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An atomistic insight into reactions and free-energy profiles of NH₃ and Ga on GaN surfaces during the epitaxial growth

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Abstract

Precursor molecules (NH₃ and Ga compounds) along with carrier gas (H₂ or N₂) used to grow GaN structures bring a large amount of hydrogen atoms which affect the growing mechanism of GaN. This has a non-negligible effect of the chemistry and diffusivity of precursors and dissociation products. To encompass the experimental difficulty in of unraveling such a complicated reaction mechanism, we resort to first principles molecular dynamics modeling, providing an atomistic insight into two major issues. The first one is the evolution of H atoms after the adsorption and dissociation of NH₃ on the growing GaN surface. The second issue is to shed light on the role of passivating hydrogen at growth conditions for a typical GaN Ga-rich (0001) surface. In the first case, reaction pathways alternative to the product of molecular hydrogen (H₂) can be realized, depending on the initial conditions and morphology of the surface, resulting in an adsorption of H atoms, thus contributing to its hydrogenation. In the second one, instead, we show how the presence of passivating H atoms at the surface, corresponding to a relatively high degree of hydrogenation, contribute to limit the diffusivity of Ga adatoms at the typical growth temperatures.

Keywords

GaN, Epitaxial Growth, Molecular Modeling, First Principles Molecular Dynamics, Free-Energy Enhanced Sampling.

1. Introduction

Gallium nitride (GaN) is well known as an important wide band gap (WBG) material having a wealth of applications in electronics and optoelectronics, particularly in light emitting diodes[1]. A new frontier of GaN has been explored exploiting its peculiar electronic properties, namely the large energy gap and the high dielectric breakdown-voltage, accompanied by a high structural stability upon heating with respect to other semiconductors such as silicon. These features grant a remarkable robustness in harsh environments, where power electronics is expected to be used[2]. Another important figure of merit of GaN with respect to its alternative competitors is its high electron mobility[3], which implies a significant gain in a frequency range higher than the current Metal-Oxide-Semiconductor Field-Effect-Transistors (MOSFETs) technology, thus translating into a better efficiency and, for this reason, in a reduced environmental impact.

Despite these well acknowledged promising properties of GaN, its performance as an electron device material is much lower than what is expected. The reason is the presence of carrier traps near the device interfaces, and more importantly the low quality of GaN thin films epitaxially grown in the fabrication of the devices. It is thus technologically demanded and also scientifically challenging to unveil atomic reactions during the epitaxial growth of GaN films. Vapor phase epitaxy with various source gas molecules is nowadays the main technique to grow GaN. In particular, metalorganic vapor phase epitaxy (MOVPE) with use of trimethylgallium (TMGa) and ammonia (NH₃) as source gas is prevailing[4-6]. These source gas molecules along with the carrier gas molecules, H₂ or N₂, or a mixture of the two, react with each other in the gas phase or in proximity of the growing GaN surface in complex ways, and atomic-level mechanisms of the reactions are just being unraveled.

Former studies, both experimental and theoretical, have evidenced that TMGa undergoes a decomposition in the gas phase, with the net result of producing in general a Ga-rich growing surface[7-12]. Calculations based on the Density-Functional Theory (DFT) combined with the free-energy evaluation of each molecule in the gas phase[8] show that a Ga adatom surface (termed Ga(ad) hereafter) with a coverage ratio $\theta_{\text{Ga}} = 1/4$ and a hydrogenated surface (termed 3Ga-H hereafter) with a coverage $\theta_{\text{H}} = 3/4$ are the energetically favorable structures under the condition in which N₂ and H₂ are the carrier gases, respectively. Those surfaces satisfy an electron-counting rule[13,14] in terms of stability of

compound semiconductor surfaces. Yet, on an experimental standpoint, the amount of Ga-adatoms, their actual localization and the amount of passivating hydrogen atoms present on the surface are, to date, still unknown despite recent computational efforts[15]. Concerning the ammonia NH_3 , former studies[16] assumed that its decomposition occurs in the gas phase, generating unsaturated fragments that bind to the surface during the growth process. However, no evidence has ever been reported to support this notion. On the contrary, time-of-flight (TOF) experiments[11-12] have at least partly addressed this issue, evidencing that NH_3 remains substantially undissociated when it comes in contact with the surface, and only a nearly negligible fraction of NH_2 is produced in the gas phase. Thus, although the stage of GaN epitaxial growth is reasonably identified as Ga-rich surface with either H-free or H-covered, the behavior of NH_3 on it remains to be clarified.

Along this line, total-energy electronic-structure calculations based on DFT have been attempted to unveil atomic reactions during GaN epitaxial growth[17-19]. The proposed reaction from those DFT calculations is that NH_3 is adsorbed on the Ga-rich surface, the subsequent NH unit after NH_3 decomposition diffuses easily to the surface step edges, and then N is incorporated into GaN films. Former studies assuming H_2 desorption in the final product, although insightful, were lacking all dynamical aspects of the reaction and a thorough investigation of other reaction channels.

