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Influences of growth parameters on the reaction pathway during GaN synthesis

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ABSTRACT

Gallium nitride (GaN) film growth is a complicated physical and chemical process including fluid flow, heat transfer, species transport and chemical reaction. Study of the reaction mechanism, i.e., the reaction pathway, is important for optimizing the growth process in the actual manufacture. In the paper, the growth pathway of GaN in a closed-coupled showerhead metal-organic chemical vapor deposition (CCS-MOCVD) reactor is investigated in detail using computational fluid dynamics (CFD). Influences of the process parameters, such as the chamber pressure, the inlet temperature, the susceptor temperature and the pre-exponential factor, on the reaction pathway are examined. The results show that increases of the chamber pressure or the inlet temperature, as well as reductions of the susceptor temperature or the pre-exponential factor lead to the adduct route dominating the growth. The deposition rate contributed by the decomposition route, however, can be enhanced dramatically by increasing the inlet temperature, the susceptor temperature and the pre-exponential factor.

1. Introduction

With the development of the electronic and photoelectric technologies, novel devices with less weight, high efficiency, low energy consumption and multi-mission adaptability are urgently demanded in the digital market. Group III-nitride materials, such as silicon carbide (SiC) and gallium nitride (GaN), have enormous advantages against traditional silicon materials [1]. The blue light emitting diodes (LEDs) with high brightness booms research of GaN-based semiconductor materials [2]. Nowadays, requirements of the materials with high frequency and stability in the 5th generation mobile networks (5G) further stimulate GaN production [3]. Metal-organic chemical vapor deposition (MOCVD) is a popular technique to produce high-quality GaN thin films. According to the flow structure and thermal design, MOCVD reactors can be divided into the horizontal planetary and the vertical closed-coupled showerhead (CCS) types [4]. The precursors (trimethylgallium and ammonia) are transported by the carrier gas into the reactor, followed by a series of complex chemical reactions in the chamber and on the wafer surfaces to form thin-film crystals.

The growth of GaN in the MOCVD reactors involves fluid flow, mass transport, heat transfer and chemical reactions. In the early experimental studies, the ex-situ measurement is usually applied to test the performance of GaN epitaxial chips. Recently, the in-situ monitoring system is established in many commercial MOCVD reactors to measure reflectance and temperature of the wafers for real-time control of the growth. However, it is hard to measure the species existing in the growth due to their short lifetime. Numerical and theoretical studies are the major tools to understand the reactions.

Some detailed chemical reaction kinetic parameters have been obtained by quantum chemistry calculation and transition state theory [5–7]. Besides, some integrated mechanisms have been also summarized from a series of other related studies [8–11]. However, the mechanism of GaN growth is still neither clear nor certain due to its complex intermediate products and reaction pathways. Besides, different growth mechanisms would have significant effects on the growth rate, the uniformity and the surface morphology. In the paper, a commercial CCS-MOCVD reactor is considered. A reasonably detailed chemical reaction model has been obtained from sufficient tests and summaries of the chemical mechanisms. The new growth mechanism contains 14 gas-phase reactions and 11 surface reactions. The gas-phase reactions involve adduct, decomposition, free radical, and ammonia-related reactions. The surface reactions include adsorption, desorption and incorporation reactions. Based on the computational fluid dynamics (CFD) theory and the growth mechanism of GaN, the distribution of multiphysic fields has been carried out. From the variation of gas-phase species and surface species, influences of the chamber pressure, susceptor temperature, inlet gas temperature and the pre-exponential factor

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of a key reaction (Section 3.5) have been discussed. Some important reactions and growth pathways have been obtained. The findings regarding the relationship between the growth pathways and the growth parameters may provide practical guidelines for researchers to know the GaN growth process better, and to improve the process parameters.

2. Mathematical models

To simulate MOCVD-grown GaN process, a series of physic problems, such as fluid flow, heat transfer, species transport and chemical reaction, should be firstly described by mathematical equations. Based on the CFD theory, a series of multi-physics fields can be obtained by solving the mass, momentum, energy, species transport equations coupled with the chemical reactions. Navier-Stokes equations are used for solving the fluid flow. Both of Fick diffusion (derived by concentration difference) and Soret diffusion (derived by temperature difference) are used for solving the species diffusion. The energy equation is adopted to solve the temperature field, involving the source items of the flow and chemical reactions. The chemical reaction adopts the laminar finite-rate model. The specific expression of the equations can be found in our previous work [12–14]. Compared with other equations, the chemical reaction is more complex and vital to the growth process. Fig. 1 shows the main chemical reactions, which are dominant in GaN growth. The MOCVD-grown GaN process is usually divided into two pathways: the decomposition route (the green dashed line) and the adduct route (the red dashed line).

