < 500 \ ^\circ \text{C})
\]

(1)

\[
\text{Ga}_{(ad)} + \text{AsH}_3 \rightarrow \text{GaAs} + \frac{3}{2} \text{H}_2 \quad (T_{sub} > 500 \ ^\circ \text{C})
\]

(1)

It was observed that there is no growth in the range of $T_{sub} < 350$ °C, i.e., Ga(CH$_3$)$_2$(ad) and Ga(CH$_3$)$_3$(ad) do not react with AsH$_3$ in the TMG-AsH$_3$ system. Monomolecular layer growth is limited by the formation of GaCH$_3$ and its reaction with AsH$_3$.
2.4 Overall reaction pathway

At lower temperature (350-500 °C), equivalently low energy, TMG decompose in the gas phase to Ga(CH$_3$)$_2$ and methyl radical, (1).

\[
\text{Ga(CH}_3)_3 \rightarrow \text{Ga(CH}_3)_2 + \text{CH}_3 \quad \text{(low energy, gas phase)}
\] (1)

After the first ligand dissociation, there are two different pathways, in the first, the Ga(CH$_3$)$_2$ keeps decomposing into GaCH$_3$ and another methyl group when it is at the gas-substrate interface, (1), and then further decomposes into free gallium atoms on the substrate surface, (1). In the second reaction, the Ga(CH$_3$)$_2$ decomposes directly into Ga and CH$_3$-CH$_3$ by reductive elimination, (1).

\[
\text{Ga(CH}_3)_2 \rightarrow \text{GaCH}_3 + 2 \text{CH}_3 \quad \text{(gas/surface)}
\] (1)

\[
\text{GaCH}_3 \rightarrow \text{Ga} + \text{CH}_3 \quad \text{(surface)}
\] (1)

\[
\text{Ga(CH}_3)_2 \rightarrow \text{Ga} + \text{H}_3\text{C-CH}_3 \quad \text{(reductive elimination)}
\] (1)

At high temperature (> 500 °C), the TMG decomposes into Ga(CH$_3$) and two methyl groups instead of the step-wise decomposition at lower temperature, (1), and the Ga(CH$_3$) further decomposes into free Ga atoms at the substrate surface, (1).

\[
\text{Ga(CH}_3)_3 \rightarrow \text{GaCH}_3 + 2 \text{CH}_3 \quad \text{(high temperature, gas phase)}
\] (1)

\[
\text{GaCH}_3 \rightarrow \text{Ga} + \text{CH}_3
\] (1)

The decomposition of AsH$_3$ forms an “arsenic cloud” in the reaction chamber. The decomposition is also step-wise:

\[
\text{AsH}_3 \rightarrow \text{AsH}_2
\] (1)

\[
\text{AsH}_3 \rightarrow \text{HAs} + \text{H} \quad \text{(surface)}
\] (1)

\[
\text{HAs} \rightarrow \text{As} + \text{H} \quad \text{(surface)}
\] (1)

The methyl groups in the surface Ga(CH$_3$) molecules are removed by the formation of methane with atomic hydrogen from the decomposition of AsH$_3$, (1).

\[
\text{H} + \text{CH}_3 \rightarrow \text{CH}_4 \quad \text{(surface)}
\] (1)
2.5 Kinetics for other systems

Investigations have been reported for the mechanism of the growth of GaAs using triethylgallium [Ga(CH₂CH₃)₃, TEG] and TMG with trimethylarsene [As(CH₃)₃, TMA], triethylarsene [As(CH₂CH₃)₃, TEA], tert-butylarsine [(CH₃)₃CAsH₂, TBA], and phenylarsine [(C₆H₅)AsH₂]. The experiments were conducted in a MOCVD reactor equipped with a recording microbalance for in-situ growth rate measurements. For example, the kinetics of the growth of GaAs were investigated by measuring growth rate as a function of temperature using the microbalance reactor while holding the partial pressure of gallium precursor (e.g., TMG) and arsenic precursor [e.g., As(CH₃)₃] constant at 0.01 and 0.05 Torr, respectively. Three different flow rates were used to determine the influence of the gas residence time.

The growth rate of GaAs with TMG and As(CH₂CH₃)₃ is higher as compared with the growth from TMG and As(CH₃)₃ because of the lower thermal stability of As(CH₂CH₃)₃ than As(CH₃)₃. Both of the two growth rates showed a strong dependence on the residence time.

Similarly, the kinetic behaviors of the TMG/TBA and TEG/TBA system were investigated under the same conditions as the TMA and TEA studies. There are two distinct regions of growth. For TMG/TBA, the deposition rate is independent at low temperature and in the intermediate temperature (around 600 °C) the dependence of the growth rate on the total flow rate is significant. This means that the growth at the lower temperature is controlled by surface reactions. The TEG/TBA system showed a similar behavior except that the maximum growth rate occurs around 450 °C while it is around 750 °C for TMG/TBA system. Also, the growth of TMG/(C₆H₅)AsH₂ was studied on the same conditions as for the Me₃Ga/tBuAsH₂ system. It was reported that the difference in the growth rate at various flow rates was related to a combination of parasitic reactions and depletion effects from deposition. From the comparison of the data, it is deduced that the effect of parasitic reactions is slightly smaller for (C₆H₅)AsH₂ than for TBA.

Two possible mechanisms for the dependence of growth rate on flow rate were proposed. The first, mass-transfer limitation was thought to be unlikely because of the high diffusivity of the gallium precursors at 1 Torr (ca. 350 cm²/s). The second, also the more likely explanation for the observed growth-rate dependence on flow rates is gas-phase depletion cause by the parasitic reactions. Since the growth efficiency is high (41% at 700 °C), the loss of precursor from the gas phase will directly affect the growth rate. It was evidenced by the differences in the growth rates between split and combined feed streams. The growth rate is lower when the reagents are combined upstream of the reactor than when they are combined inside the reactor (split stream). It is suggested that the experimental observations can be explained by a model based on the reversible formation of an adduct and the decomposition of this adduct to useless polymeric material competing with the growth of GaAs. It can be written in the form shown in (1) where kₖ and kᵣ are the forward and reverse rate constants for adduct formation, respectively, k₆ is the rate constant for the irreversible decomposition of the adduct to polymer, and kₜ is the surface reaction rate constant for the growth of GaAs. It is obvious that each step involves several elementary reactions, but there were insufficient data to provide any more detail.

\[
\text{GaAs} \overset{kₖ}{\rightleftharpoons} \text{organometallic precursors} \overset{kᵣ}{\rightarrow} \text{adduct} \overset{k₆}{\rightarrow} \text{polymeric deposits}
\]

3 Bibliography