# Direct observation of different equilibrium Ga adlayer coverages and their desorption kinetics on GaN (0001) and $(000\overline{1})$ surfaces

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We present a Ga adsorption study of both polar GaN (0001) and (000 $\overline{1}$ ) surfaces using line-of-sight quadrupole mass spectrometry as a quantitative *in situ* method. Monitoring the desorbing Ga atoms, two characteristic desorption regimes (exponential and steady-state regimes) were found that are assigned to the formation of a thin equilibrium Ga adlayer and Ga droplets on top of it. The Ga adlayer coverage differs substantially between the two surface polarities, being 1.1 monolayers on (000 $\overline{1}$ ) GaN and 2.4 monolayers on (0001) GaN. Additional temperature-dependent measurements of the surface lifetime of Ga adatoms unveil fundamental differences in the adsorbate-substrate binding energetics both for the Ga adlayers on the two surface polarities and for the Ga droplets.

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# I. INTRODUCTION

Despite outstanding achievements in the fabrication of GaN-based opto-<sup>1-4</sup> and high-power<sup>5</sup> electronic devices some of the typical features of nitride growth are still lacking a fundamental comprehension. Only recently, growth studies by metal-organic chemical vapor deposition<sup>6,7</sup> (MOCVD) and molecular beam epitaxy<sup>8–13</sup> (MBE) have pointed out that the growth mechanism and the resulting surface structure of GaN thin films are crucially sensitive to the kinetics—i.e., Ga/N flux ratio and growth temperature. Particularly, in plasma-assisted MBE desirable two-dimensional growth is commonly attained under Ga-rich conditions, suggesting that the GaN growth front is stabilized by a metallic Ga adlayer.<sup>10,11,13,14</sup>

In this context, adatom diffusion calculations<sup>15</sup> revealed that such a Ga adlayer triggers a high surface migration of nitrogen adatoms as compared to N-rich conditions, where the Ga adlayer is absent. This explains why smooth surface morphologies emerge under metal-rich conditions in contrast to the observed kinetic roughening for N-rich growth.<sup>16</sup>

Besides, wurtzite GaN exists as two inequivalent surface orientations, denoted as the N-polar  $(000\overline{1})$  and Ga-polar (0001) surface. Given the different surface atomic arrangements, the two polar GaN surfaces tend to stabilize different Ga adlayer coverages on top. In first-principles theory, the N-polar surface was found to consist of a single monolayer (ML) of Ga bonded to the outermost GaN bilayer.<sup>17</sup> In the Ga-polar case, though, the energetically most favorable surface structure is characterized by a laterally contracted Ga bilayer of  $\approx 2.3$  ML in terms of GaN atomic density.<sup>18</sup> Further theoretical investigations suggested that such a Ga bilayer activates a very efficient diffusion channel for N adatoms, specifically enhancing lateral transport between subsurface sites.<sup>19</sup> The Ga bilayer acts therefore as an auto-surfactant and proves critically important for achieving good material quality.<sup>20</sup>

The exact bilayer thickness and its adsorption properties in dynamic equilibrium have to date been, however, experimentally *not directly* measured. Modeling of Auger spectral intensities and scanning tunneling microscopy<sup>21</sup> (STM) under static conditions as well as indirect measurements by intensity variations in reflection high-energy electron diffraction (RHEED) patterns<sup>22</sup> have indicated a Ga bilayer coverage estimated somewhere between 2 and 3 ML.

Moreover, when GaN growth is performed under extremely Ga-rich conditions or at low temperatures, excess Ga forms macroscopic Ga droplets on top of the adlayer-stable GaN surface.<sup>11,12,14,23,24</sup> This entails severe consequences for device applications, as these droplets cause metallic precipitates in the layers. Lately, we have therefore emphasized the necessity for optimum GaN growth to be achieved in the immediate vicinity of the boundary condition for Ga droplet formation.<sup>11</sup> For the temperature dependence of this boundary line we found an Arrhenius behavior with an activation energy of 2.8 eV. Similar results have been obtained from RHEED studies by Hacke et al., who attributed the transition from a  $2 \times 2$  reconstruction to a  $1 \times 1$  unreconstructed structure to excess Ga remaining on the surface.14 Meanwhile, semiquantitative measurements of the Ga coverage by RHEED intensity variations<sup>12,24</sup> have posed ample inconsistencies in the activation energies for Ga desorption from Ga droplets and GaN surface.

What remains to all these issues is the lack of a quantitative *in situ* technique that has long inhibited a direct study of Ga surface coverages and their dynamic processes such as surface reactivity and desorption on GaN surfaces.

To tackle these problems, we have employed line-of-sight quadrupole mass spectrometry (QMS) as a genuine *in situ* method to *quantify* the kinetic processes of Ga adsorption and desorption. Specifically, this technique has been applied to a series of Ga wetting (i.e., adsorption) experiments on the two technologically relevant (0001) and (0001) GaN surface orientations. By monitoring the desorbing species we demonstrate a precise deconvolution of Ga atoms contained in adlayer and droplets. It is shown that the equilibrium adlayer coverage differs between the two surface polarities, consistent with the theoretical predictions. Additional temperaturedependent measurements of the surface lifetime of Ga adatoms generate further a good understanding of the representative Ga adsorbate-substrate binding energies.