Our scope here is to fill this gap and go beyond the limitations of static DFT calculations. To this aim, we resort to first principles dynamical approaches empowered by free energy sampling methods and clarify the mechanism and free energy landscape for the atomic reactions during GaN epitaxial growth for the first time. In particular, the novelty of this work is an atomistic insight into the dissociation of an adsorbed NH_3 molecule and the subsequent generation of NH_x units on a Ga-rich GaN (0001) surface, a key process of the epitaxial growth, are clarified. Without imposing the presence of any H_2 in the final product, we find the decomposition of NH_3 and subsequent NH_2 and NH incorporation in Ga-Ga weak bonds, being associated with the hydrogenation of the growth surface. Furthermore, the surface passivation by hydrogen is also investigated in terms of its effect on the mobility and diffusion of Ga adatoms. Kinetics and dynamics of Ga adatoms clarified here is essential to discuss relevant phases of the growth surface such as a two-dimensional liquid phase[18] which we have found on a pristine Ga-rich GaN (0001) surface in the past

2. Computational methods

All calculations presented in this work have been done within the DFT[20] framework. First principles molecular dynamics (FPMD) simulations have been performed according to the Car-Parrinello method[21] as implemented in the developer's version 4.3 of the CPMD code[22]. The Perdew-Burke-Ernzerhof functional[23] was used to describe the exchange and correlation interactions, complemented by the Grimme's semi-empirical formulation[24] of the long-range van der Waals dispersion. Wavefunctions representing the valence electrons are expanded on a plane-wave basis set with a cut-off of 80 Ry (1088.46 eV), whereas the core-valence interaction is described by norm conserving pseudopotentials in the analytical formulation of Goedecker, Teter and Hutter[25]. In all canonical NVT simulations the temperature was controlled by a Nosé-Hoover thermostat[26-28]. A fictitious electronic mass $\mu=340$ a.u. and a time step $\Delta t=4.0$ a.u. (0.096755 fs) used to numerically integrate the Car-Parrinello equations of motion ensured a good conservation of the constants of motion all along the dynamics. In the simulations requiring enhanced sampling methods, we have used the Blue-Moon ensemble (BME)[29] to sample the selected reaction coordinate and compute the free-energy profiles via thermodynamic integration. The specific reaction coordinate used to sample a given pathway will be given in the following sections to support the discussion. In all the BME simulations done here, the dynamics lasted for at least 3-4 ps at each sampled value of the reaction coordinate (example reported in Fig. S1 of the Supplementary Data), allowing for collection of statistically meaningful data in the last 2-3 ps after the equilibration stage, to ensure a good convergence of the BME Lagrange multiplier, monitored on-the-fly by computing its running average. A full BME simulation amounts then to about 30 ps for a sufficiently fine sampling of the reaction coordinate and for a minimization of the error bar in the calculation of the constraint forces (Fig. S2 in the Supplementary Data)

Our model system is analogous to those used in our former investigations[17,18]. Specifically, we use a slab containing 96 GaN formula units, amounting to six GaN layers with a 4x4 exposed surface. The bottom atoms are kept fixed to the bulk crystallographic positions and the resulting dangling bonds are saturated with H-like monovalent atoms[30] to saturate dangling bonds and avoid spurious reconstruction / relaxation processes. On the upper side representing the surface, four Ga adatoms (Ga(ad)) are present and one of them carries an adsorbed NH₃ molecule according to the structure found in Ref. 17. The simulation cell is a periodic box of 12.8044 x 12.8044 x 31.000 Å³ with the angle between the a and b vectors equal to 120° imposed by the hexagonal symmetry of the GaN crystal

structure. The large c value ensures sufficient empty space to accommodate the NH_3 molecules and grants a good separation from periodically repeated images. This system, shown in panel (a) of Fig. 1, amounts to 216 atoms and 884 electrons and will serve as a starting configuration for our simulations exploring reactions of NH_3 . A second system consisting of this same slab (96 GaN formula units) was prepared with the addition of one single Ga(ad) and nine H atoms bound at the Ga atoms at the surface mimicking a hydrogenated surface as in panel (b) of Fig. 1. Theoretically the stable hydrogenated surface consists of Ga-H surface bonds with the coverage^[8] $\theta_{\text{H}} = 3/4$. Furthermore, the Ga(ad) atoms are expected to coexist with those Ga-H bonds in the real system.^[15] Hence, starting from a fully hydrogenated surface, i.e. twelve H atoms in the 4×4 lateral cell, we removed progressively up to three H atoms and added one Ga(ad) on the H-free Ga atoms. The system constructed in this way fulfills the prescriptions of the electron counting rule^[13,14] and results in a thermally stable surface, shown in panel (b) of Fig. 1, used in our study of the thermal behavior of Ga(ad).

