Kinetic energy barriers on the GaN(0001) surface: A nucleation study by scanning tunneling microscopy

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Island nucleation of GaN on its (0001) surface is studied by scanning tunneling microscopy. A comparison is made between surfaces with and without excess Ga and among surfaces with different excess Ga coverages. Evidence is provided for the change of step characteristics of GaN(0001) by excess Ga adlayers, where the Ehrlich-Schwoebel effect is seen to be mediated by excess Ga coverage. For single Ga adlayer covered GaN(0001) surfaces, nucleation island densities are evaluated, which are used to derive the kinetic barriers of adatom diffusion on a terrace. A barrier of less than 1 eV is obtained for the system, and the Ga adlayers make GaN growth surfactant mediated.

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I. INTRODUCTION

The surface growth of a thin film by molecular-beam epitaxy (MBE) is governed by a few kinetic processes,[1,2] such as adatom surface diffusion and step attachment, and the determination of relevant kinetic parameters has been one of the intensively studied areas in surface science.[3–8] The developments of nucleation theories of surface growth have led to methods to derive surface kinetic parameters by examining nucleation island density and distribution,[9–11] which can be achieved by scanning tunneling microscopy (STM).[5,12,13] Up to now, most of such studies are on simple and well-understood systems, such as metals[8,13] and Si.[5,12] For GaN, a technologically important semiconductor for modern microelectronic and optoelectronic applications,[14] a much less quantitative measurement has been made. As it turns out, such a measurement is very difficult due to the complicated nature of GaN surfaces. The past experiments have revealed a rich family of surface structures and novel growth features.[15–19] Due to strong chemical bonds of GaN, diffusion of adatoms on clean GaN(0001) requires overcoming a large energy barrier,[6] which would imply inferior films at the commonly adopted growth temperatures of MBE (600–700 °C). It was thus mysterious how smooth surfaces and high quality films could be obtained experimentally under excess gallium (Ga) by MBE.[20,21] A recent theoretical investigation of adatom diffusion on a monolayer (ML) indium (In) covered GaN(0001) surface identified a novel diffusion channel underneath the In adlayer for nitrogen (N) atoms, and the diffusion barrier was about 0.5 eV.[7] For growth under excess Ga, excess Ga adlayers exist on the surface, forming the "pseudo-1×1" surface structure.[15,16,22] A similar mechanism of diffusion may thus apply, which would explain the smooth films obtained under excess Ga by MBE. However, for film growth with surface adlayers, the kinetics of nucleation may also be modified from a conventional diffusion limited mechanism to one which is surfactant mediated or reaction limited.[23,24] Another known effect on surface growth is the so called Ehrlich-Schwoebel (ES) effect,[3,4] where the additional energy barrier for adatom to diffuse across a step will have important consequences to the morphology of growth front (e.g., being smooth or rough). How surface excess Ga on GaN(0001) surface will affect the ES barrier remains to be documented, while an experimental evaluation of adatom diffusion kinetic barrier is still unavailable.

In this paper, we present an experimental investigation of the step characteristics of GaN(0001) and a derivation of the energy barrier for N adatom diffusion based on a nucleation study of the system. We identify that the nucleation kinetics of GaN under excess Ga is surfactant mediated, and the model of Kandel,[24] where adatom incorporation at steps is a rate limiting process, is relevant for such a system. The ES effect is seen to be conveniently mediated by excess Ga coverage on surface. These findings not only have important bearings to the morphological control and manipulation of the growth front of GaN during MBE, but also suggest further theoretical investigations of the system so as to identify the origin of the surface characteristics.

