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Numerical Study of AlN Growth in MOCVD Heated by Induction

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Abstract. In this paper, the process of growing aluminum nitride(AlN) film in the metal organic chemical vapor deposition(MOCVD) reactor heated by induction was simulated, and several important factors affecting the growth rate were analyzed. The purpose of this study is to explore the relationship between these factors and the growth rate of AlN films, and to provide feasible guidance for the parameter optimization of the growth of AlN film. It was concluded that compared with the pure nitrogen(N_2) or hydrogen(H_2) as the carrier gas, the growth rate was obviously improved under the conditions of using the mixed carrier gases composed of N_2 and H_2. In addition, the uniformity of AlN film and the growth rate can be improved with the increase of H_2 ratio. It was also found that the growth rate of the film gradually decreased with the increased temperature of the gases introduced into the reactor, but the uniformity increased. Dimer is the main growth precursor of the film. In the parasitic reaction, the trimer has the greatest influence on the film, and the concentration of the polymer is more susceptible to temperature changes.

1. Induction

As an important wide-bandgap III-V compound semiconductor material, AlN has been one of the ideal raw materials for making high-frequency and high-power devices since its discovery[1]. AlN has excellent electrical properties, high breakdown voltage, and strong thermal conductivity and radiation resistance[2]. In the III-V composite semiconductor material, the Al and N bonds have a relatively strong chemical bond energy when combined with Ga and In in the tri-group element, and the Al-N bond energy is as high as 2.88 eV[3]. At present, the preparation of AlN thin films is mainly carried out by metal organic chemical vapor deposition (MOCVD) technology[4]. During preparation, due to the high bond energy of Al-N, it has a stronger parasitic reaction in the process of growing AlN film, which makes it difficult to increase the growth rate and uniformity of the AlN film[5]. In order to meet the high quality and easy integration of electronic devices at lower cost, high quality AlN films have always been our goal. For this reason, domestic and foreign scholars have done a lot of research on the high quality AlN thin films grown by MOCVD. Mihopoulos et al. first proposed a chemical reaction model for MOCVD growth of AlN, and through the simulation of AlN growth, it was found that when the AlN film was grown, changing the temperature and pressure would affect the polymer, the growth rate and the uniformity of the film[6]. LU Qing et al. modeled and simulated AlN, and found that the increase of pressure would enhance the parasitic reaction. They also found that dimer is the main precursor of film growth, and terpolymer is the main source of nanoparticles[7]. Kaiwen Pu et al. proposed a new dynamic model of MOCVD growing AlN. Through the simulation of this model, they found that the addition

path was the main path of AlN thin film growth, and the growth rate would decrease with the increase of reaction chamber pressure[8]. The research of these scholars further reveals the complex physicochemical changes in the growth process of AlN films, and explores the factors affecting the growth of AlN films. These results are of great significance to improve the actual growth quality of AlN thin films. In this work, the growth of AlN film in the MOCVD reactor by induction heating was simulated and the effects of parasitic reactions in the boundary layer of gas flow above the substrate on the growth of AlN film were studied.

2. Model of growth of AlN film by MOCVD

There are two main chemical paths involved in the growth of AlN films by MOCVD: Pyrolysis path and addition path. First, the source gases TMAl and NH_3 and carrier gas H_2 (or N_2) enter the reactor through the separation inlet. Under the pyrolysis path, TMAl is thermally decomposed to generate DMA1 and MMAl[9]. DMAl and MMAl are further decomposed to form MMAl and Al ions in the process of approaching the substrate, and finally the aluminum-containing material reaching the substrate participates in the growth reaction of AlN film. In the addition path, TMAl first reacts with NH_3 to form $TMAl:NH_3$, which is very rapid because the reaction does not require activation. In addition, the reversible reaction of $TMGa:NH_3$ formed by the reaction with TMGa and NH_3 is different, due to the high bond energy of Al-N, it is easier for $TMAl:NH_3$ to eliminate CH_4 to generate $DMAlNH_2$[10,11], which makes the reaction of TMAl and NH_3 irreversible. $DMAlNH_2$ is easily polymerized at a high temperature to form a polymer $(DMAlNH_2)_n$, n is 2, 3, 4, 5. The larger n is, the larger the diameter of the polymer particles is, and the larger particles are easily affected by the hot swimming force and difficult to reach the substrate[12]. The Al-containing material reaching the substrate participates in the growth of the AlN film. However, there are a lot of parasitic reactions in the addition path. We need to study the addition path to explore the details of the addition path.