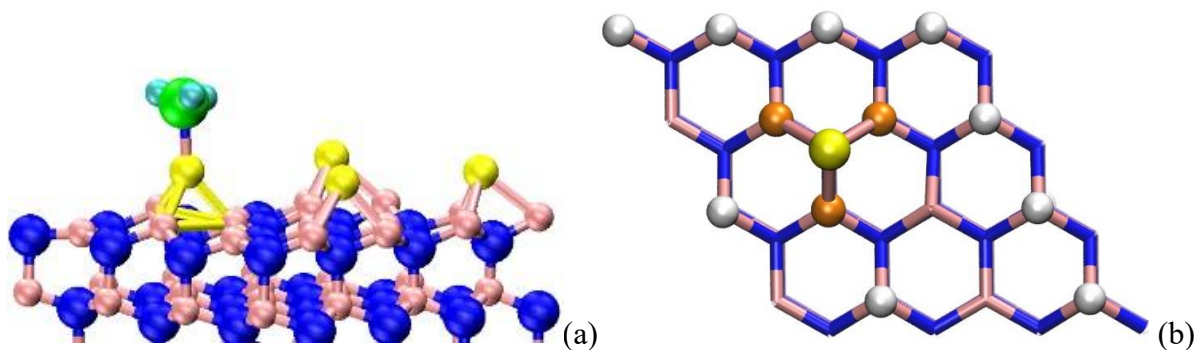


Fig. 1. (a) GaN Ga-rich (0001) surface with the adsorbed NH_3 molecule for the model system used in the simulations of the NH_3 dissociation. The color code for the atoms is white for H, blue for N, pink for Ga in the substrate. The N atom of the NH_3 is colored in green, its H atoms in cyan and Ga(ad) in yellow for clarity. (b) Top view of the model system of the initial configuration used to study the thermal behavior of Ga(ad) on an H-passivated surface. The color code is identical to the one used in panel (a) with all the H atoms at the surface in white and the Ga atoms bound to Ga(ad) highlighted in orange for clarity.

3. Results and discussion

3.1 Stability of the adsorbed NH₃ molecule

We started our analysis by questioning the stability of the NH₃ molecule adsorbed onto a growing Ga-rich GaN (0001) surface. Our initial condition is sketched in Fig. 1 (a), representing an NH₃ molecule adsorbed on top of one of the Ga(ad) adatoms present at the surface. We recall that our previous static DFT calculations[17] have shown that NH₃ is adsorbed either on the Ga(ad) atom or on the regular surface Ga atom (called T1 site). However, clarification of dynamics and stability of the NH₃ at finite temperature among the possible adsorption sites escape the capability of static calculations. Yet, thermal and entropy effects are likely to play an important role in the behavior of the adsorbed NH₃. To unveil this point, we did FPMD simulations on the structure shown in Fig. 1(a), within the Car-Parrinello framework, complemented by the BME enhanced sampling, to search for dynamical confirmations or possible alternative adsorption sites. Since the adsorption of an NH₃ molecule is basically a barrierless process[17,19], an attempt at desorbing this molecule from the Ga(ad) to which it is bound should either result in a spontaneous bond formation onto a nearby Ga(ad) or in an adsorption to some other site, not necessarily Ga(ad), available on the Ga-rich GaN (0001) surface. To this aim, we used as a reaction coordinate the Ga(ad)-NH₃ chemical bond distance, $x = |\mathbf{R}(\text{N}) - \mathbf{R}(\text{Ga}(\text{ad}))|$, and we sampled the cleavage of this bond by gradually increasing this bond length. To disentangle the thermal motion effects typical of the 1300 K growth temperature, which will be included in the next sections targeting the hydrogenation/dehydrogenation, we here did these NVT simulations at a target temperature of 500 K, where Ga(ad) atoms are not yet in a diffusive regime. The result is summarized in Fig. 2, where the red curve shows the free energy profile ΔF as provided by the BME after thermodynamic integration of the averaged Lagrange multiplier[29], $\langle \lambda \rangle_t$, used to complement the Car-Parrinello Lagrangean L^{CP} with the BME constraint in the standard way, $L^{\text{CP}} \rightarrow L^{\text{CP}} + \lambda[x(\mathbf{R}_i) - x_i]$. As detailed in Ref. 29, $x(\mathbf{R}_i)$ is the analytical expression of the constraint and x_i its sampled numerical value. Thus, the free energy profile reads

$$\Delta F = \int_{x_0}^{x_1} \langle \lambda \rangle_t dx \quad (1)$$

where the value x_0 refers to the initial Ga(ad)-NH₃ chemical bond and x_1 each one of the fifteen sampled values evidenced by red diamonds in the figure. By increasing until bond breaking the Ga(ad)-NH₃ distance, at a value of about 3.0 Å, the free energy cost to disrupt this bond amounts to 0.23 eV, while the corresponding total energy

difference ΔE , where the total energy is intended as the sum of the ionic kinetic energy E_I^k and the Kohn-Sham DFT functional E^{DFT} ($E = E_I^k + E^{\text{DFT}}$ black line in Fig. 2), is slightly higher, $\Delta E = 0.44$ eV.