II. EXPERIMENT

GaN growth by MBE and surface examinations by STM were conducted in a multichamber ultrahigh vacuum (UHV) system, where the MBE reactor was connected to an array of surface analysis tools, including STM, via UHV interlocks.[25] The substrate used in this experiment was GaN-on-SiC(0001) (TDI, Inc.). Following a heat treatment at 600–700 °C in UHV, a clean surface was obtained, on top of which a ~0.2 μm thick GaN buffer was grown at 620 °C. The latter was for the improved morphology as well as for the required surface structures, characteristic of excess Ga covered GaN(0001) surfaces.[16,26] After the buffer layer deposition, the sample was either briefly annealed at ~600 °C or immediately brought to a low temperature in the range of 340–520 °C, ready for subsequent island nucleation experiment. The latter was achieved by resuming the source fluxes for a shorter period of time (10–15 s), resulting in submonolayer (~0.2 ML) GaN deposition. Afterward, the sample was thermally quenched by switching off the heating current flowed through the sample and then transferred to the adjacent STM chamber for examination at room temperature. In

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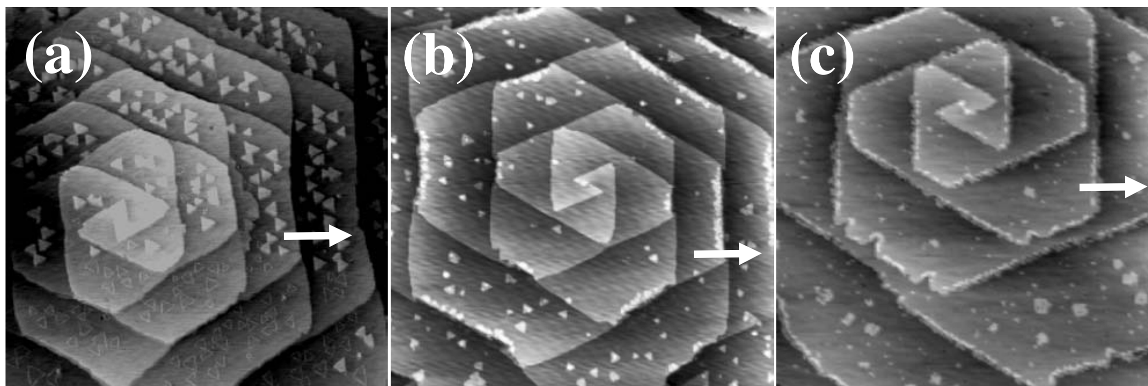

FIG. 1. STM images showing nucleation islands on surfaces with (a) excess Ga bilayer, (b) excess Ga monolayer and (c) no excess Ga. The white arrows point to the $[10\bar{1}0]$ direction. The image size is 350×350 nm^2.

the STM experiment, the tunneling current was 0.1 nA and the sample bias was −2.5 V.

III. RESULTS AND DISCUSSION

Before presenting the nucleation data, we firstly remark that it is essential to identify the growth regimes of the experiments. In addition to excess Ga versus excess N conditions,[25] one may further distinguish three growth regimes for the case of excess Ga.[26] At high Ga coverage, the surface contains 2 ML excess Ga. The nucleation islands usually show a distinct triangular shape and appear as the "ghosts" in STM micrographs.[19] The nucleation process involves site exchange between atoms of the deposit and surface Ga, and the critical island size appears to be zero.[27] Reducing Ga coverage leads to a surface covered by a single layer of excess Ga. Islands formed on such a surface are the "bare" islands according to Ref. 26. For surfaces without excess Ga, which is obtained by using the N-rich conditions of MBE, the islands lose their distinct triangular shape but show higher densities.[28] All of these reflect a change of surface adatom kinetics upon the variation of surface Ga coverage on GaN(0001).

In the following, we first study the island spatial distribution on terraces under different surface conditions, by which the ES barriers and their changes with Ga coverage can be referred to. Then, the island density on a terrace is measured, from which adatom diffusion kinetics and the energy barrier for N adatom surface diffusion are derived for the ML Ga covered surfaces.

