Roles of V/III ratio and mixture degree in GaN growth: CFD and MD simulation study*

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To understand the mechanism of Gallium nitride (GaN) film growth is of great importance for their potential applications. In this paper, we investigate the growth behavior of the GaN film by combining computational fluid dynamics (CFD) and molecular dynamics (MD) simulations. Both of the simulations show that V/III mixture degree can have important impacts on the deposition behavior, and it is found that the more uniform the mixture is, the better the growth is. Besides, by using MD simulations, we illustrate the whole process of the GaN growth. Furthermore, we also find that the V/III ratio can affect the final roughness of the GaN film. When the V/III ratio is high, the surface of final GaN film is smooth. The present study provides insights into GaN growth from the macroscopic and microscopic views, which may provide some suggestions on better experimental GaN preparation.

Keywords: GaN growth, computational fluid dynamics, molecular dynamics

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1. Introduction

Gallium nitride (GaN) is one of the most promising wide-band-gap semiconductors which may have potential applications in optoelectronic devices, the blue and ultraviolet wavelengths, and high-temperature high-power electronic devices.[1–4] In the past several years, a number of notable advances have been reported in the growth of GaN.[5–7] However, the success of GaN-based electronic and optoelectronic devices is limited by the lack of high-quality lattice-matched substrates, and the difficulty in controlling electronic properties.[8–10] Several growth techniques including molecular beam epitaxy (MBE), metal-organic chemical vapour deposition (MOCVD), and hydride vapor phase epitaxy (HVPE) have been developed to deposit GaN.[11,12]

Meanwhile, many theoretical methods including Monte Carlo (MC), molecular dynamics (MD), *ab initio*, and computational fluid dynamics (CFD), can provide some useful results in epitaxial growth and investigate the related factors that may affect the growth.[13–20] Wang *et al.* used Monte Carlo simulations to study the effects of substrate temperature, Ga flux on growth rate, and growth front quality.[21] Gong *et al.* discussed the growth behavior of GaN film along the non-polar [1 1 −2 0] direction using MD simulations.[22] Chen *et al.* investigated the process of wurtzite GaN film growth, including the appearance of films at the early stage, regulation of growth, structure of the surface, and the dynamic features by using MD simulations with the Coulomb–Buckingham potential.[23] Safvi *et al.* investigated the effect of geometry on the GaN growth and considered V/III ratio near the substrate as a key parameter that may influence GaN crystalline quality.[24] By combining the computational fluid dynamics and kinetic Monte Carlo method, Fu *et al.* presented a multiscale modeling of fluid dynamics and thermodynamics to study the chemical and physical growth process of GaN in a standard MOCVD reactor.[25]

In this work, we combine the conventional CFD method with the microscopic MD scheme to study the dynamics of GaN film growth. The CFD method is used to study the influence of substrate rotation on the deposition of GaN, while the MD method is applied to explore the growth behavior of GaN at the atomic level.

2. Model and methods

In the CFD simulations, we use the HVPE reactor to grow GaN thick film. The simulations are conducted in 3D domain by using the finite-element method, and are carried out in a home-built, vertical HVPE reactor. Figure 1 shows the schematic illustration of the cross section of the reactor. Since the conversion rate of HCl to GaCl is higher than 95%, we only simulate the conversion of GaCl to GaN in order to reduce the amount of calculation.[26] Before setting up the model, some assumptions are formulated: (1) the gas mixer is treated as a continuum; (2) laminar gas flow conditions exist; (3) the no-

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slip boundary condition is satisfied (i.e., the velocity of the gas at the wall is equal to the velocity of the wall); (4) the equation of the state obeys the ideal gas law; (5) the gas obtained by reaction has no effect on results. Besides, we do not consider the gas-phase pre-reaction in our simulations because previous studies have shown that the effect of pre-reaction on the GaN growth is not obvious.[26–30] Actually, even if the phase pre-reaction is considered, previous studies have shown that the effect of pre-reaction on the GaN growth is not obvious.[29,30] Moreover, an incompressible fluid model is adopted in the simulations and the flow here is considered as steady flow. The equations for conservation of mass, momentum, and energy are solved with the boundary conditions in Ref. [31]. Gas inlets and gas outlets are defined as velocity inlet and pressure-outlet, respectively.