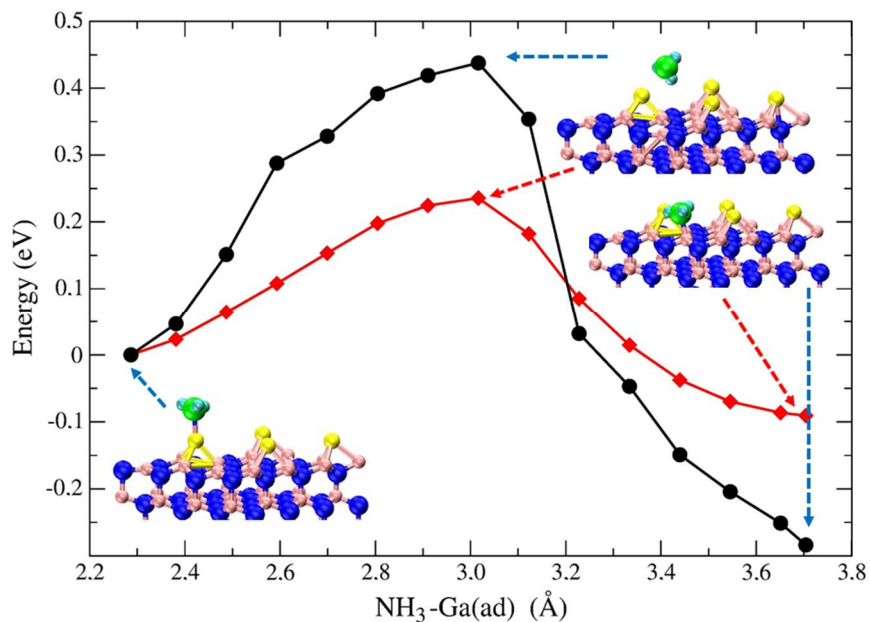


Fig. 2. Free (red) and total (black) energy profiles for the NH_3 desorption reaction sampled via BME. The reaction coordinate is the Ga(ad)-NH_3 bond distance, and the stick-and-ball insets show the average configuration of the main steps of the reaction pathway. The red diamonds and black circles correspond to the values of the reaction coordinate sampled whereas the lines are intended as a guide to the eye. The atoms color code is identical to the one of Fig. 1.



Fig. 3. Side and top views of the stable structure found in which the NH_3 is adsorbed on a Ga(T1) atom, highlighted inside the red circle. Details are provided in the text and the color code for the atoms is identical to the former figures.

These free and total energy barriers are not so high and can be easily crossed at the high temperatures (1300 K) used in MOVPE. What we observe is that the desorption of the NH₃ molecule from the Ga(ad) site allows the ammonia to go back temporarily to the gas phase conditions. Yet, instead of simply flying away from the surface, this NH₃ diffuses on the surface and visits other sites, including a nearby Ga(ad). Eventually, in a spontaneous way, it forms a new chemical bond not with another Ga(ad) but with a “regular” Ga atom of the surface (T1 site). This configuration, shown in detail in Fig. 3, is energetically more stable than the Ga(ad)-NH₃ one by $\Delta F = 0.10$ eV and $\Delta E = 0.28$ eV in terms of free and total energy, respectively.

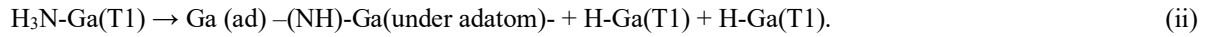
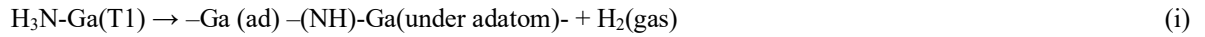
The fact that the total energy curve displays an energetically lower final value with respect to the free energy profile is not surprising and is ascribed to the insufficiency of the selected reaction coordinate in catching the features of a new chemical bond formation. Indeed, this was not our scope and, anyhow, the selected constraint does not bias in any way the final product, which is just the stable result of the NH₃ migration on the surface. This somehow unexpected result is then free from any possible biasing and corresponds to a situation that the system self-selected. A continuation of this simulation at the end of the process, i.e. at the value $x=3.70$ Å of the reaction coordinate, was done within a standard canonical NVT dynamics by removing any BME constraint. Nonetheless, this adsorbed NH₃ remains stable and does not undergo any other diffusion or dissociation process at least on the time scale of the simulation (~30 ps). We then assumed that this is a consistent and reliable configuration to be considered for the dissociation process of the ammonia molecule. An interesting feature is the fact that at the beginning of the simulation, the Ga(ad)-NH₃ distance is 2.23 ± 0.02 Å, corresponding to the left value of the plot in Fig. 2, whereas the final product is characterized by a bond length Ga(T1)-NH₃ = 1.91 ± 0.03 Å, the mean value and deviation being computed on the dynamical trajectories. These geometrical values are already an indicator of the fact that the shorter bond, Ga(T1)-NH₃, is indeed a more stable configuration, being this distance basically equivalent to those of bulk Ga-N bonds (1.90-1.95 Å).

To get a better insight into this issue, we analyzed the local electronic structure in terms of Wannier function centers (WFCs)[31] (see Supplementary Data, Fig. S3) of the Ga(ad) and Ga(T1) sites. What emerges from this analysis is that the Ga(ad) carrying three rather long (~2.46 Å) makes relatively weak bonds with the three Ga(T1) sites with WFCs not localized along the Ga(ad)-Ga(T1) bond axis, as expected for a regular homopolar bond, but at a distance of 0.41 Å from the bond axis (see Fig. S4 of the Supplementary Data) with an associated spread of 1.64 Å, much