# **II. EXPERIMENT**

The Ga desorption experiments were carried out in a V80H MBE system designed by VG Semicon using a standard effusion cell for Ga. To monitor the desorbing Ga atoms, a quadrupole mass spectrometer was mounted in direct line of sight to the wafer, as described in our earlier work.<sup>25,26</sup> Prior to the experiments, the desorbing Ga flux was calibrated by measuring the partial pressure of the <sup>69</sup>Ga isotope for a sequence of incident Ga fluxes evaporated onto a sapphire substrate at high enough temperatures, so that all impinging Ga desorbs completely.<sup>13,25</sup> A linear relationship of  $2.5 \times 10^{-10}$  mbar/ML sec<sup>-1</sup> was obtained which allows a precise quantification of desorbing Ga in units of ML.

To facilitate heating of the substrates by radiation, their back sides were coated with a TiW refractory metal. The substrate temperature was then measured by a pyrometer with a maximum sensitivity at 940 nm.

The N-polar  $(000\overline{1})$  and Ga-polar (0001) GaN surfaces were prepared by different growth techniques. The former was produced by nucleating and growing  $\approx 1 \ \mu m$  GaN directly on c-plane sapphire in our MBE system with active nitrogen supplied by a rf plasma source. Under growth conditions of Ga/N=4 and a temperature of 730 °C the RHEED pattern resulted in a streaky  $1 \times 1$  phase, which transformed to a  $3 \times 3$  reconstruction upon cooling below 300 °C. Such a reconstruction is a direct evidence of the obtained N-polar GaN surface.<sup>27</sup> The Ga-polar surface was prepared by growing  $\approx 2 \ \mu m$  GaN on sapphire by MOCVD (University of Gent, Belgium). In order to guarantee a surface free of any contamination, we have overgrown this template homoepitaxially with  $\approx 0.5 \ \mu m$  GaN, using the same conditions as for the growth of N-polar GaN. The final RHEED pattern showed a smooth  $1 \times 1$  surface with no additional reconstruction.

Each of these two polar GaN surfaces have been subjected to two sets of Ga wetting experiments in the absence of a nitrogen flux. The first set was realized by evaporating short pulses of Ga onto the GaN surfaces by opening and closing the shutter of the Ga effusion cell. The shutter sequences ranged from 1 to 20 sec and the substrate temperature was kept constant at 650 °C. The Ga flux was set to 0.25 ML/sec: thus, the shutter sequences corresponded to an



FIG. 1. Ga desorption vs time for a series of Ga pulses deposited on a GaN (0001) surface at constant 650 °C. The measurements in (a) illustrate a close-up view of the first few Ga pulses, while (b) shows also longer pulses. The Ga pulses correspond to shutter sequences ranging from 1 to 20 sec (and coverages of  $\theta$ = 0.25–5 ML). The level  $\phi^{\text{sat}}$ , at which the peak of the desorption signal saturates and steady-state desorption sets in, indicates the accumulation of excess Ga on the surface (i.e., Ga droplet regime).

amount of deposited Ga between 0.25 and 5 ML. Then our QMS setup was used to monitor the desorbing Ga signal from the sample surface.

In the second series the surface lifetime of Ga adatoms was determined by measuring the desorption from 14 ML of Ga (Ga flux = 1.75 ML/sec) deposited onto the GaN surfaces and by varying the substrate temperature between 620 and 700 °C. Care has been taken that this temperature range was well below the onset for thermal decomposition of GaN (>750 °C),<sup>28</sup> in order to exclude additional desorption from GaN and changes in surface structure due to thermally induced roughening.

#### **III. RESULTS**

### A. Transition Ga-adlayer-droplet regime

# 1. Ga adatoms on a GaN $(000\overline{1})$ surface

The Ga desorption measurements of the first series of wetting experiments are illustrated in Figs. 1-3. To explain the main features we focus first on a closeup view of the typical Ga desorption behavior on a N-polar GaN surface

[Fig. 1(a)]. Initializing the very first Ga pulse, the shutter of the Ga effusion cell is opened for only 1 sec and a nominal amount of  $\theta = 0.25$  ML Ga is deposited onto the surface. During this shutter sequence, Ga starts desorbing, evidenced by a rise of the partial pressure signal of the <sup>69</sup>Ga isotope to a certain peak level. Upon closure of the Ga shutter, the Ga desorption signal then decays exponentially to zero. For the second Ga pulse (shutter sequence=2 sec—i.e., Ga coverage  $\theta = 0.5$  ML), we observe an identical desorption behavior, but notice that the desorption peak has increased. Obvious from the additional Ga pulses, this peak rises continuously with surface coverage until it saturates at a Ga coverage of  $\theta \approx 1$  ML. Concurrent with the peak saturation, the desorption signal changes in shape for Ga coverages exceeding 1 ML, since there is no immediate decay after shuttering. Instead, an equilibrium plateau along with steady-state desorption appears. This situation becomes even more evident when we extend the Ga pulses to higher Ga coverages [see Fig. 1(b)]. As a clear trend, we find that with increasing Ga coverages the duration of the steady-state desorption is getting longer. By integrating the area below each single desorption signal, we obtain exactly the same amount of Ga as has been deposited nominally. This proves that over time all adsorbed Ga atoms desorb completely and no Ga remains on the surface, giving convincingly the direct relation between the Ga desorption signal and the adsorbed Ga surface coverage.