At present, the widely used MOCVD reactor are horizontal and vertical [13,14]. In this paper, the electromagnetically heated and cold wall MOCVD reactor model shown in Figure 1 is used. Because the reactor is two-dimensionally axisymmetric, an axisymmetric model is used in order to reduce the amount of calculation. The finite element method is used to calculate the coupled electromagnetic field, thermal field and flow field.
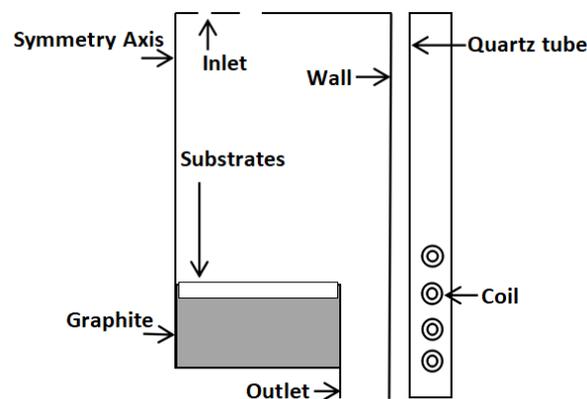

Figure 1. Model of MOCVD reaction chamber

The simplified electromagnetic equation is [15]:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial A}{\partial r}\right) + \frac{\partial^2 A}{\partial z^2} = j\mu\omega\sigma A - \mu J_c \qquad (1)$$

where ω is angular frequency of the alternating current, σ is the electrical conductivity, μ is magnetic permeability and J_c is the current density applied to the coils.

The heat, momentum, and mass transfers of the gases are governed by four conservation equations that are coupled together: continuity equation [16]:

$$\frac{\partial \rho}{\partial t} + div(\rho U) = 0 \qquad (2)$$

where ρ is density, t is time, U is gas velocity vector.

Momentum, species conservation and energy equations are generalized into one generic equation[17]:

$$\frac{\partial(\rho\phi)}{\partial t} + div(\rho U\phi) = div(\Gamma_\phi grad\phi) + S_\phi \qquad (3)$$

Where div is gradient operator，$U = iu + jv + kw$，$\phi = u,v,w,T$，$\Gamma_\Phi = \eta, k/c_p$ or ρD_{ij}，(k is thermal conductivity, η viscosity, c_p specific heat, D_{ij} binary diffusion coefficient) corresponding to momentum, species conservation or energy equations, respectively. S_ϕ is called source term.

For the inlet, in order to reduce the pre-reaction of the reaction gas, two inlets are used. TMAl and NH$_3$ are carried into the reactor through different inlets carried by the H$_2$(or N$_2$). For the outlet, the pressure boundary conditions are set. For the wall surfaces of the substrate and the walls of the reactor, the velocity is assumed to be zero and the material gradient is zero.

3. Numerical simulation and analysis

*3.1 Influence of carrier gases composition on growth rate of AlN film*
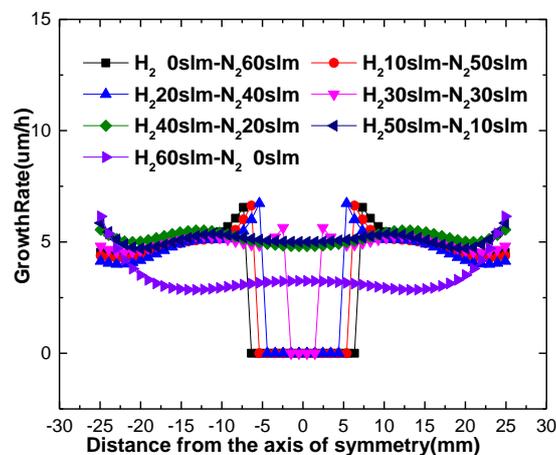
Figure 2. Influence of carrier gas composition on growth rate of film

In order to investigate the influence of the composition of carrier gases on the growth rate of AlN film, the simulation was carried out by changing the ratio of hydrogen and nitrogen in the carrier gases while the total gas flow rate is unchanged. Carrier gas as a transport gas, the traditional MOCVD chemical reaction has two explanations, one believes that carrier gas does not participate in chemical reactions as a pure transport gas, the other considers that the carrier gases participate in the chemical reaction, but their action is similar to that of the catalytic reaction, which has an effect on the intermediate process of the chemical reaction and has no effect on the final product of the reaction. As shown in Figure 2, the experiment took seven sets of carrier gases values: H$_2$ 0-10-20-30-40-50-60 slm; N$_2$ 60-50-40-30-20-10-0 slm. From the simulation results, it was found that in the case of a low hydrogen content, the 0 growth rate region appeared on the substrate. As the hydrogen component increases, the region with a zero growth rate gradually decreases, and when the hydrogen content exceeds half of the total carrier gases, the zero growth region completely disappears. However, as the hydrogen component continues to increase, the growth rate of the substrate film is significantly reduced, and the growth rate is the lowest when only hydrogen is contained, which indicates that the hydrogen is involved in the growth of AlN films compared to nitrogen in the carrier gas, and it has a significant effect on the growth rate and uniformity of film.