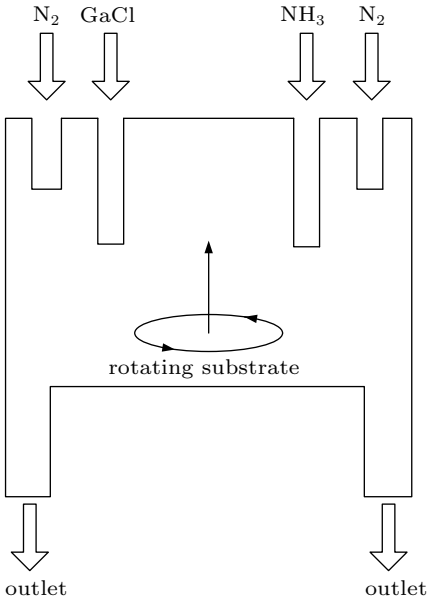


Fig. 1. Schematic structure of a new style vertical HVPE reactor.

In our molecular dynamic simulations, we apply the Tersoff potential instead of other types of potentials to model the interactions of Ga–Ga, Ga–N, and N–N because Tersoff potential is very similar to the second-moment approximation of the bond order potential and parameterizations of Tersoff potential have better phase transferability.[32] Our MD simulations apply the velocity–Verlet integration algorithm and the integration time step $\Delta t = 0.5$ fs. Additionally, 5 ns of growth is simulated. The GaN substrate is performed in the NVT ensembles by using Nose–Hoover thermostat algorithm, and the temperature is set as 1300 K unless otherwise stated. Besides, the NVE ensemble is used to control the free GaN atoms above the substrate.[22] The size of the simulation box is $6.78 \times 6.78 \times 8.0$ nm^3, and the periodic boundary conditions are adopted in x and y directions, while the reflect wall is applied in the z direction. All MD simulations in this work are carried out by using the software package Lammps (12 Jun 2011).

3. Results and discussion

Figure 2 shows the growth rate of GaN (which reveals the characteristics of the deposition uniformity) on the substrate with different rotation rates (i.e., the varying mixture degree). It is found that the deposition uniformity becomes better with the increase of the substrate rotation. When the substrate does not rotate, GaN deposition on the substrate is rather non-uniform. In this situation, the growth rate of GaN is high on one side of the substrate, and is low on the other side. When the substrate rotates, the source of Ga and N flows into the reactor space in all directions. As a result, the mixture degree becomes good. As shown in Fig. 3, when the substrate rotates properly, the gas of *GaCl* and NH_3 around the substrate can be fully mixed. While in the unmixed case, the fluctuation of V/III ratio is very large. The reason is that the substrate rotation results in averaging the instantaneous growth rate distribution, which provides the non-uniformity in the GaN deposition. Besides, because the rotation can induce the flowing of reactor gas to the end of the substrate, the growth rate of GaN is higher on the end of the substrate. Moreover, the gas diffuses intensely in the chamber and then pushes the local streamlines towards the substrate surface, which in turn enhances the heat and mass transfer there.[33] Therefore, the uniformity of growth rate and the epilayer flatness can be improved.

Compared with fluid dynamics simulations which can give some physical pictures from the macroscopic viewpoint, molecular dynamic simulations may be better for understanding in depth the mechanism of GaN film growth to some extent because it can provide insights from the microscopic viewpoint.

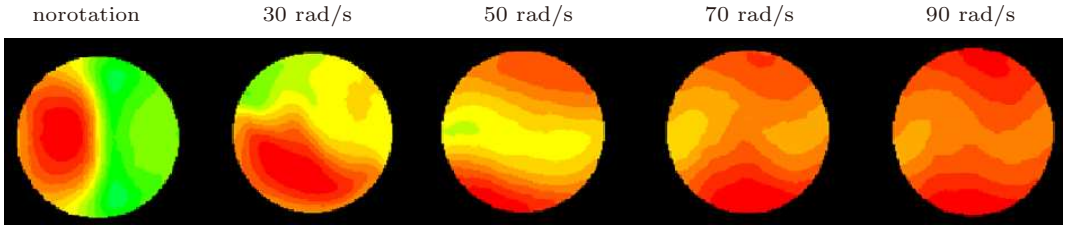


Fig. 2. (color online) Growth rate of GaN on the substrate with different rotation rates (by CFD).