larger than the WFCs spreads of 1.02 Å of all the other Ga-N bonds of the system which are well centered along their bond axis. Another electronic structure feature worthy of note is the local dipole moment of the Ga(ad) atoms with respect to Ga(T1) ones. This local dipole moment is directly available as $\mathbf{P} = \sum_I Z_I \mathbf{R}_I - \sum_n f_n \mathbf{r}_n$ being Z_I and \mathbf{R}_I the valence charge and ionic position of the Ga atom I and f_n and \mathbf{r}_n the occupation number (=1 in our spin-unrestricted approach) and position of the closest WFCs. As reported in Fig. S5 of the Supplementary Data, we found that for Ga adatoms not carrying the adsorbed NH₃ molecule the dipole moment is mainly orthogonal to the surface with a value $|\mathbf{P}_z| = 7.43 \pm 0.40$ D, whereas for Ga(T1) sites (also in this case not bound to NH₃), this same dipole moment reduces to $|\mathbf{P}_z| = 0.53 \pm 0.21$ D, thus accounting for a higher stability of T1 sites in comparison with Ga(ad) ones. This electronic structure analysis seems then to corroborate the conclusions drawn from the energetic and structural results of our simulations.

3.2 Dissociation of the adsorbed NH₃ molecule

The dissociation of the NH₃ molecule bound to the growing Ga-rich GaN (0001) surface has been a matter of both speculations and, only recently, simulations. Namely, the possible pathways that the release of H atoms from an adsorbed NH₃ could be realized can be summarized into two alternative reaction channels:



The first one has been the target of a former DFT-based investigation[17,19] starting from the Ga(ad)-NH₃ configuration and assuming the presence of a released H₂ molecule in the gas phase as a final product. At variance with our former study, here we do not impose neither a specific final structure nor *a priori* assumed mechanism. Again, we work in the NVT canonical ensemble, consistently with the simulation protocol of the previous paragraph. The temperature is set to the experimental value of MOVPE (1300 K) and BME simulations are done by using as a reaction coordinate the coordination number of N with its three H atoms around. The analytical representation of the (continuous) coordination number used in our simulation is the one proposed by M. Sprik[32], specifically

$$N_{coord} = \sum_{i=1}^3 F_i(|\mathbf{R}(N) - \mathbf{R}(H_i)|) \quad (2)$$

with the continuous coordination number described by a Fermi-like distribution function $F_i(r)=1/\{\exp[k(r-r_c)]+1\}$. Here, the two parameters k and r_c represent respectively the decay constant and the cut-off radius beyond which an H atom is no longer chemically bound to N, being $r=|\mathbf{R}(\text{N})-\mathbf{R}(\text{H}_i)|$ the distance between the N atom of NH_3 and each one of the three H atoms bound to it. In this specific case, following Ref. 32 and keeping in mind that a regular N-H bond in ammonia is equivalent to 1.012 Å, we adopted $k = 3.40 \text{ \AA}^{-1}$ and $r_c=1.80 \text{ \AA}$. This cut-off radius ensures that weak N-H bonds, including possible hydrogen bonds, are not accounted for in determining a permanent breaking of the chemical bond. With this computational set-up and by starting from the configuration shown in Fig. 3, we progressively reduced the coordination number of N with its H atoms via BME simulations. The free (red) and total (black) energy profiles obtained are shown in Fig. 4. In the initial configuration, the adsorbed NH_3 is located at the T1 site found in the former simulation and represented by the last right inset of Fig. 2. This is the conditions in which the coordination number is equal to 3. A nearby Ga(ad) is present on the surface, not too far from this T1 site. Yet, the Ga(T1)- NH_3 chemical bond is rather stable.

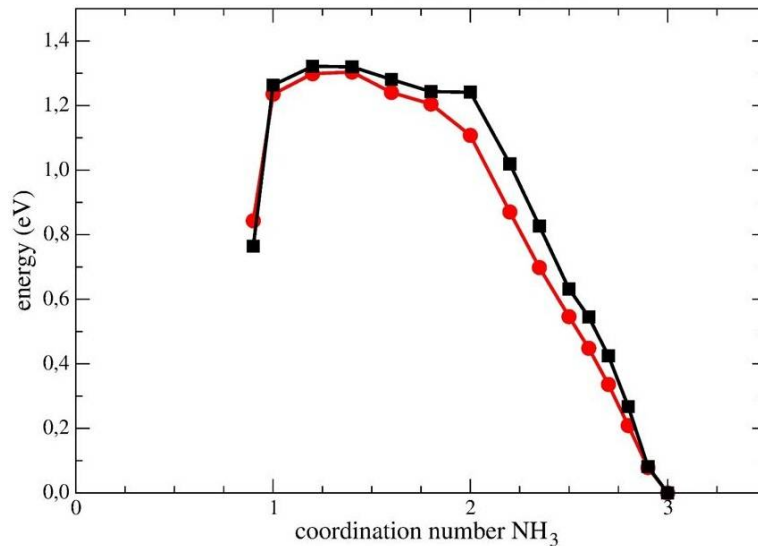


Fig. 4. Free (red) and total (black) energy profiles for the dissociation of an NH_3 molecule adsorbed on a Ga-rich GaN (0001) surface at 1300 K. The reaction coordinate is the coordination number of N with its three neighbor H atoms as explained in the text. The sampled values of the reaction coordinates are highlighted by symbols as in Fig. 2, whereas the solid lines are intended as a guide to the eye.

