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Computational study of adsorption, diffusion, and dissociation of precursor species on the GaN (0001) surface during GaN MOCVD

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ABSTRACT

The adsorption, diffusion, and dissociation of precursor species, MMGa (monomethylgallium) and NH_3, on the GaN (0001) surface have been investigated using the DFT (density functional theory) calculation combined with a GaN (0001) surface cluster model. The energetics of NH_3(ad) dissociation on the surface proposed the dissociation of NH_3(ad) via NH_2(ad) to NH(ad) was facile with small activation barriers. A combined analysis with surface diffusion of adatoms demonstrated Ga(ad) and NH(ad) become primary reactant species for 2D film growth, and N(ad) develops into a nucleation center. Our studies suggest the control of NH_3(ad) dissociation are essential to improve epitaxial film quality as well as Ga-rich condition. In addition, the adsorbability of H(ad)s resulted from NH_3(ad) dissociation were found to influence on the surface chemistry during film growth.

Much attention has been paid to the light-emitting diode (LED) in an emerging market of general lighting, as a potential alternative of incandescent light bulbs and fluorescent lamps [1,2]. Recently, highly efficient GaN-based blue and green LEDs combined with an yttrium aluminum garnet (YAG) phosphor became one of the most popular white LED technologies [3]. The metal organic chemical vapor deposition (MOCVD) using trimethyl group III precursors and ammonia (NH_3) has been commercially employed to grow epitaxial LED structure on sapphire substrate; p-GaN|InGaN/GaN MQW|n-GaN|u-GaN|Sapphire [1,2]. Opposing to the great progress in device fabrication of GaN-based LEDs, the attempts to understand the underlying growth mechanism, essential to improve epitaxial film quality in a systematical way, have been limited due to the difficulty of experimental analysis under real CVD conditions. Computational simulations instead have been employed to investigate the electronic structures of GaN surfaces and the initial stage of GaN epitaxial growth [4–6]. However, thermochemical processes on GaN surface have not been explored in much detail. The surface diffusion of Ga(ad) and N(ad) were treated to an extent in the discussion of stability and polarity of the GaN (0001) surface [7]. The adsorption of NH_3, O_2, and hydrogen on the GaN (0001) surface were investigated only in some details [8–11]. Those works were rudimentary compared to the extensive computational studies of adsorption and dissociation of NH_3 on Si(100) and (111) surfaces [12,13].

We have thus performed a comprehensive study of adsorption, diffusion, and dissociation of various reactant species on the Ga-terminated GaN (0001) surface using density functional theory (DFT) calculations combined with the cluster approximation. The energetics for those surface processes was computationally calculated. A $Ga_{13}N_{13}H_{24}$ cluster was employed to emulate the Ga-terminated ideal GaN (0001) surface. Details for the cluster were found elsewhere [8,9]. Computing capacity was also considered for the selection. All calculations were carried out with *GAUSSIAN 03*, using the B3LYP (Becke, three-parameter, Lee-Yang-Parr) model chemistry and split basis sets – LanL2DZ (Los Alamos effective core potential plus double-Z) for Ga and 6-31G(d) for other elements [14–16]. Molecular geometries were optimized with hydrogen edge atoms in the $Ga_{13}N_{13}H_{24}$ cluster fixed and others relaxed. The transition state (TS) was located using the Berny algorithm as implemented in *GAUSSIAN 03* [14]. The *Materials Studio 4.2* was used for the visualization of the results.

Adsorption of monomethylgallium (MMGa) and NH_3 on the Ga-terminated GaN (0001) surface: It was presented that the trimethylgallium (TMGa) precursor for GaN MOCVD readily decomposes via dimethylgallium (DMGa) to MMGa in the gas phase as soon as the first methyl dissociation is activated and the third methyl dissociation from MMGa counters a reinforced significant barrier [17]. A thermodynamic calculation by Cardelino et al., in accordance, demonstrated that the main species in the gas phase in trimethylindium (TMIn) decomposition are C_2H_6 and monomethylindium (MMIn) at an elevated temperature [18]. Now that the N–H bond energy in NH_3 is ~94 kcal/mol, the initial reactant species on the surface will be MMGa and NH_3. The adsorption energies (ΔE_{ads}) of MMGa and NH_3 on the surface were −65.3 and −33.0 kcal/mol, respectively, calculated by the following expression:

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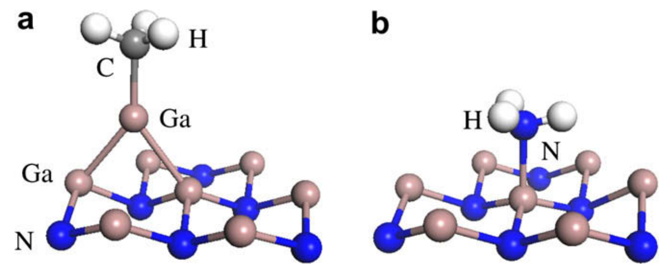