These firsthand results clearly point out that depending on the Ga surface coverage two distinct desorption regimes exist: a monoexponential and a steady-state regime. The transition between the two occurs at a critical Ga coverage  $\theta^{\text{crit}} = 1$  ML. The exponential regime features a decreasing desorption rate with time, while the steady-state regime represents an overall very high desorption rate. These differences imply that Ga on a (0001) GaN surface must be adsorbed in two different states: (a) as a Ga adlayer up to a maximum coverage of  $\approx 1$  ML and (b) as excess Ga in a rather weakly adsorbed state on top of the adlayer.

To evaluate the nature of the excess Ga, we investigated the time evolution of the steady-state behavior for various Ga coverages. For this purpose, we defined a characteristic steady-state desorption time  $t^D$  as the duration between the closure of the shutter and the drop-off in steady-state desorption (see also Fig. 3). The desorption time  $t^D$  was found to scale linearly with the deposited Ga coverage, being longer for higher coverages. This indicates that the weakly adsorbed Ga is accumulated on the surface as some excess Ga reservoir, which might eventually develop macroscopic Ga droplets by a ripening process.<sup>12,29</sup> Simultaneous RHEED intensity observations support this evolution in desorption qualitatively. They exhibited a low-contrast streaked pattern during steady-state desorption that converted to a higher contrast  $1 \times 1$  phase at the final drop-off. RHEED patterns of low intensity contrast were previously assumed to stem from shadowing effects of droplets during very metal-rich conditions in GaN (Ref. 12) and AlN (Ref. 30) growth. For our low excess Ga coverages, though, we believe that the accumulated Ga resembles more or less a continuous metallic Ga film with possibly very small-sized droplets. In fact, the de-



FIG. 2. Ga desorption for a series of Ga pulses deposited on a GaN (0001) surface at 650 °C. Shutter sequences and Ga coverages are the same as in Fig. 1. The saturation of the desorption peak at  $\phi^{\text{sat}}$  and the onset of steady-state desorption give again the transition to the Ga droplet regime.

sorption of macroscopic Ga droplets deviates from the steady-state behavior in that they give rise to additional desorption.<sup>31</sup> However, for simplicity we refer the accumulated excess Ga from now on to Ga droplets.

### 2. Ga adatoms on a GaN (0001) surface

Quite different desorption features occur when Ga pulses are adsorbed on a Ga-polar GaN surface (Fig. 2). Depending on the Ga surface coverage, we can basically differentiate here between three essential desorption regimes.

(a) For submonolayer coverages ( $\theta < 1$  ML) we observe again a fast rise followed by a monoexponential decay of the Ga desorption signal, similar to the N-polar case. The decay, however, proceeds by a much slower rate on Ga-polar GaN (note the difference in the time scale for the two cases).

(b) For Ga coverages above 1 ML, the desorption peak rises continuously with surface coverage, until it saturates at  $\theta^{\text{crit}} \approx 2.7$  ML. In this range (1 ML <  $\theta$  < 2.7 ML), the decay of the desorption signal deviates substantially from the typical monoexponential behavior by indicating a rather complicated looking process, which will be investigated later.

(c) Exceeding the critical Ga coverage ( $\theta > 2.7$  ML) yields again a steady-state desorption due to the accumulation of excess Ga on the surface (i.e., Ga droplet regime).

In accordance with the N-polar case, the transition between the subcritical and steady-state regimes allows us here to also discriminate between a Ga adlayer and excess Ga as droplets on top. Strikingly, the maximum Ga adlayer coverage on Ga-polar GaN has thus a thickness of  $\approx 2.7$  ML, which is by far higher than the  $\approx 1$ -ML-thick analogon on N-polar GaN.

### 3. Ga adlayer in dynamic equilibrium

In the following, we place special emphasis on the final stage of the steady-state desorption by going to even higher Ga coverages. The details of this study are exemplified in Fig. 3 for a total amount of 14 ML of Ga deposited on a N-polar and a Ga-polar GaN surface at 650 °C.



FIG. 3. Ga desorption of 14 ML of Ga deposited on a GaN (000 $\overline{1}$ ) (black curve) and a GaN (0001) surface (gray curve) at constant 650 °C. Integrating the areas below the desorption signals facilitates a precise deconvolution of Ga contained in both Ga drop-lets and the residual adlayer: Ga adlayer coverages are 1.1 ML on a GaN (000 $\overline{1}$ ) and 2.4 ML on a GaN (0001) surface, respectively ( $t^D$  denotes the steady-state desorption time and  $\tau^A$  is the characteristic adlayer decay time).