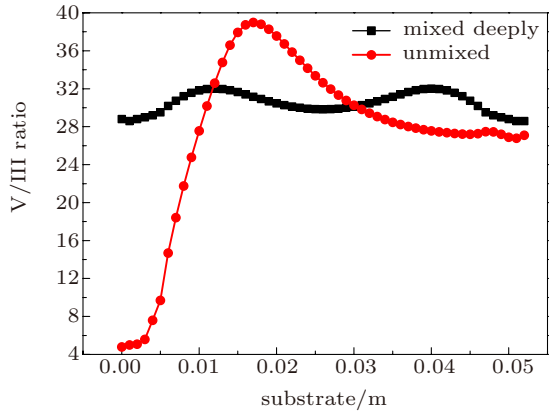


Fig. 3. (color online) V/III ratio distribution along the central line of the substrate (by CFD).

Figure 4 shows that our MD simulation system contains two different kinds of GaN: one is the GaN substrate (1800 Ga atoms and 1800 N atoms are arranged with the lattice constant $a = 3.189$ Å and $c = 5.185$ Å), and the other is free Ga and N atoms (the total number of atoms of Ga, N, is 1200, while the respective number varies with the V/III ratio). The perpendicular axis of the substrate is along the polar direction [0001] (i.e., the Z direction in our simulations). Particularly, in order to prevent crystal drift due to the atom momentum transfer, atoms in the bottom two planes are fixed during the MD simulations.

As shown in Figs. 4(a) and 4(b), at first, the free Ga and N atoms move randomly in all directions. Then, some N atoms will diffuse onto the GaN film, and can be deposited on the substrate because of the effective attraction between Ga atoms on the substrate surface and the free N atoms. At the same time of deposition, some N atoms may re-evaporate from the substrate. It should be noted that Ga atoms diffuse slower than N atoms because of its greater mass. Then some free Ga atoms will also reach the substrate and, if it happens to attach to a Ga atom on the substrate, the free Ga atom will deposit on the substrate since the diffusion energy barrier (for Ga adatoms on Ga polar) is 0.7 eV. On the contrary, if it meets N atoms which have been deposited before, it may not form a bond because here the diffusion energy barrier (for Ga adatoms on N polar) is about 1.8 eV, much higher than that in the former case (see Figs. 4(c) and 4(d). At last, the system will keep balanced, i.e., most of the free atoms have been deposited on the surface and they will just diffuse on the substrate surface (see Figs. 4(e) and 4(f)).

In the following sections, we will study the effects of V/III ratio and mixture degree on the growth behavior in detail. As shown in Fig. 5, our results show that the V/III ratio (ξ) plays an important role in the final balance. When ξ is lower, since the total number is fixed, there are fewer free N atoms. As a result, an N atom may not readily form a bond with the Ga atoms on the substrate, which in turn will cause the bad deposition of a free Ga atom. Besides, according to Zhou *et al.*,[32] lower ξ may also induce the weak evaporation of N atoms, i.e., the "self-adjustment" of N atoms becomes weaker. Therefore, the surface is rough and the crystallinity is bad under the lower V/III condition. As shown in Figs. 5(a), 5(c), and 5(e), with the increase of ξ, the surface becomes smoother. In order to provide more quantitative data of the roughness, we calculate the height distribution of the final GaN film (see Figs. 5(b), 5(d), and 5(f)). For higher ξ, there only exists one sharp peak in the distribution and the other peaks are much lower, indicating that the growth is better and is laminar growth. While for lower ξ, the peak is not that sharp, which means that the growth is worse and is island growth. Interestingly, our CFD result also shows that the V/III ratio is larger than 1.0 for the films of best quality. Though there exists some difference of the definition of V/III ratio between CFD and MD simulations,[34,35] the two results are consistent with each other to a large extent, and both of the simulations show that the higher ξ is better for the growth.

