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Gallium desorption kinetics on (0001) GaN surface during the growth of GaN by molecular-beam epitaxy

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Gallium (Ga) surface desorption behavior was investigated using reflection high-energy electron diffraction during the GaN growth. It was found that the desorption of Ga atoms from the (0001) GaN surfaces under different III-V ratio dependents on the coverage of adsorbed atoms. Doing so led to desorption energies of 2.76 eV for Ga droplets, 1.24–1.89 eV for Ga under Ga-rich growth conditions, and 0.82 eV – 0.94 eV for Ga under stoichiometric growth conditions. Moreover, the variation of the GaN surface morphology under different III-V ratios on porous templates supports the conclusion that Ga desorption energy depends on the coverage, and the III/V ratio dominates the growth mode. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2166478]

Molecular-beam epitaxy (MBE) is an established method for synthesizing GaN-based heterostructures for devices where high-purity and precise control of layer thickness are required.[1] The extensive work on epitaxy of GaN for device applications[2–9] is in contrast to the relatively few studies on the physics of growth itself. MBE studies indicated that the growth mechanisms and the resulting surface structure of GaN thin films are crucially sensitive to the kinetics, i.e., Ga/N flux ratio and growth temperature.[10–13] It was reported that the GaN growth is stabilized by a metallic Ga adlayer, which is commonly attained under Ga-rich conditions or near Ga-rich conditions.

The Ga desorption process has been studied previously by mass spectrometry[14,15] and reflection high-energy electron diffraction (RHEED)[12,13,16] techniques, however with a large degree of inconsistency. The activation energies reported for Ga desorption span 0.4 eV–5.1 eV,[13–20] while the typically reported value for GaN decomposition is near 3.6 eV.[21] Even though the growth conditions affect the desorption energy,[19,20] there is no systematic study of Ga desorption energy as a function of the Ga surface coverage. In this work, we analyze the desorption energy as a function of the Ga coverage by monitoring the intensity of RHEED specular beam during GaN growth in plasma-assisted MBE (PAMBE) under different temperatures and III/V ratios.

The experiments were carried out using a PAMBE system equipped with two conventional Ga effusion cells for the metallic species and a radio-frequency plasma source for the nitrogen. The (0001) oriented GaN templates grown by metalorganic chemical vapor deposition on sapphire were used as substrates. The GaN epilayers were grown on these substrates in the temperature range of 648 °C to 773 °C. The acceleration voltage for *in situ* RHEED was 13.9 kV with a fixed filament current at 1.4 A resulting in a fixed emission current. The intensity of the RHEED specular beam was monitored when the growth was stable. The desorption energy was determined from the relationship between the intensity and substrate temperature for a given III/V ratio. To study the growth modes under different conditions, atomic force microscopy (AFM) surface topology image was carried out which allowed the investigation of the surface morphology of GaN regrown on porous GaN templates under different III-V ratios for a substrate temperature of 700 °C.

During the GaN growth, Ga atoms are incorporated into the GaN epilayer with active nitrogen, adsorbed on the surface to form a Ga adlayer, or re-evaporated from the Ga adlayer.[13] The incorporation, adsorption and desorption processes reach a statistical equilibrium when GaN growth proceeds under steady conditions, in which case the desorption rate constant can be expressed as[22]

$$k = \nu_0 \exp(-E_{\mathrm{des}}/k_B T), \tag{1}$$

where ν_0 is the attempt frequency. At GaN growth temperatures used by MBE (in the range of 650 °C–780 °C), the Ga adatoms do not condense into a reconstruction, but rather represent a liquidlike film.[23] The RHEED electron beam is scattered just by the top layers of the periodic GaN surface. However, Ga adlayer on GaN surface does not diffract the electron beams; on the contrary, this disordered film causes an attenuation of the RHEED specular beam intensity.[24] The Ga adlayer is a monolayer during the growth, therefore, the intensity of the RHEED is related with the number of Ga atoms on the surface. The smaller the desorption rate of Ga is, the more Ga atoms stick on the GaN surface forming Ga adlayer and reducing the RHEED intensity. As a result, the dependence of the desorption rate represented by the RHEED intensity versus substrate temperatures provides the opportunity to study the desorption kinetics of Ga. We interpret the relationship between the RHEED intensity and the desorption energy as an exponential, given by

$$I \sim \exp(-E_{\mathrm{des}}/k_B T_s). \tag{2}$$

The Ga atoms desorbs from the surface at a substrate temperature T_s with the desorption energy E_{des}.