Due to the high amount of excess Ga, we notice first a very long period of steady-state desorption,  $t^D$ , which is of the same order for both polar surfaces. However, when the excess Ga droplets are depleted and the steady-state desorption ceases, we observe subsequently either a monoexponential decay (on N-polar GaN) or the complicated "tail-like" decay (on Ga-polar GaN). Integrating the area below these two types of decaying signals (i.e., the right-hand side of the dashed line) gives the remaining Ga coverage. From this and several other extended Ga pulses the residual Ga coverage was found to be independent of the initially adsorbed Ga coverage and amounts to  $\theta = 1.1 \pm 0.1$  ML for N-polar GaN, while it equals  $\theta = 2.4 \pm 0.2$  ML on Ga-polar GaN.

Moreover, these values are also independent of the substrate temperature within the experimental error. Note that these residual Ga coverages reflect exactly the maximum Ga adlayer coverages as evaluated from Figs. 1 and 2. This means that during the steady-state desorption of excess Ga the whole Ga adlayer is kept fully in dynamic equilibrium and is depleted only afterwards. Most remarkable, these measured Ga adlayer coverages are in sound agreement with recent theoretical predictions: the energetically most favorable Ga adlayer coverages have been determined to 1 ML on GaN (000 $\overline{1}$ ) and to a 2.33-ML laterally contracted Ga bilayer on GaN (0001).<sup>17,18</sup>

The  $\approx$ 2.4-ML-thick Ga bilayer on a Ga-polar GaN surface was found to desorb in a complicated fashion. First, there is a quick exponential decay (similar to the  $\approx$ 1-ML adlayer decay in the N-polar case), which is followed by a much slower desorption term. We assume that these two terms can be attributed to the desorption of two individual monolayers adding up to the whole bilayer decay: the quick decay refers to a top ML and the subsequent slow decay corresponds to a bottom ML. Based on this concept, the typical decay times  $\tau^A$  of the individual monolayers differ severely. Consequently, we expect drastically different interaction strengths between the respective monolayer and the underlying GaN surface.

Indeed, evidence for such a bilayer split-up into single monolayers is further endorsed in the next section, where the representative adsorbate-substrate binding energetics will be given at every desorption stage. Also, a model is presented in the discussion, which resolves the decay of a laterally contracted Ga bilayer structure on the basis of simple differential rate equations.

# B. Surface lifetime of Ga adatoms

During the second series of wetting experiments, we extend the previous findings by a temperature-dependent study of the desorption from the Ga adlayer and droplets. For this investigation, we deposited an equal amount of 14 ML of Ga onto the respective GaN surface for a wide set of substrate temperatures and, as before, monitored the desorbing Ga atoms.

# 1. Ga lifetime on GaN $(000\overline{1})$

An exemplary extract of these measurements is given in Fig. 4(a) for the case of N-polar GaN. We observe clearly that with increasing temperature the overall desorption time becomes shorter. Consequently, this leads to an elevated Ga desorption signal, since the total amount of deposited Ga is constant throughout the entire study.

Based on these features, we are able to determine one of the key measures in adsorption theory: the mean surface lifetime of adatoms. Such measurements of Ga adatom lifetimes have been studied already quite early for submonolayer coverages on GaAs (Ref. 32) and GaN (Ref. 33). In our case, though, we have to apply an evaluation scheme that considers adatom lifetimes in both the Ga droplets and adlayer. If  $t^{D}$  is—as earlier introduced—the desorption time during steady-state desorption of Ga droplets and  $\theta_D$  the amount of Ga contained in droplets, then the mean Ga adatom lifetime in droplets is simply expressed by  $\tau^D = t^D / \theta_D$ . To assess the characteristic Ga adatom lifetime in the remaining adlayer, the monoexponential decay of the Ga desorption signal provides useful information. Since the Ga surface population n decays in first-order kinetics by n $\propto \exp(-t/\tau^A)$ , where t is the time, the mean adatom lifetime in the adlayer is then equivalent to the decay time  $\tau^A$ . Using these expressions, the Ga adatom lifetime in the droplets and adlayer varies by approximately  $\tau^D = 3 - 85$  sec and  $\tau^A$ =4-170 sec in the 620-700 °C temperature range (the superscripts D and A refer to droplets and adlayer). As intuitionally expected, adatoms remain longer in the adlayer, due to a stronger bonding mechanism to the GaN surface compared to the weakly adsorbed excess Ga in the droplets.