During the simulation, at the experimental temperature $T = 1300$ K, the high mobility of the Ga(ad) atoms[17] brings one of these highly mobile Ga(ad) in proximity of the NH_3 at the T1 site allowing for the formation of a metastable state. This metastable state corresponds to the coordination number of about 1.8 in Fig. 4. In these conditions, the first H atoms has been released and diffuses on the GaN surface quite rapidly, thanks to the high temperature, until it realizes a stable chemical bond with a nearby Ga atom. This first stage of the dissociation mechanism supports the notion of a contribution of the NH_3 dissociation to the hydrogenation of the surface, at least on pristine Ga-rich systems. Thus, upon release of the first hydrogen atom, we reach a situation in which part of the second reaction pathway hypothesized is realized, namely



with the structure corresponding to the snapshots shown in panel (a) of Fig. 5.

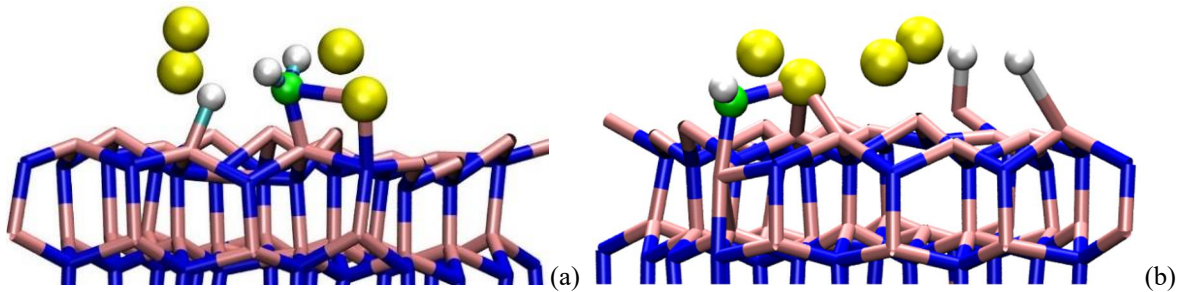
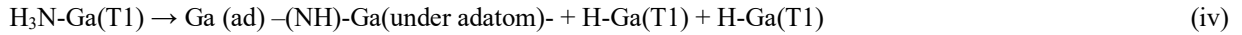


Fig. 5. Configurations realized upon release of the first (a) and second (b) hydrogen atom from the adsorbed NH_3 molecule. The Ga(ad) atoms (evidenced in yellow) not chemically bound to N are highly dynamical, as well as the released H atoms on the surface, at 1300 K in line with what has been found in Ref. 18. The two snapshots represent the same system along the dynamical BM trajectory but rotated of about 90° with respect to each other for clarity of presentation.

In this condition, this intermediate structure is characterized by bond lengths of $\text{Ga(ad)-(NH}_2\text{)} = 2.20 \pm 0.05 \text{ \AA}$, and $\text{(NH}_2\text{)-Ga(under adatom)} = 2.06 \pm 0.03 \text{ \AA}$, with an angle $\text{Ga(ad)-(NH}_2\text{)-Ga(under adatom)} = 78.0 \pm 14.0^\circ$ due to the high

temperature and consequently highly dynamical structure. For comparison, Ga-N bonds in the bulk GaN substrate amount to $\sim 1.98 \text{ \AA}$ with Ga-N-Ga angles of 120° . The formation of a chemical bond Ga(ad)-(NH₂) confirms the fact that the Ga(ad)-Ga are rather weak, as supported by the electronic structure analysis reported in the Supplementary Data and discussed in the former paragraph. This triggers the insertion of the N atom in the structure as a seed for the GaN growing process. The energetic cost to release this first H atoms amounts to $\Delta F = 1.20 \text{ eV}$ and $\Delta E = 1.24 \text{ eV}$ and, according to our energy profiles, represents the rate limiting step of the reaction. In fact, the subsequent H release requires the overcoming of a modest additional barrier of about 0.1 eV , facilitated by the over-coordination of N which becomes fourfold with two chemical bonds with Ga atoms and two with H atoms. This situation corresponds to the maxima of the free and total energy profiles at the value 1.0 of the coordination number, amounting to 1.30 and 1.32 eV , respectively, before dropping down to 0.8 and 0.76 eV when the second H atom is released from the adsorbed NH₂. This final step along the sampled reaction pathway completes the realization of the mechanism (ii) as



with the stable structure shown in panel (b) of Fig. 5. In this condition, beside the stable structure Ga(ad)-(NH)-Ga(under adatom)-, the diffusing Ga(ad) and released H atoms are wandering on the surface, these diffusion processes being enhanced by the high temperature. On a structural standpoint, the geometrical parameters of this Ga(ad)-(NH)-Ga(under adatom)- configuration become Ga(ad)-(NH) = $2.04 \pm 0.02 \text{ \AA}$, (NH)-Ga(under adatom) = $2.05 \pm 0.01 \text{ \AA}$ and the angle Ga(ad)-(NH)-Ga(under adatom) = $111.0 \pm 10.0^\circ$, thus less (dynamically) dispersed than the former intermediate structure.