A. Step kinetics of GaN(0001)

Figure 1 shows the STM images depicting the surfaces after submonolayer deposition at 400 °C but on different starting surfaces. In Fig. 1(a), the Ga coverage is a bilayer (BL) and the islands appear ghost (the lower half of the image) and "normal" (the upper half of the image). The latter are converted from the ghost by STM scanning.[19,27] For the surface of Fig. 1(b) prepared under a slight excess Ga flux, the triangular islands are the bare islands.[26] They differ from the normal islands in Fig. 1(a) by their sizes (smaller), spatial distributions (closer to steps), as well as the fact that upon Ga wetting, they transfer to the ghost, as detailed in Ref. 26. Finally, for growth under stoichiometric or slight excess N condition, the islands become circular in shape, smaller in size, and high in density [Fig. 1(c)].[28] Another observation in Fig. 1 is the step characteristics for different surfaces. As the GaN buffer surface contains spiral mounds,[29] the steps at the mound sides are double layers perpendicular to $\langle 10\bar{1}0 \rangle$ but debunched single layers at the corners of the hexagon, characteristic of the wurtzite GaN(0001) surface.[18,28] For nucleation on surfaces with 2 ML excess Ga, the islands are seen to locate away from descending steps but close to ascending steps, irrespective of the step heights [see, e.g., Fig. 1(a)]. On surfaces without excess Ga [Fig. 1(c)], islands accumulate near the edges of descending steps of all heights. For surfaces with excess Ga ML [Fig. 1(b)], however, one observes a mixed feature where islands accumulate at descending double layer steps but stay away from single layer steps.

Figure 2 shows spatial distributions of islands across terraces bounded by ascending steps on the left and descending steps on the right. In obtaining the data, we record the space coordinate of each island relative to the central line of the terrace, and the histograms summarize islands from many different terraces of the same surface without excess Ga in Fig. 2(a) but with excess Ga BLs in Fig. 2(b). For the former case [Fig. 2(a)] where coalescence of islands has occurred near the descending steps due to high island density [as in Fig. 1(c)], the number of island near descending steps can be underestimated. Despite this and the existence of statistical errors, the skewness of island distributions is clearly discernible. For surfaces without excess Ga the island number peaks on the right of the terrace, being closer to descending step. On the other hand, for the surface with Ga BLs, more islands are found to the left side of the terrace. The dark lines in Fig. 2 represent the least-squares fittings of the distributions by a parabolic function. According to Ref. 30, if there exists an asymmetry between ascending and descending steps, adatom density distribution on the terrace is an inverted parabola with the peak being shifted from the terrace center.[2,30] The skewness of the island distribution seen in Fig. 2 may thus

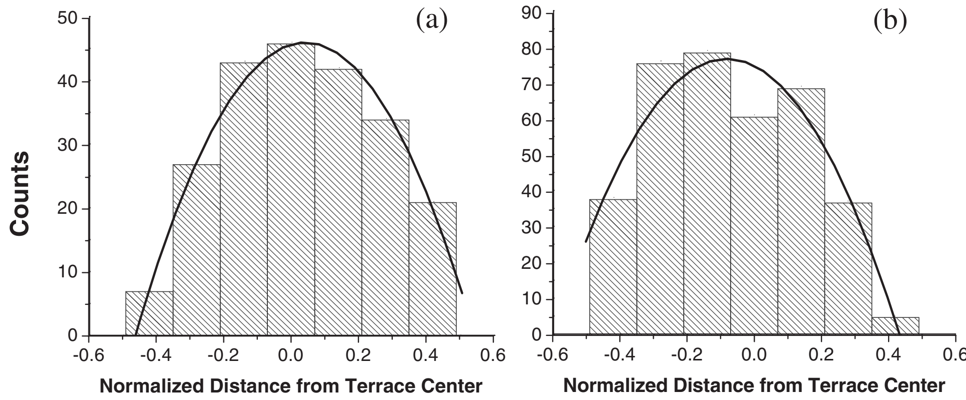

FIG. 2. Spatial distribution of islands across terraces. The descending (ascending) step edge is on the right (left). (a) is for a surface without excess Ga, whereas (b) plots the data for a surface with BL excess Ga. The solid lines in both figures represent the least-squares fitting of the distribution by a parabolic function.

reflect a similar adatom density distribution and, so, the asymmetry of steps in adatom incorporation.[2] Comparing Figs. 2(a) and 2(b), it is clear that the step kinetic coefficients are modified by excess Ga adlayers. We argue that for a clean surface without excess Ga, the step edges are effective sinks for adatoms from the lower terraces, while for adatoms from the upper terraces, there exists an ES barrier that hinders adatom incorporation from the above. Consequently, adatoms accumulate at descending steps, leading to high nucleation rates and therefore more islands near the step edges. For surfaces with excess Ga BL, the abundant Ga atoms likely passivate the steps of all heights, changing the character of the steps into ones showing an inverse ES effect, where adatom incorporation into a step from below becomes difficult. For surfaces with ML excess Ga, however, the Ga atom may only passivate steps of single layer high but not those of double layers. As a result, one observes islands accumulating at the edges of descending BL steps but not of single BL steps.

