Molecular dynamics simulations of atomic assembly in the process of GaN film growth

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A R T I C L E  I N F O

Article history:
Received 11 March 2009
Received in revised form 20 July 2009
Accepted 31 July 2009

PACS:
61.30.Hn
68.43.Jk
31.15.at

Keywords:
Molecular dynamics simulation
Epitaxial growth
GaN film

A B S T R A C T

Molecular dynamics simulations using a Coulomb–Buckingham potential have been used to investigate the process of wurtzite GaN films growth, including the appearance of films in early stage, regulation of growth, structure of the surface and the dynamic features. The simulations show that the N atoms and Ga atoms are absorbed on the lattice of substrate and take on a distinct sandwich structure. Time evolution of the mean square displacements and diffusion coefficient of the deposited atoms are observed, the results show that the clusters will become stable with the increase of time steps and the atoms reach the initial stable state after 25 ps; N atoms reach the equilibrium positions more quickly than Ga atoms. It is proved by radial distribution function and the ratio of vacancy of every deposited layer that the crystalline characters of the films will become better as the time steps increase and weaker from bottom to top.

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1. Introduction

Gallium nitride (GaN) and related alloys provide enormous benefits in optoelectronic and electronic devices [1]. GaN film is particularly interesting because their band gaps can be conveniently engineered [2]. GaN films can be grown on many kinds of substrates, such as silicon, sapphire [3] and SiC [4]. However, because of the high mismatch in lattice constant and thermal expansion coefficients between these substrates and GaN, cracks and high density of dislocations [5,6] still exist, which impedes the fabrication of devices. High quality optoelectronic GaN thin films must have a highly perfect crystal lattice, a stoichiometric composition, and contain a low defect concentration [2]. So we choose GaN bulk as substrate to improve the quality of GaN films in this paper.

Theoretically, many calculation methods can provide accurate results for the epitaxial growth and cluster structures [7–15]. Monte Carlo (MC) method considers only configuration space without detailed dynamics. However, molecular dynamics (MD) simulation in which the atoms are modeled as pointlike particles in an empirical potential field can show more dynamic details, providing complete information about position and momentum at all times. So, MD method provides an outstanding means for simulating the capture of vapor atoms by a solid surface and the subsequent mechanisms of atomic assembly including thermally activated migration of atoms on a surface [2].

The structural and thermodynamic properties of GaN have been successfully described using MD method with Tersoff potential or Coulomb–Buckingham potential model [16–20]. Not all potentials that adequately describe the static properties of a crystal are able to simulate its growth and correctly predict film amorphous structures. The modeling of vapor deposition is one of the most stringent tests of an interatomic potential. Coulomb–Buckingham potential can predict relatively large antisite defect energies. This is important for the correct simulation of the crystalline growth, which requires that adatoms condensed on random sites to reconstruct to the correct sites in the corresponding sublattice.

In this paper, MD simulations using a Coulomb–Buckingham potential have been used to investigate the process of wurtzite GaN films growth. We provide an evidence that the potential is valid to describe both static and dynamic properties. Mean square displacements and diffusion coefficient of the deposited atoms are observed to study the diffusion properties of atoms. Radial distribution function of every deposited layer is computed to investigate the crystalline character of the films. All these results will give a better understanding of the atomic assembly and structural properties in the process of GaN films growth.
2. Simulation method and potential function

The numbers of atoms and the time steps of the simulation in MD are limited by the hardware restrictions. Nevertheless, MD is applicable to analyzing the behavior of deposited atoms at small scales, and useful for understanding the deposition mechanisms [21]. Here, we introduce a reduced MD unit in terms of which all physical quantities will be expressed. The wurtzite form of GaN is hexagonal closely packed. The gallium atoms in structures are coordinated by four nitrogen atoms and vice versa. A computational wurtzite GaN substrate crystal (2.5 nm × 4 nm × 1 nm) is created using lattice constants a = 3.189 Å, c = 5.185 Å. It contains five Ga-planes and four N-planes in the z-direction, totalling 584 Ga atoms and 464 N atoms. They are all fixed during the simulation. Incidence atoms are 464 Ga atoms and 464 N atoms, their initial positions are random and the incidence angle is assumed to be normal to the growth surface, the injected atoms are all assigned a remote kinetic energy of 0.24656 eV, which is similar to Refs. [22, 23]. Such thermalized fluxes are analogous to those of a molecular beam epitaxy (MBE) or a high pressure sputtering process. The incidence atoms fall at the same time and the interatomic forces between them are considered.