For further proof, determination of the activation energies for these desorption processes can give more proper insight. Applying the Frenkel equation for the adatom lifetime,<sup>34</sup>

$$\tau = \frac{1}{\nu_0} \exp\left(\frac{E}{kT}\right),\tag{1}$$



FIG. 4. (a) Temperature-dependent Ga desorption vs time for 14 ML of Ga adsorbed on a GaN (000 $\overline{1}$ ) surface; the duration of the steady-state desorption and the decay time of the adlayer yield (b) the mean Ga adatom lifetime  $\tau$  in Ga droplets and adlayer as a function of 1/kT. The gradients of the curves give the activation energies for desorption from droplets ( $E^D = 3.1 \text{ eV}$ ) and adlayer ( $E^A = 3.7 \text{ eV}$ ). Alternatively, plotting the Ga partial pressure level during steady-state desorption of Ga droplets yields an identical activation energy.

where  $\nu_0$  is the adatom-surface vibrational frequency, *T* the substrate temperature, and *k* the Boltzmann constant, the adatoms face an activation process for desorption with a characteristic energy *E*. An Arrhenius-type fit to the data [Fig. 4(b)] results in activation energies for Ga desorption from the droplets and adlayer equal to  $E^D = 3.1$  eV and  $E^A = 3.7$  eV, respectively. The activation energy for Ga desorption from droplets can even be evaluated by a more simple routine. Plotting the inverse of the Ga partial pressure signal during steady-state desorption as a function of 1/kT yields also  $E^D = 3.1$  eV [see upper curve in Fig. 4(b)].

### 2. Ga lifetime on GaN (0001)

A similar, but more complex picture emerges when we want to derive Ga adatom lifetimes on Ga-polar GaN surfaces. Akin to the N-polar case, both the overall desorption time and the partial pressure level of the Ga desorption signal scale with substrate temperature [Fig. 5(a)].

The only difference though arises from the complicated desorption process of the Ga bilayer structure. In detail, we propose that this characteristic bilayer decay represents a superposition of separate terms which correspond to the deple-



FIG. 5. (a) Temperature-dependent Ga desorption vs time for 14 ML of Ga adsorbed on a GaN (0001) surface yielding (b) the mean Ga adatom lifetime  $\tau$  in Ga droplets and both single monolayers of the Ga bilayer structure as a function of 1/kT. The activation energies for desorption from droplets and monolayers are  $E^D = 3.2 \text{ eV}$ ,  $E^T = 3.7 \text{ eV}$ , and  $E^B = 4.9 \text{ eV}$ .

tion of a top and a bottom monolayer (see the Discussion). According to this, we can deconvolve Ga adatom lifetimes in the individual monolayers by fitting the initial and final parts of the decaying Ga signal to two exponential functions (i.e., dashed lines denoted by  $\tau^T$  and  $\tau^B$ ) and using the same expressions as introduced above. The intermediate part of the bilayer decay can be neglected for this evaluation, but will be explained as a central feature in the discussion. The resulting lifetimes plotted as a function of inverse substrate temperature are shown in Fig. 5(b).

Due to the different degrees of bond strengths in the respective layers, Ga adatom lifetimes are the shortest in droplets, a little longer in the top layer and very long in the bottom layer of the Ga bilayer. This is further reflected by the activation energies for desorption from Ga droplets and the single monolayers, which were determined to  $E^D = 3.2 \text{ eV}$ ,  $E^T = 3.7 \text{ eV}$ , and  $E^B = 4.9 \text{ eV}$ , respectively (the superscripts D, T, and B refer to droplets, top ML, and bottom ML). To give an overview, all the key parameters describing the Ga desorption energetics ( $E, \nu_0, \tau$ ) are summarized in Table I for both polar GaN surfaces.

Previous indirect techniques have highlighted a wide scatter in the activation energy for Ga desorption from droplets, ranging from 2.4 to 5.1 eV.<sup>11,12,14,24,35</sup> For statistical reasons, we performed additional Ga wetting experiments to identify

TABLE I. Characteristic parameters for Ga desorption from both (0001) and (0001) GaN surfaces: *E* denotes the activation energy,  $\nu_0$  the adatom-surface vibrational frequency, and  $\tau$  is the mean Ga adatom surface lifetime (the values for the lifetime given below are restricted to a temperature range from 620 to 700 °C).

GaN surface	Layer	<i>E</i> [eV]	$\nu_0$ [Hz]	$\tau$ [sec]
(0001)	Bottom ML Top ML Droplets	4.9 3.7 3.2	$6.6 \times 10^{24}$ $6.2 \times 10^{18}$ $1.9 \times 10^{16}$	5-750 3.3-125 2.5-60
(0001)	Adlayer Droplets	3.7 3.1	$\begin{array}{c} 4.5 \times 10^{18} \\ 4.1 \times 10^{15} \end{array}$	4.3–170 3.5–85

the accuracy of this specific activation energy. Altogether, we have carried out four such experiments on the two GaN surface orientations, including also one set of rough GaN surfaces which has been grown under N-rich conditions. The activation energies have then been derived by the two equivalent techniques as described in Sec. III B 1 (i.e., desorption time  $t^D$  and steady-state partial pressure level). The average activation energy for desorption from Ga droplets results thus in  $\overline{E}^D = 3.1 \pm 0.2$  eV, independent of the underlying GaN surface orientation and surface roughness.