This apparent mediation of step characteristics by excess Ga on surface will have very important consequences to the morphological control of the growth front. Indeed, it has been established that an ES barrier may lead to mound formation and thus rough surfaces.[1,31,32] On the other hand, an inverse ES effect may give rise to step bunching.[1,30] Therefore, different surface Ga coverages, which change the ES barriers of the surface, will lead to different morphologies of the growing surfaces. This effect can be utilized to achieve different structures for special device applications.

B. Adatom diffusion barrier on GaN

In this section, we turn to examine adatom diffusion kinetics on flat terraces. We shall derive the energy barrier for adatom diffusion from the nucleation data. According to the theories of surface nucleation, the density of islands saturates at the maximum value N_m in the aggregation regime,[1,2,5,9–11]

$$N_m = \eta\left(\frac{F}{D_0}\right)^{\chi} \exp\left(\frac{E^*}{kT}\right), \tag{1}$$

where η is a dimensionless number of the order of unity, F is the deposition flux, k is the Boltzmann constant, and T is the temperature. The diffusion prefactor $D_0 = \nu_0/3$, where ν_0 is the attempt frequency. For conventional diffusion limited growth, the exponent χ and the effective energy E^* are, respectively,

$$\chi = i/(i+2) \text{ and } E^* = (iE_d + E_i)/(i+2), \tag{2}$$

where i is the critical island size for nucleation, E_d is the energy barrier of diffusion, and E_i is the binding energy of a cluster of size i ($E_{i=1}=0$).[9] For a surfactant mediated or reaction-limited growth, where adatom incorporation at steps requires overcoming an additional energy barrier E_s, Kandel derived that[24]

$$\chi = 2i/(i+3), \quad E^* = 2(iE_d + iE_s + E_i)/(i+3). \tag{3}$$

By measuring the temperature dependence of the island density $N_m(T)$, one is thus able to derive the energy barrier(s) of surface kinetics using Eqs. (1)–(3).[8]

In the following, we concentrate on adatom diffusion kinetics on surfaces with ML excess Ga, similar to that of Fig. 1(b). For the other surface states, the data are less reliable due to high surface roughness and/or defective when prepared under excess N,[20] or for BL Ga covered surfaces, they are not useful for deriving the barrier E_d due to the zero critical size of nucleation.[33]

Figure 3 plots the island density as a function of deposi-

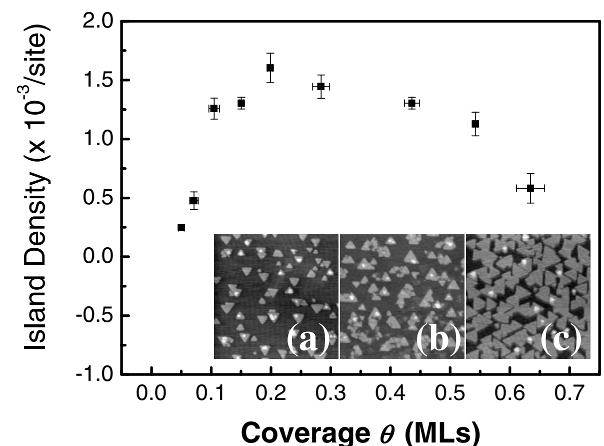

FIG. 3. Island densities as a function of deposition coverage. The insets show a few representative images of the surfaces at the coverage of (a) 0.15, ML (b) 0.2 ML, and (c) 0.6 ML. The image size is 100×100 nm^2 for all.