A system that is bounded but free of physical walls can be constructed by resorting to periodic boundary conditions. An atom that leaves the simulation region through a particular opposite face [21].

In order to simulate clusters containing more than several hundred atoms, it is necessary to resort to an empirical interatomic potential used to describe the interatomic forces [20]. There are two kinds of atoms in the system: crystallized atoms which are already deposited on the epitaxial layer as well as in the substrate and free atoms which are far away from the substrate. We use Coulomb–Buckingham potential function to indicate different effects caused by different kinds of atoms. Here, the Buckingham model is used as the short-range potential. The long-range potential is the coulomb potential. Expression term in the Buckingham potential provides a better description of strong repulsion due to the overlap of the closed shell electron clouds, which is important in simulation of bombardment by energetic atoms or ions, etc. When atoms lie in the crystalline thin film, the distance between two atoms is small and the short-range potential plays an important role. However, other atoms are far away from the substrate (free atoms), the longer distances between atoms lead to a rapid reduction of the short-range potential, the long-range potential has a main effect on the free atoms.

\[ V_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} + V_{short}(r_{ij}) \]  

(1)

\[ V_{short}(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - C_{ij} r_{ij}^{-6} \]  

(2)

where \( Z_i \) or \( Z_j \) is an effective charge. Here the charges are taken to be -2e and 2e, respectively. \( A_{ij} \) and \( \rho_{ij} \) are the parameters of repulsion, \( r_{ij} \) is the distance between atoms \( i \) and \( j \). \( C_{ij} \) is the Van der Waals constant. The Buckingham potential parameters are shown in Table 1 [20].

Velocity-Verlet algorithm is adopted in this simulation. The simulated time step length \( dt \) is 5 fs. First, initial atom position and velocity are known, the positions of atoms in the next step can be computed by the formula

\[ r_i^{(n+1)} = r_i^{(n)} + \frac{v_i^{(n)} + v_i^{(n+1)}}{2} \times \frac{dt^2}{m} \]  

(3)

Then, the velocities of atoms in the step can be acquired from formula

\[ v_i^{(n+1)} = v_i^{(n)} + \frac{dt \times (F_i^{(n+1)} + F_i^{(n)})}{2 \times m} \]  

(4)

The force of interaction can be obtained from formula

\[ F_i = \sum_{j \neq i} (-\nabla V_i(r_{ij})) \]  

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3. Results and discussion

The lateral views of substrate and injected atoms at 0, 5, 25 and 50 ps are shown, respectively, in Fig. 1.

From Fig. 1, we can find that the atoms deposit quickly toward the substrate as the velocities of atoms are large in the earlier period. Some atoms reevaporate from the surface of substrate, others are adsorbed by the substrate and diffused quickly on the surface of substrate. After 5 ps, the atoms diffuse slowly to find their equilibrium positions, the deposited clusters reach the initial stable state in the first 25 ps. The crystallinity of films will be improved with the increase of time steps. The simulations show that the N atoms and Ga atoms are absorbed on the lattice of substrate and take on a distinct sandwich structure. The film structure is in a large part determined by the surface atom migration distance. The deposition rate in MD simulations must be greater than that in the experiments, which significantly reduces the surface diffusion time before adatoms are buried by new arrivals. During deposition, there are more and more vacancies in the layers with the increase of the thickness of films, upper atoms in amorphous embryos are not mobile enough to quickly migrate within these regions. The amorphous embryos then quickly accumulate resulting in the formation of a fully amorphous structure on the upper layers. So, the crystallinity is significantly worsened with the increase of the number of film layers. In order to explain this result well, RDF of the first three deposited layers and the ratio of vacancy in the first three deposited layers are investigated. The results are self-consistent.

3.1. Mean square displacements and diffusion coefficient of the deposited atoms

Time evolution of the mean square displacements (MSD) and diffusion coefficient of the deposited atoms can describe the diffusion of atoms appropriately. They are computed by the formula

\[ MSD = \langle (r_i(t) - r_i(0))^2 \rangle \]  

(6)

\[ D = \frac{1}{6t} \langle (r_i(t) - r_i(0))^2 \rangle \]  

(7)

\( r_i(0) \) is the initial position of atom \( i \) and \( r_i(t) \) is the position of atom \( i \) at the time of \( t \). MSD of the deposited atoms at different
time are plotted in Fig. 2. Diffusion coefficients of the deposited atoms at different time are plotted in Fig. 3.