### **IV. DISCUSSION**

### A. Model for Ga bilayer decay

As obvious from Figs. 3 and 4, the  $\approx$ 1.1-ML Ga adlayer coverage on the N-polar GaN surface is prone to decay by a simple monoexponential law. The  $\approx$ 2.4-ML-thick Ga bilayer on Ga-polar GaN follows, however, a more complicated desorption process. To understand the latter process, we offer a basic model that involves the decay of two single monolayers adding up to the observed bilayer desorption. For this reason, we assume that the Ga bilayer structure can be split up into  $\approx 1$  ML of Ga above the last Ga-terminated GaN layer (i.e., bottom monolayer) and a Ga toplayer containing  $\approx$ 1.4 ML in terms of GaN atomic density (1 ML=1.14  $\times 10^{15}$  atoms/cm<sup>2</sup>). Such an arrangement has actually been validated from some of the previous experiments [in Fig. 5(a)] by simply integrating the area below each single desorption term. Independent of substrate temperature, the amount of Ga referring to the initial fast decay yielded 1.4  $\pm 0.2$  ML (i.e., top ML), while the subsequent tail-like decay gave exactly the remaining  $\approx 1$  ML (bottom ML). According to first-principles total energy calculations by Northrup *et al.*,<sup>18</sup> this bilayer split-up represents the energetically most favorable surface structure under Ga-rich conditions. In this case, the Ga bottom ML matches the underlying substrate and therefore features a Ga-Ga in-plane separation corresponding to the  $1 \times 1$  GaN surface ( $\approx 3.2$  Å). The Ga top layer, on the other hand, faces lateral contraction with respect to the substrate, allowing  $\approx 1.4$  ML of Ga atoms being squeezed into its plane. This benefits a reduction in the surface free energy along with the Ga-Ga in-plane spacing having almost values typical for liquid Ga ( $\approx 2.7$  Å).<sup>18</sup> This situation is schematically drawn in the insert of Fig. 6(a).

Applying these concepts, we find that a qualitatively and quantitatively correct description of the entire bilayer desorption process relies on the implementation of three essential desorption stages. In the following, each stage is modeled by a set of differential rate equations which describe the time evolution of the individual layer coverages  $\theta$  and give exactly the desorbing Ga fluxes  $\phi$ .

(A) *Relaxation stage*. During this very first stage, we suggest that only the laterally contracted  $\approx 1.4$ -ML top layer desorbs, which fosters a simultaneous self-relaxation process. Formally speaking, with Ga atoms desorbing from the strained top layer, the Ga-Ga in-plane spacing becomes gradually larger. When the top layer coverage  $\theta^T$  decreases to 1 ML (i.e., total bilayer coverage=2 ML), full relaxation is finally accomplished and the Ga-Ga separation complies with the underlying bottom ML as well as the GaN surface. Ideally, during relaxation the Ga atoms in the top layer keep the bottom ML can escape. The following differential equations describe this situation for both top and bottom monolayer in the effective range of  $1.0 < \theta^T(t) < 1.4$  ML:

$$\phi^{T}(t) = -\frac{d\,\theta^{T}(t)}{dt} = \theta^{T}(t)a,\tag{2}$$

$$\phi^B(t) = -\frac{d\,\theta^B(t)}{dt} = 0. \tag{3}$$

Subjected to the initial conditions of  $\theta_0^T = 1.4$  ML and  $\theta_0^B = 1.0$  ML, the bottom monolayer remains entirely unaffected, while the coverage of the top layer decreases by a simple exponential law. With  $a = \nu_0^T \exp(-E^T/kT)$ , denoted as the desorption probability from the top layer, this term depends only on the substrate temperature *T*, the activation energy for desorption  $E^T$ , and the adatom-surface vibrational frequency  $\nu_0^T$  [similar to the Frenkel equation (1)].

(B) Transfer stage. Starting from a fully relaxed top layer  $(\theta^T = 1 \text{ ML})$ , Ga atoms keep desorbing as in the relaxation stage. But with the gradual decrease in  $\theta^T$  over time [0]  $<\theta^{T}(t)<1.0$  ML], the surface of the bottom ML becomes increasingly bare, allowing atoms from the bottom part to desorb as well. While this occurs, we suppose that subsequently Ga atoms from the top layer hop down and nourish the bottom ML, in order to keep it fully populated. From an energetical point of view, this transfer process is reasonable, since Ga atoms are more strongly bound in the bottom layer and do not face an activation barrier for downhill transport.<sup>36</sup> Under these assumptions, the overall coverage of the bottom layer remains constant at  $\theta^B = 1.0$  ML, while the top layer follows a rather fast depletion given by both its characteristic desorption and the transfer mechanism. With the desorption probability  $b = \nu_0^B \exp(-E^B/kT)$  for the bottom layer, this stage is then characterized by the following equations:

$$\frac{d\,\theta^{T}(t)}{dt} = \phi^{T}(t) + \text{transfer} = \theta^{T}(t)a + \text{transfer}, \quad (4)$$

$$-\frac{d\,\theta^{B}(t)}{dt} = \phi^{B}(t) - \text{transfer} = (\,\theta_{0}^{B} - \theta^{T}(t))b - \text{transfer} = 0.$$
(5)