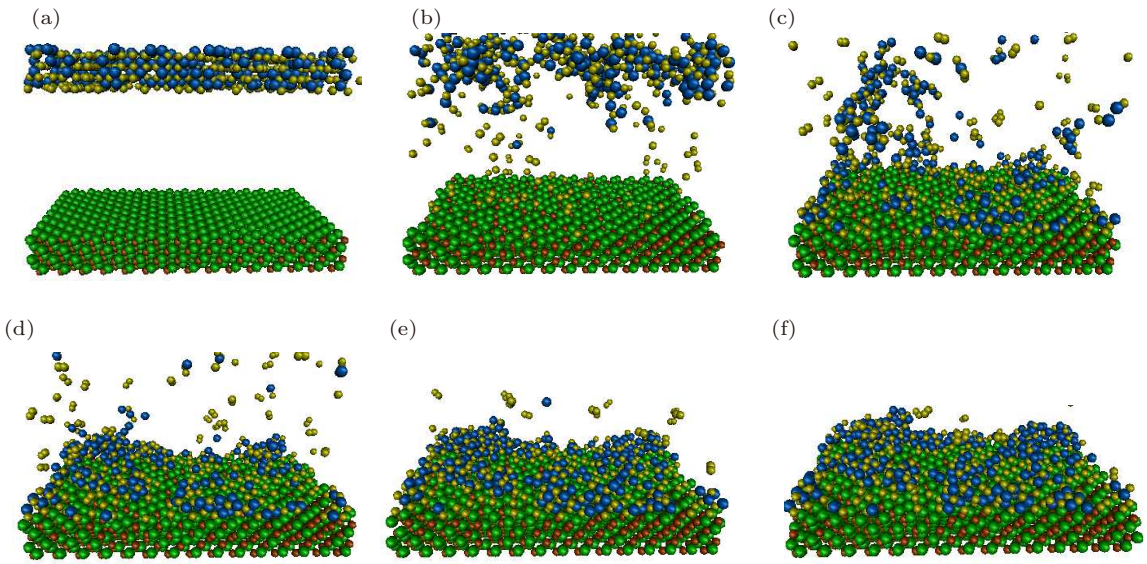


Fig. 4. (color online) (a) t=0.0 ns; (b) t=0.1 ns; (c) t=0.5 ns; (d) t=1.0 ns; (e) t=2.0 ns; (f) t=5.0 ns. In all snapshots, green beads represent the Ga atoms on the substrate; blue beads stand for the free Ga atoms; orange beads mark the N atoms on the substrate; yellow beads are the free N atoms.

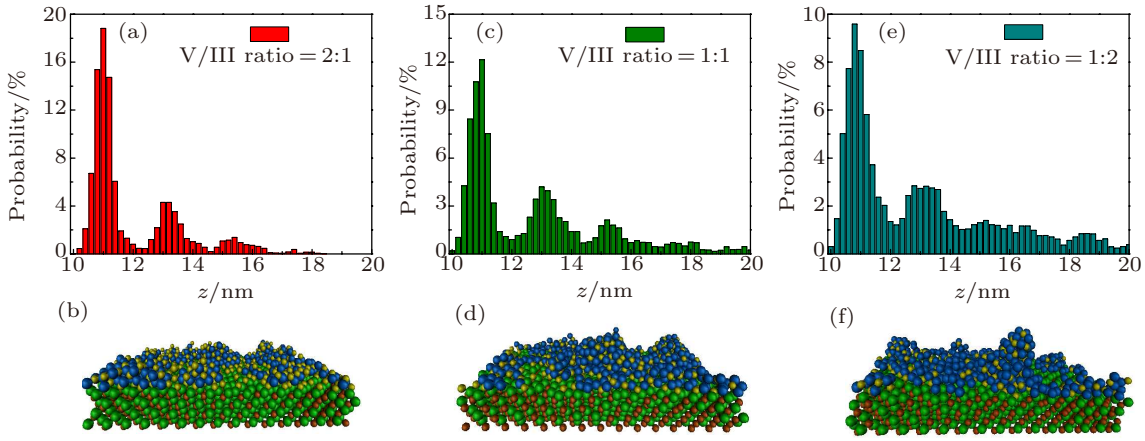


Fig. 5. (color online) Effect of V/III ratio on the final balance. (a), (c), and (e): the final surface morphology of the GaN film; (b), (d), and (f): the height distribution of the height of the final GaN film.