The decomposition route is the start of the growth, and consists of a series of pyrolytic reactions. The first step of decomposition route is the cracking of TMGa to dimethyl gallium (DMGa) with a methyl radical loss. In a similar way, DMGa and monomethylgallium (MMGa) decompose to MMGa and Ga due to high temperature, respectively. The decomposition route was first reported by Jackoet al. [15] with three first-order reactions above. These phenomena are similar to the decomposition of trimethylaluminum (TMAl) [16]. More specific reaction mechanisms were carried out as experiments of the modern MOCVD-grown GaN process, and chemical reaction kinetic parameters of the decomposition mechanism became available [17–20]. The detailed chemical formulas and their kinetic parameters can be found in Table 1 (G1-G3). Compared with the decomposition route, the adduct route is more complicated and hard to be observed by experimental methods. It is generally acknowledged that the electron acceptor TMG (Lewis acid) and the electron donor ammonia (Lewis base) share an electron pair to form TMG:NH_3 (Lewis adduct) [21]. This reaction can easily occur at room temperature. The pre-exponential factor of the reaction is depended on the bimolecular collision rate of the reactants [10]. The Lewis adduct is not stable in a high-temperature environment, and it may decomposes into TMG and ammonia (reversible reaction) or decomposes into DMG:NH_2 (amide) with a released methane. The trimer (or ring compound), $(DMG:NH_2)_3$, is formed by the collision of three amides. The generation of these oligomers is proved to lead an initial gas-phase nucleation and particle growth [22]. The final reaction of the adduct route is unidentified and usually regarded as the decomposition of the trimer into low molecular weight species with a quantity of methane released [9]. The adduct route consists of above six reactions which can be found in Table 1 (G4-G9).

Although the decomposition and adduct routes in the GaN growth pathway are dominant, the free radical and ammonia related reactions also cannot be ignored. Due to the main products of the decomposition route, methyl, three important reversible reactions (Table 1 G10-G12) associated are added to the kinetic model. Ammonia is the most popular nitride source for the MOCVD growth of the V-Nitride. The pyrolysis of ammonia can be obviously observed at the temperature range from 2000 to 3200 K [23]. However, in the temperature range of a typical MOCVD-grown GaN, Monnery et al. found that conversion of ammonia was less than 25% between 1123 and 1323 K at an atmospheric pressure [24]. Therefore, the pyrolysis of ammonia is not the main pathway to affect GaN growth. Instead of the pyrolysis, two chemical reactions (Table 1 G13-G14), which are mostly occurred, are included in the growth mechanism.

Parasitic reactions consist of recombination of the gas-phase nucleation of the adducts by the adduct route, the metal-containing fragments by the decomposition route and the particle formation. It also leads to a waste of the precursors, and makes the film surface morphology non-uniform. Many researchers have performed theoretical and experimental studies regarding the topic [25–32]. However, the mechanism of the parasitic reaction is still absent from the literature, and kinetic parameters of the parasitic reactions are not available. Therefore, analysis of the reaction pathway could help people understand the parasitic reactions in theory.

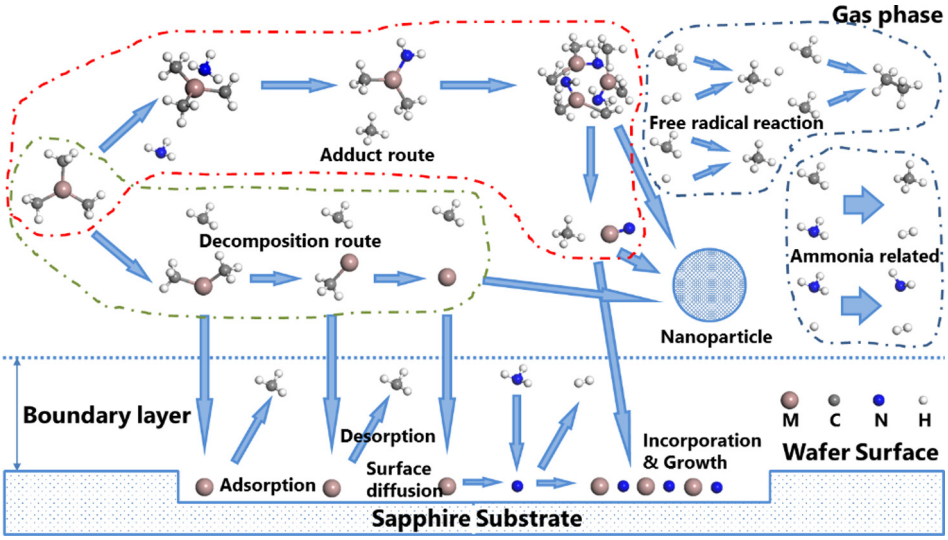

Fig. 1. Chemical reaction pathway during MOCVD-grown GaN. (M = metal atom, C = carbon, N = nitrogen, and H = hydrogen).