(C) Bottom ML decay stage. When finally the top layer is completely depleted ( $\theta^T = 0$ ), the coverage of the bottom ML starts to decrease by a simple exponential law, similar to the relaxation of the top layer in stage (A). For this stage we can therefore set up the equations by

$$\phi^T(t) = -\frac{d\,\theta^T(t)}{dt} = 0,\tag{6}$$

$$\phi^B(t) = -\frac{d\,\theta^B(t)}{dt} = \theta^B(t)b\,. \tag{7}$$

For this model, each stage proves necessary to explain the experimentally observed bilayer decay. By analytically integrating the expressions (2)–(7), we obtained easily the evolution of the individual layer coverages  $\theta$  and desorbing Ga fluxes  $\phi$ . The results and the experimental data for a substrate temperature of 640 °C are illustrated in Fig. 6, with the contributions of the single layers marked by dashed lines. Taking the activation energies  $E^{(T,B)}$  as derived in Sec. III B 2 and by adapting only the prefactors  $\nu_0^{(T,B)}$ , our proposed model achieves reasonable consistence with the experimental desorption data [see Fig. 6(b)], even explaining the two pronounced kinks. To further confirm our model, we have also calculated the bilayer decay for higher temperatures. In close match with the experimental data, we found that with increasing temperature the desorption probabilities a and b become larger, which consequently leads to a much faster decay. Associated with this, the transfer stage gets gradually shorter and almost disappears for very high temperatures of  $\approx 700$  °C.

#### **B.** Ga bond strengths on GaN $(000\overline{1})$ and (0001)

As a consequence of polarity, the (0001) and (0001) GaN surfaces differ crucially in the atomic geometry of the surface terminating atoms. In the N-polar (0001) case each Ga surface atom has ideally three dangling bonds, in contrast to only one in the Ga-polar (0001) case.<sup>15</sup> This causes the Gapolar surface to produce strongly directed  $sp_z$  orbitals, while the N-polar surface is characterized by delocalized metallic bonds between the surface atoms. The latter leads therefore to a substantially weaker adsorbate-substrate interaction. Based on these considerations, it is comprehensible why in dynamic equilibrium only  $\approx 1.1$  ML of Ga can be stabilized on a (0001) GaN surface.

The polarity-related differences in adsorbate-substrate bonding are further reflected by the mean Ga lifetimes and activation energies for Ga desorption from the adlayer. Ga adatoms interacting directly with the GaN substrate (i.e., monolayer coverages) face a much lower activation energy for desorption from a N-polar surface (3.7 eV), as compared to a Ga-polar surface (4.9 eV). On the other hand, the later-



FIG. 6. Modeled evolution of (a) the Ga coverage  $\theta$  and (b) the desorbing Ga flux  $\phi$  from a decaying laterally contracted 2.4-ML Ga bilayer on a Ga-polar GaN surface at 640 °C. Splitting up the bilayer into single monolayers proves important to resolve the complicated three-stage decay featuring (A) the relaxation stage, (B) the transfer stage, and (C) the bottom ML decay stage. The contribution of each individual layer (*T*, top; *B*, bottom) is represented by dashed lines. Note the reasonable agreement with experimental data points (open circles), using a = 0.0115 Hz, b = 0.009 Hz, and the activation energies derived from Fig. 5.

ally contracted top part of the Ga bilayer on Ga-polar GaN exhibits desorption properties comparable to the Ga adlayer on N-polar GaN ( $E^T \approx E^A \approx 3.7 \text{ eV}$ ). Backed by theoretical, STM, and Auger electron spectroscopical studies,<sup>17,18,21</sup> these results suggest an overall stronger bonded Ga adlaver on Ga-polar GaN than on a N-polar surface. The different metallic adlayer configurations also cast a severe influence on surface diffusion mechanisms of N adatoms, in letting them experience a much lower diffusion barrier on a Gapolar compared to a N-polar GaN surface.<sup>15,19</sup> Furthermore, we reckon that these broadly differing bonding and diffusion properties might pose a strong effect on both impurity incorporation and defect formation during GaN growth. Some studies pointed out that GaN grown along the (0001) orien-tation exhibits smoother surfaces<sup>37–39</sup> and alleviates p-type doping by Mg, whereas residual impurities such as C and O are more likely to incorporate on a  $(000\overline{1})$  polar surface.<sup>40,41</sup>