Figure 1 shows the typical trend of the variation of RHEED specular beam intensity during GaN growth at different substrate temperatures under the stoichiometric conditions. Since the growth temperature range is small, it can beassumed that the desorption energy changes caused by the Ga adlayer coverage varying under different substrate temperatures is negligible. Therefore, the desorption energy can be treated as a constant and calculated by the zeroth-order desorption kinetics. The exponential relationship in Fig. 1

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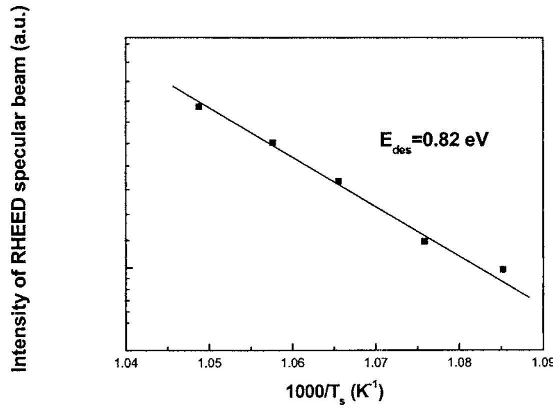

FIG. 1. Variation of the RHEED specular beam intensity during the GaN growth for substrate temperatures from 648 °C to 680 °C under stoichiometric growth condition. The Ga cell temperature is kept constant at 1140 °C, and the pressure is 8×10^{-6} Torr.

supports this assumption, and a desorption energy of $E_{des}=0.82\pm0.02$ eV is determined by using Eq. (2).

Interestingly, it was found that the desorption energy changes for different growth conditions. Higher Ga desorption energies resulted for higher III/V ratios. In the transition regime, the desorption energies are in the range of 0.82 to 0.94 eV, slightly increasing with the number of Ga atoms on the surface. Under Ga-rich conditions, the desorption energies are found to be 1.24 to 1.89 eV. Finally, the desorption energy is 2.76 ± 0.02 eV in the Ga-droplet regime, where the coverage of the Ga adlayer is approximately 100%. Note that in Ref. 15, much higher desorption energies have been reported. However, in their experiments GaN was covered with Ga metal without nitrogen being impingent on the surface. Therefore, one should be careful in comparison of desorption of Ga in these two cases.

Table I lists the deduced Ga desorption energies for different III/V ratios on the GaN surface at different substrate temperatures. It is clear that the growth environment affects the Ga desorption energy. This phenomenon can be explained by the dependence of the desorption energy on the bond strength which is determined by the separation between atoms. A simple approach based on the Madelung model[25] allows a basic understanding of the relationship between the cohesive energy and the separation between atoms:

$$U(r_0) = -\frac{N\alpha q^2}{r_0}\left(1-\frac{\rho}{r_0}\right), \tag{3}$$

Equation (3) shows the total energy of the crystal of 2N ions at their equilibrium atomic separation r_0, while α is the Madelung constant and the parameter ρ is of the order of $0.1r_0$. In the framework of the above model, it is clear that the bond energy has a reciprocal relationship to the separation, r_0.Under the steady-state condition of GaN growth, the equilibrium separation r_0 between Ga–Ga atoms depends on the surface coverage conditions, and the average in-plane separation r between Ga–Ga atoms can be related to the Ga coverage C as follows:

$$C(r) \propto 1/r^2. \tag{4}$$

Ultimately, the relationship between the Ga desorption energies and surface coverage can be deduced.

In our study, the Ga desorption energy is determined to be 2.76 eV under Ga very rich conditions with a Ga coverage about 100%. This result is very close to the cohesive energy of Ga (2.81 eV),[25] defined as that energy required to remove a Ga atom from a Ga reservoir. Since this condition corresponds to a Ga-Ga separation of 2.7Å,[26,27] the coverage of Ga under different growth conditions can be calculated based on these values by

$$C(r) = C_{100\%}\left[\frac{r_{100\%}}{r}\right]^2, \tag{5}$$

with $r_{100\%}=2.7$ Å. The results are listed in Table II.

TABLE II. Desorption energies with different Ga-Ga separation and coverage.