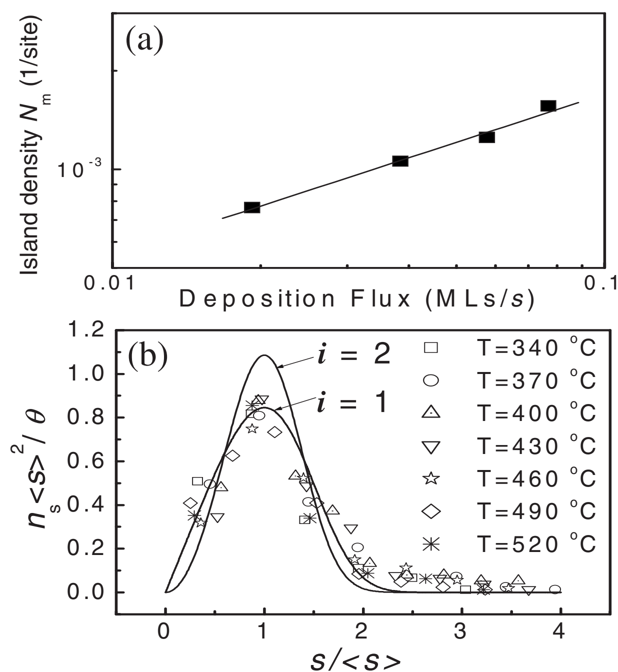

FIG. 4. (a) Double logarithm plot of the island density versus deposition flux. The solid line represents the best fit of the data. (b) Scaled island density $n_s\langle s\rangle^2/\theta = f_i(s/\langle s\rangle)$ for different temperatures. The lines are theoretical curves of f_i for $i=1$ and $i=2$ (Ref. 36).

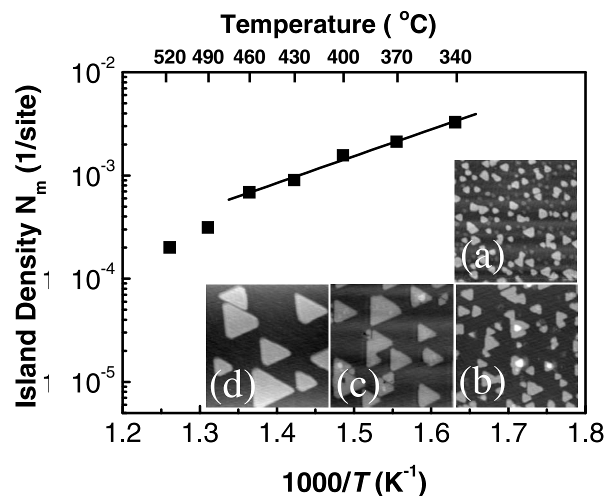

FIG. 5. Arrhenius plot of the island density as a function of deposition temperature. The straight line represents least-squares fitting of the data. The insets show some examples of the surfaces following GaN depositions at (a) $T=340$ °C, (b) 400 °C, (c) 460 °C, and (d) 490 °C (image size: 50×50 nm^2).

tion coverage θ for the specific growth condition of $F=0.02$ ML/s and $T=400$ °C. The insets show a few examples of the surfaces. In calculating the island densities, we have limited ourselves to regions away from surface steps, so the effect of the latter is minimized. The deposition coverage is estimated from the sizes of the islands. As expected, the island density increases initially at low coverage due to nucleation, but decreases at later stages due to coalescence. It saturates in the aggregation regime, which occurs at about 0.2 ML.

Figures 4(a) and 5 summarize the flux and temperature dependences of the saturated island densities following the same 0.2 ± 0.03 ML GaN deposition. According to Eq. (1), the data of $N_m(F)$ may be used to derive the scaling exponent χ, and the least-square fitting of the data in Fig. 4(a) results in a value of $\chi\approx0.49\pm0.04$. From Eqs. (2) or (3), this will suggest a critical nucleation size of $i=2$ or $i=1$, depending on the growth mechanism (diffusion versus reaction limited). However, we remark that due to the narrow range of N fluxes producible from the plasma unit in this experiment, the exponent χ derived from Fig. 4(a) could be erroneous by a large margin. Therefore, we have also examined the size distribution of islands, as shown in Fig. 4(b). According to the scaling theory of surface nucleation,[34–36] $n_s(\theta)=\frac{\theta}{\langle s\rangle^2}f_i(s/\langle s\rangle)$, where n_s is the density of islands with size s, and $\langle s\rangle$ represents the average size of the islands. The scaling function $f_i(s/\langle s\rangle)$ depends on the parameter i, which are plotted in the figure for $i=1$ and $i=2$.[36] A comparison between experiments and theory suggests that $i=1$, which agrees with the assignment made above, assuming that the growth is reaction limited. Additional support for $i=1$ and the reaction-limited mechanism may be found from the temperature dependence of N_m, as shown in Fig. 5 and discussed below.