We remark that this two-step reaction pathway can well be the consequence of the selected reaction coordinate in which the coordination number of N with H decreases first to 2 and then to 1. This choice of the reaction coordinate includes the possibility of the simultaneous dissociation of two H atoms from NH₃. However, in view of the energetics resulting from our BME simulations, such a concerted release of both hydrogen atoms at the same time requires a higher cost and, as such, would result in a much harder realization than the subsequent steps depicted here. An interesting consequence of the formation of a stable Ga(ad)-(NH)-Ga(under adatom)- even at the high deposition temperature (1300 K) is the fact that one of the Ga(ad) atoms is eventually tightly bound to the surface and do no longer participate to the formation of a two-dimensional liquid state[18]. This particular reaction channel has the advantage of consolidating the growing GaN network by blocking, upon formation of stable chemical bonds, the free

diffusion of the Ga adatom, while, at the same time, contributes to the hydrogen passivation (discussed in the next paragraph) of the growing structure. This provides a novel insight into the complicated mechanisms regulating the vapor-phase deposition process and complements the previous DFT-based outcome[15]. Also in this case, the weak Ga(ad)-Ga bonds play the role of the trigger for the incorporation of N inside the growing structure. The fact that, in this case, the dissociation of the adsorbed NH_3 occurs very close to a non-hydrogenated surface, makes easier for H atoms to diffuse and bind to the exposed surface, instead of trying to “meet” in a gas phase above to the surface and combine into an H_2 molecule. Thus, this reaction channel represents a viable alternative to the H_2 production route and the realization of the first or the second reaction pathway indicated at the beginning of this paragraph is likely to be dependent on the initial conditions, i.e., the actual site where the ammonia molecule is bound to the surface and the amount of hydrogenation of the surface

3.3 Effects of surface hydrogenation on the Ga(ad) at the GaN growth temperature

Former studies, including ours, focused almost exclusively on pristine GaN surfaces. Far from being a limitation, the absence of hydrogen atoms passivating the simulated surface provides a good template to disentangle problems related to the role of the environment in the growth process. Yet, a general GaN growing surface is expected to be at least partly passivated by hydrogen, especially when H_2 molecules are used as carrier. Based on this observation, Kangawa and coworkers[9] could identify a phase diagram of the GaN surface and its dependency on the environmental conditions such as gas pressure and temperature were rationalized in a recent work[15]. Another recent study dedicated to the role of hydrogen as a passivating agent[33] has shown that H can affect to some extents the structure of GaN. More generally, hydrogen has mainly been considered as a major player in catalysis processes[34] involved in GaN systems, without deepening the analysis into the implications for MOVPE produced GaN films. A deeper insight into the role of hydrogen in surface reconstruction and morphology of a growing GaN structure was proposed twenty years ago by van de Walle and Neugebauer[35] and, despite being a bit outdated, that work still represents one of the more reliable studies even nowadays. From the rich literature part of which is summarized here, it emerges that hydrogen is ubiquitous in growth processes and a variable amount of it is expected to be present on the growing GaN surface. Nonetheless, the high growth temperature (1300 K) prevents a precise experimental identification of the H-covered surface and moreover knowledge of the dynamics of H atoms on the growth surface is completely lacking.

As shown in the former paragraph, H is not just an irrelevant byproduct released in the gas phase after the dissociation process of a precursor NH_3 . Instead, if suitable sites are present on the growing surface, H atoms can easily diffuse and form stable chemical bonds. In an attempt at figuring out at least one of the roles of H, we here inspect the Ga-rich GaN (0001) surface on which we have formerly identified the presence of a two-dimensional liquid state realized by the thermal motion of Ga(ad) atoms at the typical experimental temperature (1300 K) of MOVPE. Specifically, we aim at understanding if and to which extent the hydrogenation of this surface affects the diffusion of Ga(ad). For this scope, we constructed the model system shown in Fig. 1 (b) in which one single Ga(ad) is present on the surface and all the other exposed Ga atoms are passivated by H. We gradually removed from one to three H atoms and on each of these models we performed a 20 ps unconstrained FPMD at 300 K in the canonical NVT ensemble. Only in the case in which three H atoms were removed we could obtain a stable structure. This is not surprising, since these conditions satisfy the electron counting rule[13,14] as explained in the methodological section. On the other hand, we had no experimental hint about the amount of hydrogenation of a growing GaN surface, thus we could rely solely on our virtual experiments. For the sake of completeness, we remark that a higher H coverage, excluding the presence of Ga(ad), has been ruled out[14] and does not represent a realistic experimental situation.

On the stable system carrying nine passivating H atoms and one Ga(ad) we performed a progressive heating from 300 K to 1300 K in about 45 ps, equilibrating the system at different steps, from 300 to 1000 K as shown in the left panel of Fig. 6, until reaching the experimental growth temperature of 1300 K where the dynamics lasted for about 40 ps.