Moreover, we also pay attention to the effect of mixture degree η on the growth behavior. Similar to the results obtained by using CFD, our MD simulation results also show that the mixture ratio can obviously affect the final balance. However, instead of rotating the system to increase the mixture degree, we just choose the different initial states to denote the different mixture degree in MD simulations. As shown in Fig. 6, with the increase of initial mixture degree, the final morphology of the growth film is smoother. The reason is that the initial structure of Ga and N atoms is well mixed and it should be good for the later growth. Nevertheless, the nonuniform mixture of GaN atoms will cause the higher local energy (i.e., the local temperature will become higher), which may stimulate the diffusion of the free atoms according to the well-known Einstein relationship (i.e., $D \propto T$), and in turn will improve the mixture degree. In this sense, the initial mixture degree will not play a dominant role in the final balance. By comparing the two cases of $\eta = 0.5$ and $\eta = 1.0$, it is found that the final balance is approximately the same.

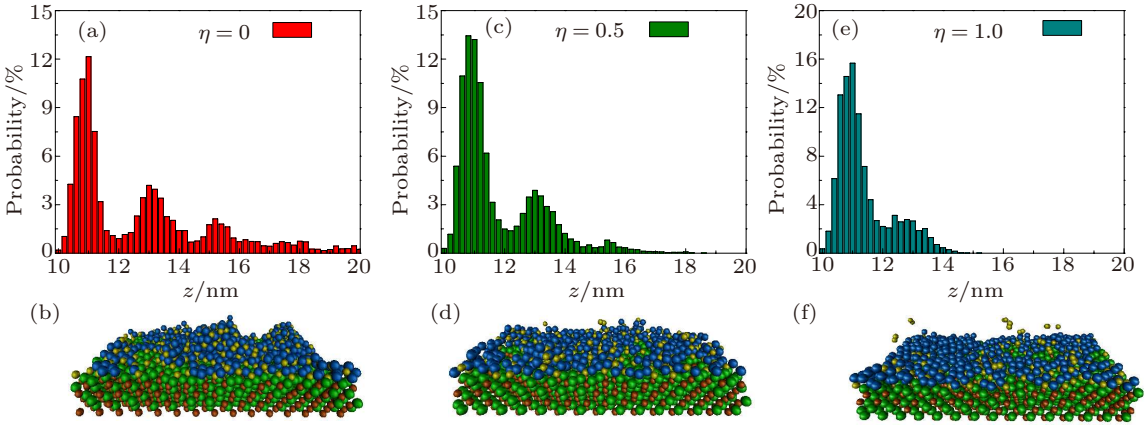


Fig. 6. Effect of initial mixture degree on the final balance. (a), (c), and (e): the final surface morphology of the GaN film; (b), (d), and (f): the height distribution of the final GaN film. The $\eta = 1.0$ indicates that the mixture of free Ga and N atoms is perfect; while $\eta = 0.0$ means free Ga and N atoms separate at the beginning.

4. Conclusion

In this paper, we have studied the growth behavior of GaN film. By using CFD simulations, we find that the uniformity of the deposition becomes better with the increase of substrate rotation. Besides, in order to gain further insights into the growth behavior of GaN film, we apply the molecular dynamics to study the mechanism of atomic deposition of GaN film. By using MD simulations, we have shown the whole process of GaN film growth. Moreover, it is found that not only the V/III ratio but also the V/III mixture degree can have important impacts on the deposition behavior, namely, a higher V/III ratio is preferable while the mixture degree may have a threshold value, above which the growth may become good. Importantly, the two simulation methods (i.e., MD and CFD) correspond to the experimental methods of PA MBE and HVPE, respectively, and the results obtained by the two meth-

ods are in good agreement to some extent. The present result shows that the growth behavior can be well controlled by the external environment, which may provide some useful guidelines for better preparation of GaN film in future experiments.

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