According to Eq. (1), the logarithm of N_m is linearly dependent on the inverse of temperature T with the slope E^*/k and intercept related to ν_0, so long as the parameter i is well defined and unchanged as T varies. The experimental data in Fig. 5 do seem to follow a straight line, except for the two data points at high temperatures (i.e., $T=490$ and 520 °C). The latter may reflect a change of i as temperature increases.[8] However, our analysis of island size scaling [Fig. 4(b)] did not indicate such. On the other hand, at high temperatures, the density of islands becomes low, which not only leads to larger errors in island counting, but also makes the effect of surface steps on nucleation stronger. Therefore, we have chosen to leave out these two data points during the line fitting, and the resulted line slope is 2.59 ± 0.15 while the intercept is -6.70 ± 0.23.

The fitted slope of 2.59 ± 0.15 translates into an effective energy of $E^*\approx0.52\pm0.03$ eV. Taking $i=1$, and thus $E_i=0$, and assuming the growth to be reaction limited per the above discussion, by Eq. (3), the sum E_d+E_s will be 1.04 ± 0.06 eV, and the attempt frequency is $\nu_0\sim10^{12\pm0.5}$. Under the surface and flux conditions of the experiment (i.e., Ga excess), diffusion of N atoms is relevant. So, the energy barriers derived above will represent N adatom kinetics on GaN(0001). Since the barrier for atom attachment to steps, E_s, is a positive value, the above result suggests a barrier for diffusion, E_d, to be less than 1 eV. Such a small diffusion energy cannot be accounted for on a clean surface.[6] Hence, the existence of excess Ga on surface must have increased the diffusivity of N atoms. Based on the study of Neugebauer *et al.*,[7] N adatom diffusion takes place below the metallic adlayer with far lower an energy barrier ($E_d\sim0.5$ eV for diffusion underneath excess In adlayer). Therefore, the above result seems to lend an experimental support to the theoretical prediction.

Had we not assumed the reaction-limited mechanism but instead a diffusion limited growth, by Eq. (2), the energy

barrier of diffusion would be $E_d = 3E^* \approx 1.56 \pm 0.09$ eV for $i=1$ or $2E_d + E_i \approx 2.08 \pm 0.12$ eV for $i=2$. For the former, though the value of $E_d \sim 1.56$ eV compares well with a theoretical value of 1.4 eV for N diffusion on clean GaN(0001) surfaces,[6] the attempt frequency derived is of the order of $10^{19\pm0.7}$, which is unphysically high. For the case of $i=2$, on the other hand, the attempt frequency is of the right order (i.e., $\sim 10^{12}$); however, the energy of $2E_d + E_i \approx 2.08$ eV seems to be out of range. The binding energy E_i for GaN is about 2 eV,[37,38] so the energy of diffusion E_d would become too small to be reasonable. Consequently, we believe that the mechanism of GaN nucleation on surfaces with ML Ga is unlikely the conventional diffusion limited aggregation but a reaction-limited process.

IV. SUMMARY

An experimental investigation of surface adatom kinetics during MBE of GaN has been conducted for surfaces with different Ga coverages. We reveal different step characteristics, where a normal ES barrier seems to exist at steps on clean surfaces whereas an inverse ES effect is suggested for Ga passivated steps. For adatom diffusion kinetics on a terrace, the nucleation data point to a surfactant-mediated process on ML Ga covered surfaces. The diffusion energy barrier for nitrogen adatoms is derived to be less than 1 eV, which is again consistent with the assignment that surface Ga enhances adatom diffusion on GaN(1000).

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