III/N ratio	1.0	1.2	1.5	2.2	2.4	∞
E_{des}(±0.02 eV)	0.82	0.94	1.24	1.59	1.89	2.76
In plane Ga–Ga Separation (Å)	9.2	8	6.1	4.8	4	2.7
Coverage (%)	8.6	11.4	19.6	31.6	45.6	100

When taken with diffusion energy, the desorption energy can be used to predict growth regimes where layer by layer or even lateral epitaxy may be possible. Figure 2(a) shows a typical AFM image of GaN epilayers etched in molten KOH for 1 min, which are later used as templates for further growth. The pores on the template have a hexagonal shape of about 200 nm in width and 50 nm in depth. After a 0.8 μm thick GaN regrown by MBE on these templates, the surface morphologies vary under different growth conditions. Under stoichiometric conditions [Fig. 2(b)], hexagonal pits still appear on the surface with a depth of 50 nm which is similar to that of the substrate. However, under Ga-rich condition [Fig. 2(c)], the surface of GaN is atomically smooth without pits.

This phenomenon indicates that the III/V ratio dominates the surface processes, which in turn strongly affect the surface morphology. As discussed, the desorption energy falls in the range of 0.82–2.76 eV with increasing III/V ratio, meanwhile the diffusion energy changes from 0.4 eV under Ga-rich conditions, to 1.8 eV under N-rich conditions.[28,29] For stoichiometric conditions, the diffusion energy is taken as 1.1 eV. Furthermore, under stoichiometric conditions the diffusion energy is larger or comparable to the desorption energy. Consequently, Ga will incorporate into the GaN film with N at the arrival site or desorb from the surface instead of dif-

TABLE I. Summary of Ga desorption energies for different Ga III/V ratios on the GaN surface at different substrate temperatures indicated in the "T_s range" row.

Ga density in Ga monolayers						
Growth condition	Transition regime		Ga-rich regime			Ga-droplet regime
E_{des}(±0.02 eV)	0.82	0.94	1.24	1.59	1.89	2.76
T_s range (°C)	648–680	659–696	667–727	692–749	752–773	751–774

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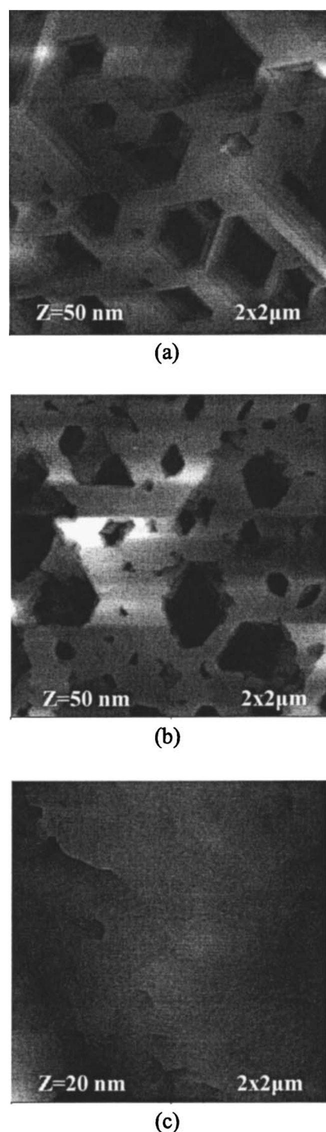

FIG. 2. Dependence of surface morphology of GaN for different III-V ratios during growth at 700 °C on KOH etched GaN templates. (a) Etched template; Surface morphologies of GaN growth for 2 h on (b) stoichiometric; and (c) Ga-rich conditions, respectively .

fusing to a new site. In contrast, the diffusion energy is smaller than the desorption energy under Ga-rich conditions that provide higher Ga surface coverage. In that case, the Ga atoms are very mobile and they prefer to move about on the surface to find a site with lower local potential energy, such as the edge of a step or the bottom of a pit.[30] As a result, the GaN growth mechanism follows the layer-by-layer growth mode with the pores being filled and the surface turning smooth as growth proceeds.

In summary, we investigated the Ga desorption kinetics on GaN (0001) surfaces using RHEED during GaN growth. We found that the desorption energy of Ga depends on the Ga coverage which is determined by the III/V ratio. For a very high III/V ratio, the desorption energy is 2.76 eV with the coverage being about 100%, while the desorption energy is about 0.82 eV under the stoichiometric growth condition with the coverage being about 10%. The variation in the desorption energy with the III/V ratio is attributed to the difference in the *in plane* Ga-Ga separation on the Ga adlayer surface. Controlling the III/V ratio, different growth modes of GaN in MBE growth are obtained as a result of competition between the desorption and diffusion processes.

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