3.2 Influence of temperature of gases flowing into reactor from inlets on growth rate and uniformity of Substrate film
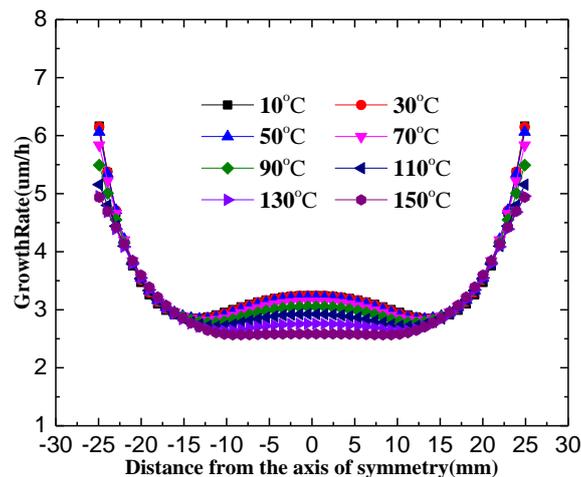

Figure 3. Influence of gas temperature on growth rate of film

In order to study the influence of the temperature of gases flow into the reactor from inlets on the growth rate and uniformity of the film, 8 kinds of gas temperature are set shown in Figure 3. It can be seen that the average growth rate of the film is higher under the conditions of the gas temperature of 10°C, but the uniformity of the film is not optimal. As the gas temperature increases, the growth rate in the central region of the substrate gradually decreases, while the edge region does not change too much. At 150°C, the uniformity of the central region of the substrate (from -15mm to 15mm) is significantly improved. This may be the temperature gradient between the substrate and the inlets becomes smaller as the gas temperature increases. In the process of DMAlNH$_2$ transported to the substrate, it is easier to generate polypolymers, especially for the concentration of tetramer and pentamer, which leads to the waste of source gases. However, the uniformity of the film becomes better with the increase of the gas temperature.

3.3 Influence of boundary layer parasitic reactions on flim growth

The boundary layer above the substrate is the portion closest to the growth region of the substrate, and is also the portion that has the greatest influence on the film growth. It is important to study the chemical reactions and material changes in the boundary layer to improve the growth rate and uniformity of the film. We studied the concentration of the polymer in the boundary layer, including: (DMAlNH$_2$)$_n$, n is 2, 3, 4, 5. In order to explore the influence of the concentration the analysis is focused on the polymer at the distance of 1 mm above the substrate.

From Figure 4(a), it can be seen that (DMAlNH$_2$)$_2$ decreases gradually with the increase of the temperature of gases flowing into the reactor from the inlets. The concentration of the polymer shown in Figure 4(b), Figure 4(c) and Figure 4(d) increases as the gas temperature increases. It can be seen that only the trend of the dimer with the gas temperature is consistent with the trend of the film with the gas temperature. It can be inferred that the (DMA1NH$_2$)$_2$ substance in the addition path is the main precursor of AlN film growth. At the same time, it is also found that the concentration of (DMAlNH$_2$)$_3$ was the highest in the polymer, the concentration of (DMAlNH$_2$)$_5$ was slightly lower, and the concentration of (DMAlNH$_2$)$_4$ was the lowest. It can be seen that in the polymer produced by the parasitic reaction, (DMA1NH$_2$)$_3$ has a mainly influence on the growth of the film, (DMAlNH$_2$)$_4$ has the weakest influence on the growth of the film. It can also be inferred that the tetramer has the worst stability in the polymer, and it is easily decomposed when it is heated. It is found that changing the gas temperature has a greater impact on the polymer. In Figure 4, the concentration of (DMAlNH$_2$)$_5$ at 150°C is an order of magnitude larger than that at 300°C, and (DMAlNH$_2$)$_3$ is still an order of magnitude change at a concentration of 150°C compared to a concentration of 30°C, The variation trend of (DMAlNH$_2$)$_4$ with the gas