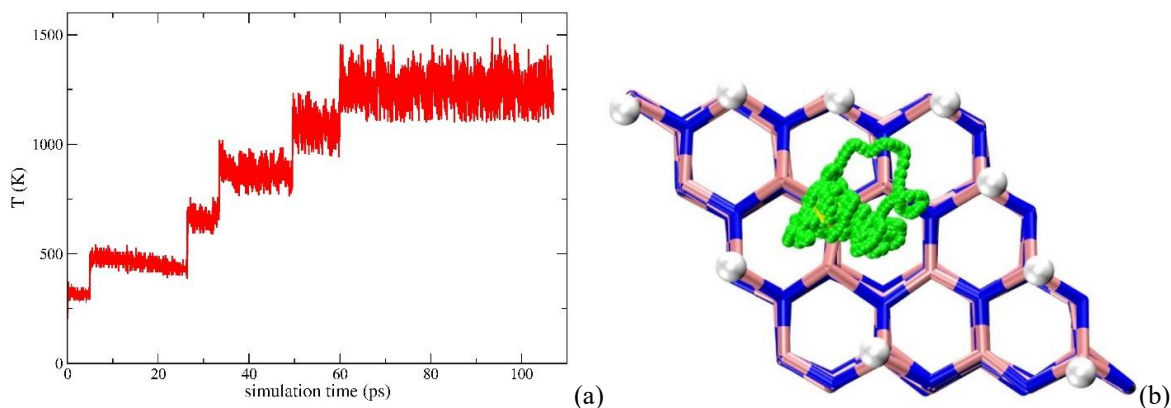


Fig. 6. (a) Heating process of the partially hydrogenated GaN (0001) surface carrying one Ga(ad) at 1300 K. (b) The trajectory highlighted by green spheres shows the diffusion path of this Ga(ad) at 1300 K. The color code of the remaining atoms is identical to all former figures.

All along the heating process, the H atoms oscillate with amplitudes gradually increasing as the temperature rises, but without dissociating, diffusing, or leaving the GaN surface. Conversely, the Ga(ad) remains stable on its initial position for $T < 1300$ K but diffuses quite rapidly at 1300 K in a way not too different from what was found on the H-free surface[18]. A substantial difference is due to the presence of H atoms passivating the surface: These H atoms tightly bound to Ga atoms, provide a strong boundary limiting the motion of the Ga(ad) as sketched in Fig. 6. The cage formed by the surrounding H atoms bound to the Ga of the substrate becomes a restricted area in which the Ga(ad) is allowed to diffuse and this, in turn, reduces the diffusion coefficient of this diffusing Ga(ad) to $0.186 \times 10^{-4} \text{ cm}^2/\text{s}$. Indeed, this value is about 1/3 of the analogous estimation ($0.492 \times 10^{-4} \text{ cm}^2/\text{s}$) computed, by integrating the velocity-velocity autocorrelation function of Ga(ad), as formerly done on a pristine surface[18] with no H-passivation and four Ga(ad) present on the exposed surface. It seems then that the presence of H, either coming from the deposition conditions (environment) or resulting from the de-hydrogenation of precursor molecules, has not only a negative effect in the sense that makes the hydrogen passivated surface less reactive to approaching ammonia or TMGa, but can concur to reduce the diffusion of Ga(ad). It is most likely the interplay of these two factors, presence of active binding sites and limitations to surficial diffusion due to H, that should be considered for a more comprehensive picture of the complicated MOVPE process

4. Conclusion

By resorting to first-principles molecular-dynamics (FPMD) simulations in the Car-Parrinello scheme, empowered by the Blue-Moon ensemble free-energy sampling technique, we have explored reaction pathways and free-energy landscape of ammonia NH_3 and Ga adatom during the GaN epitaxial growth. We have found that the NH_3 can be adsorbed on top of different Ga sites and, without evaporation, wanders among those sites with the free-energy barriers of a few tenths of eV, resulting in a rather high stability of the adsorbed NH_3 precursor molecule. We have then found that the NH_3 is decomposed into NH_2 and subsequently NH with the dissociated H atoms not being evaporated but adsorbed on Ga atoms nearby. This process of the decomposition of NH_3 turns out to be the two-step process in which NH_2 first intervenes into a weak bond of a Ga adatom (Ga(ad)) and a regular Ga surface atom (Ga(T1)), and subsequently NH_2 releases one additional H by overcoming a low energy barrier (~ 0.1 eV), thus becoming the – Ga(ad)-NH-Ga(T1)- configuration. This structure is the starting point for the growth reaction as postulated in our

previous static density-functional calculations. A novelty of the present FPMD simulations is that this decomposition of NH_3 is associated with spontaneous hydrogenation of GaN surface. We have indeed found that this hydrogenation suppresses the diffusion of the Ga adatom, thus contributing to stabilize the growing GaN system: The calculated diffusion constant at 1300 K, $0.186 \times 10^{-4} \text{ cm}^2/\text{s}$, is 1/3 of the previously value obtained on an H-free surface. Dynamical aspects and free-energy profiles of atomic reactions clarified for the first time by the present FPMD simulations are important prerequisite to unveil mechanisms of GaN epitaxial growth.

5. Credit authorship contribution statement

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

6. Declaration of Competing Interest

The authors declare no competing financial interest.

7. Supplementary Data

The following files are available free of charge. Example of time evolution and running average of a BME constrained dynamics, computed constraint force, electronic structure analysis in terms of maximally localized Wannier function centers and bonding properties of adsorbed NH_3 , Ga(ad) and Ga(T1)

8. ACKNOWLEDGMENTS

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Graphical Abstract