While our Ga adatom lifetimes and activation energies are the first ever reported *direct* measures for the binding energetics on a N-polar GaN surface, various other groups have paid more attention to the Ga-polar surface. In an early work, Guha et al.<sup>33</sup> employed also the mass spectrometry technique to determine Ga adatom lifetimes on a (0001) GaN surface. but restricted themselves only to submonolayer coverages and a high-temperature range of 680-750 °C. While the lifetimes in the low end of this interval coincide with our results [i.e.,  $\tau^B(690 \,^\circ\text{C}) \approx 5 \,\text{sec}$ ], their activation energy for desorption with 2.2 eV is much lower (compared to our value of 4.9 eV). Adelmann et al. deduced the Ga coverage indirectly from measurements of the variation in the RHEED Bragg spot intensity in a similarly high-temperature range.<sup>12,24</sup> For the RHEED transition between mono- and bilayer desorption they have reported two different activation energies: i.e., 3.7 eV (Ref. 12) versus 5.2 eV (Ref. 24). Moreover, Ga desorption studies by mass spectrometry have also been carried out in the presence of NH<sub>3</sub>.<sup>42,43</sup> The obtained activation energies for the desorption of submonolayer coverages were considerably lower: i.e., 1.4 eV in the 625-740 °C range and 0.4 eV in the 740-825 °C range.43 The low activation energies were speculated to arise from complex surface bonding mechanisms involving hydrogen.

### C. Desorption from Ga droplets

As demonstrated, excess Ga accumulates on the adlaverstable GaN surface, when depositing Ga fluxes that exceed the critical adlayer coverage (i.e., 1.1 ML on N-polar and 2.4 ML on Ga-polar GaN). We earlier referred this accumulation of excess Ga to a regime where Ga droplets might eventually evolve after a certain time (i.e., droplet regime). As a key point, we noticed that during the steady-state desorption of these Ga droplets the adlayer is sustained in full dynamic equilibrium. This implies that during the desorption an adatom transfer mechanism must be active, similar to what we have proposed for the bilayer decay (Sec. IV A). In other words, if Ga atoms from the adlayer happen to desorb, subsequently atoms from the excess Ga reservoir will nourish the adlayer. We can easily understand this situation when considering our evaluated relations for the activation energies, where  $E^D \le E^A$  and  $E^D \le E^T \le E^B$  hold true. Furthermore, due to the stronger bond strength for Ga adatoms in the adlayer, the adlayer represents a system of lower energy as compared to the Ga droplet reservoir. Along with this concept, the surface free energy of the whole Ga adlayerdroplet assembly can thus be minimized.<sup>44</sup>

These energetical considerations also suit the model for the laterally contracted Ga bilayer.<sup>18</sup> While the bottom ML of Ga matches the in-plane lattice parameter of the underlying GaN and hence faces the highest bond strength, the top  $\approx 1.4$ ML exhibits a weaker substrate interaction and a Ga-Ga inplane spacing approching a value typical for liquid Ga. Excess Ga atoms accumulated in droplets on top experience the weakest interaction, given that they are completely out of registry with the substrate lattice.

Our previous *ex situ* investigation<sup>11</sup> of the boundary condition between the Ga adlayer and droplet regime as well as

results from RHEED reconstructions by Hacke *et al.*<sup>14</sup> yielded an activation energy of ~2.8 eV for this transition. So far, this is the closest ever reported value to our directly determined activation energy for Ga desorption from droplets (i.e.,  $\bar{E}^D = 3.1 \pm 0.2 \text{ eV}$ ). All these separately acquired values agree convincingly with the activation energy for Ga evaporation from bulk Ga, which equals 2.9 eV.<sup>45</sup> Much higher activation energies for Ga desorption from droplets have been unveiled from RHEED intensity variations by Adelmann *et al.* on GaN (0001) surfaces, being 4.8 eV (Ref. 12) with incident N and 5.1 eV (Ref. 24) without N. The differences in their activation energies were speculated to rely on an interplay between N flux and the nucleation of Ga droplets.

### V. CONCLUSIONS

In summary, our Ga adsorption studies by *in situ* line-ofsight QMS demonstrated directly that an equilibrium adlayer of Ga can be stabilized on a GaN surface. The adlayer coverage was found to depend fundamentally on the GaN surface orientation. While on a GaN ( $000\overline{1}$ ) surface preferentially 1.1 ML of Ga can be stabilized, the respective Ga adlayer thickness amounts to 2.4 ML on a GaN (0001) surface. Remarkably, these results are in profound consistence with recent theoretical predictions.

We have further shown that the desorption of the 2.4-MLthick laterally contracted Ga bilayer underlies a complicated three-stage process. With the split-up of this bilayer into single monolayers, its characteristic decay was found to consist essentially of a relaxation phase of the top layer, a subsequent adatom transfer from top to bottom layer, and finally an exponential decay of the bottom layer. Additional temperature-dependent measurements of the Ga adatom lifetime revealed that the bottom part is more strongly bound than the top part of the bilayer, given by the activation energies for desorption being 4.9 eV versus 3.7 eV, respectively. The single Ga adlayer present on the  $(000\overline{1})$  GaN surface exhibits a comparable desorption energy of 3.7 eV.

Moreover, for both surface polarities additional Ga surplus leads inevitably to the accumulation of metallic Ga droplets on top of the adlayer. Ga bound in droplets was found to prevail in the weakest bound state of all possible adatom surface arrangements, resulting in the lowest activation energy for Ga desorption of  $\bar{E}^D = 3.1 \pm 0.2$  eV. This value agrees well with the evaporation energy from liquid Ga and does not depend on the underlying GaN surface polarity or the surface roughness.

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