temperature is between them. Therefore, it is concluded that the change of gas temperature has a greater influence on the polymer.
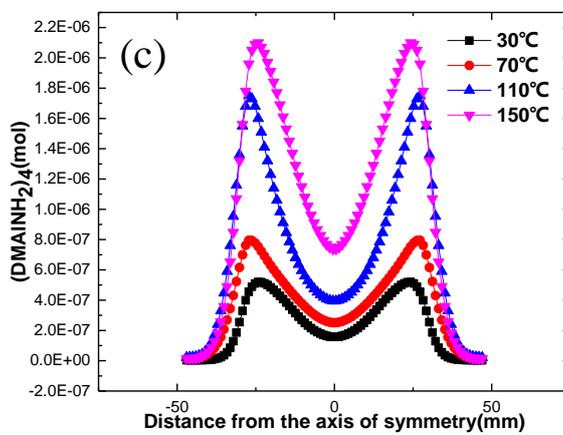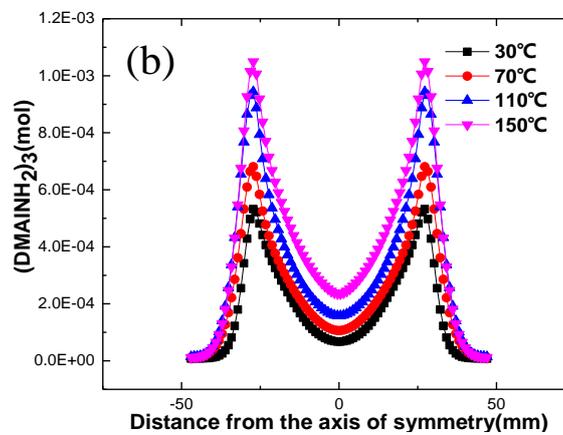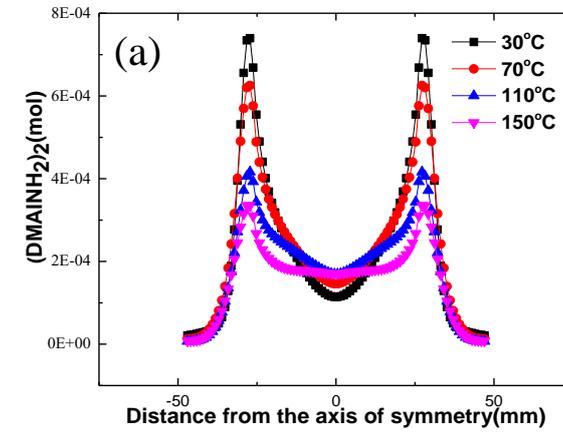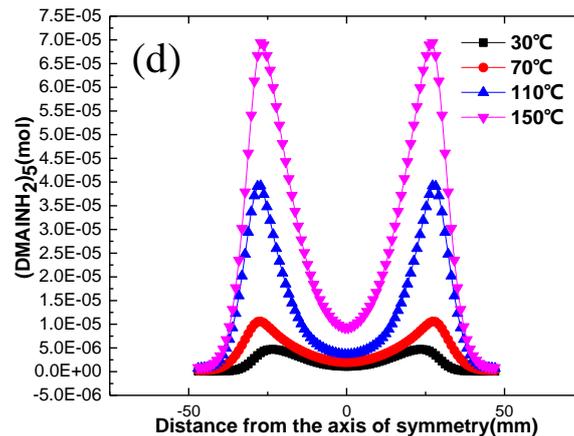
Figure 4. (a)Relationship between $(DMAlNH_2)_2$ and inlet gas temperature ; (b)Relationship between $(DMAlNH_2)_3$ and inlet gas temperature ; (c)Relationship between $(DMAlNH_2)_4$ and inlet gas temperature; (d)Relationship between $(DMAlNH_2)_5$ and inlet gas temperature

4. Conclusions

In this paper, the electromagnetic heating type MOCVD growing AlN film is simulated by analyzing the simulation results, which is found that compared with pure N_2 (or H_2) as the carrier gas, the mixed carrier gases of N_2 and H_2 can improve the growth rate and uniformity of AlN film. The growth rate and uniformity of AlN film can be improved with the increase of hydrogen ratio. As the temperature of gases flowing into the reactor from the inlets increases, the growth rate of the AlN film gradually decreases, but the uniformity of film increases. Dimer is the main growth precursor of the substrate film. In the parasitic reaction, the trimer has the greatest influence on the substrate film, and the concentration of the polymer is more susceptible to temperature changes.

Acknowledgments

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