As shown in Fig. 2, injected atoms deposit quickly, so the MSD of the deposited atoms increase rapidly within the first several steps. After that, the MSD of N atoms varies slowly around a stable value until the end of the simulation, but the MSD of Ga atoms increases gradually until the end of 25 ps and reaches the value of N atoms, then varies slowly around the stable value until the end of the simulation, which indicate that the system has reached an approximately stable state. The process shows that N atoms reach the equilibrium positions more quickly than Ga atoms and the amplitude excursion of Ga atoms is bigger than that of N atoms. The phenomenon can be easily understood because the N adatoms are less likely to reevaporate when they strike a Ga-terminated surface.

In Fig. 3, the diffusion coefficient of the deposited atoms will decrease with increasing time steps. Eventually, when MSD reaches a stable value, diffusion coefficient will begin to drop to
the minimum. Diffusion coefficient of N atoms is bigger than that of Ga atoms before 25 ps, and they become close after 25 ps, which shows that the deposited atoms reach the equilibrium positions at about 25 ps.

The limiting diffusion length indicated in Fig. 3 is much smaller than that in experiments. This is because the deposition rate in MD simulations must be orders of magnitudes greater than that in the experiments, namely our beams of atoms in the simulations are extremely dense compared with those in experiments, which significantly reduces the surface diffusion time before adatoms are buried by new arrivals.

3.2. Radial distribution function of the first three deposited layers

Radial distribution function (RDF) $g(r)$ is used to analyse the structure of the films. RDF represents the ratio of the number density of the atoms within a spherical shell or a ring area centred at a reference atom [21]. The definition of $g(r)$ implies that is proportional to the probability of finding an atom in the volume or area element $dr$ at a distance $r$ from a given atom. Here we use the two-dimensional RDF as shown in formula (8) to investigate the structural properties of the first three deposited layers.

$$g(r) \approx \frac{n(r)}{2\pi r_0^2 dr}$$ (8)

$n(r)$ is the number of atoms in a torus of radius $r$ and thickness $dr$ surrounding the atom, $r_0$ represents the average number density of atoms in the perfect crystal.

When $r$ is small, $g(r)$ implies the assembly state and the distance between the bonds. When $r$ is big enough, $g(r)$ becomes flat or even tends towards a constant because the ratio of finding the atoms at the fixed distance is almost the same. The RDF not only addresses the local structure, but also gives information as to whether long-range crystalline order exists. The sharpness of the RDF peaks, separation of the peaks and the presence of additional peaks imply the degree of ordering [23].

Fig. 4 shows the RDF curves, in which all atoms in the first three deposited layers are monitored. Obviously, the curves in Fig. 4(b) are more ordered than those in Fig. 4(a), the RDF peaks in Fig. 4(b) are sharper and separate quickly, there are more additional peaks in Fig. 4(b). However, in Fig. 4(a), the corresponding peaks are lower and wider, some even disappear, which indicates the disordered structure of the films. All of these show that the crystallinity of films will be improved with the increase of time steps. From Fig. 4(b), we can find that the sharpness of the RDF peaks of the three layers becomes worse from bottom to top, which indicates that the crystalline character of the films becomes weaker from bottom to top. As the simulation takes only 50 ps, the deposited dimers tend more and more difficulty to be broken, the rate of breaking and reconstruction of dimers will decrease. Not all the atoms can find their equilibrium positions in this short time and the growth will become amorphouslike with the increase of deposited layers. In Figs. 5 and 6, the number of deposited atoms in the first three layers will increase as the time increases; the ratio of vacancy in the first three layers will decrease with the increase of time and decrease from top to bottom. N atoms reach the equilibrium positions more quickly than Ga atoms. With the reduction of the free atoms, the crystalline character of the films will become weak. Of course the un-symmetric free Ga and N atoms contribute to the different speeds towards their equilibrium positions. In our future work, N:Ga flux ratio effects on the quality of films and the speeds to their equilibrium positions will be investigated.
4. Conclusions

Molecular dynamics simulations using a Coulomb–Buckingham potential have been used to investigate the atomic assembly in the process of wurtzite GaN films growth. The results show that the N atoms and Ga atoms are absorbed on the lattice of substrate and take on a distinct sandwich structure; the clusters will become stable with the increase of time steps and the atoms reach the initial stable state after 25 ps; N atoms reach the equilibrium positions more quickly than Ga atoms. It is also proved that the crystalline character of the films will become better as the time steps increase and weaker from bottom to top. All of these conclusions are important to the industrial production of GaN films.

Acknowledgments

This work is supported by the National 863 High Technology Research and Development Program of China (Grant no. 2009AA032405) and the National Natural Science Foundation of China (Grant no. 60644004).

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