Fig. 1. Optimized geometries of MMGa(ad) (a) and NH_3(ad) (b) on the Ga-terminated GaN (0001) surface. Hydrogen edge atoms and the third/fourth (Ga/N) layers in the $Ga_{13}N_{13}H_{24}$ cluster were omitted for simplicity.

$$\Delta E_{ads} = E(\text{adsorbate/substrate}) - [E(\text{adsorbate}) + E(\text{substrate})] \quad (1)$$

where E(adsorbate/substrate), E(adsorbate), and E(substrate) are the calculated local minimum electronic energies of the adsorbate/substrate system, isolated adsorbate (MMGa or NH_3), and substrate ($Ga_{13}N_{13}H_{24}$ cluster), respectively. The GaN (0001) surface, terminated by triply bonded Ga atoms, showed no significant reconstruction and the doublet state was the most stable. The much lower adsorption tendency of NH_3 to MMGa on the surface explains the high V/III ratio (2000–10000) typically employed in GaN MOCVD.

Decomposition of MMGa(ad) and NH_3(ad) on the Ga-terminated GaN (0001) surface: The optimized geometries of MMGa(ad) and NH_3(ad) on the Ga-terminated GaN (0001) surface are presented in Fig. 1.

The MMGa(ad) is stabilized by changing its bond characteristic to form sp^2 hybridization with two adjacent Ga surface atoms [17]. The homolysis of the methyl ligand from MMGa(ad) had a barrier energy of 64.5 kcal/mol to leave behind Ga(ad) on the surface, calculated by the following expression:

$$\Delta E_{homolysis} = E(\text{GaCH}_3(\text{ad}) \text{ on } Ga_{13}N_{13}H_{24} \text{ cluster}) - [E(\text{Ga(ad) on } Ga_{13}N_{13}H_{24} \text{ cluster}) + E(^{\cdot}\text{CH}_3(\text{g}))] \quad (2)$$

The barrier is almost equivalent to the adsorption energy (ΔE_{ads}) of MMGa. In fact, there found two local minima for the resulting Ga(ad) on the Ga-terminated GaN (0001) surface; on top of nitrogen in the second layer (T_4) and void (H_3). The Ga(ad) is more stable on T_4 site than on H_3 site by 12.7 kcal/mol. For comparison, N(ad) is the opposite by 12.8 kcal/mol. It is consistent with the results presented by Wang et al. [4]. The NH_3(ad) meanwhile rests on top of one of the Ga surface atoms bonded by sp^3 hybridization, as shown in Fig. 1. Nai-Xia et al. also predicted the same geometry for NH_3 adsorption on the GaN (0001) surface [8]. They claimed that the dissociation of NH_3(ad) to NH_2(ad) + H(ad) was thermodynamically preferred by decreasing the total energy of 0.95 eV (21.9 kcal/mol) [8]. The energetics of NH_3(ad) dissociation on the Ga-terminated GaN (0001) surface was calculated including the transition state as presented in Fig. 2.

The activation energy was 8.5 kcal/mol, suggesting that the dissociation of NH_3(ad) to NH_2(ad) + H(ad) is very facile. The thermodynamic driving force was a lot significant by the total energy decrease of 54.7 kcal/mol, compared to 21.9 kcal/mol calculated by Nai-Xia et al., while the NH_3 adsorption energy (ΔE_{ads}) of −33.0 kcal/mol (see Fig. 2) was comparable to the value of −29.2 kcal/mol in their calculations. It is caused probably by the different positions of the resulting NH_2(ad) and H(ad). For some reason, they placed H(ad) on top of the center surface Ga atom and let NH_2(ad) bonded to peripheral surface Ga atoms for **1-p** [8]. The resulting NH_2(ad) is stabilized again by sp^3 hybridization with two adjacent surface Ga atoms. A further dissociation of NH_2(ad) and NH(ad) was also examined as presented in Fig. 3. In each initial (base) geometry for the dissociation of NH_2(ad) or NH(ad), the resulting H(ad) in the previous dissociation was assumed to hop out of the vicinity.

There are two possible pathways of the dissociation of NH_2(ad) and NH(ad) because two local minima exist with respect to the positions of NH(ad) and N(ad) (T_4 and H_3 sites). It is noted that the activation energy for the dissociation of NH_2(ad) is as low as 16.8 kcal/mol (see Fig. 3a), presenting that the NH_2(ad) dissociation is also kinetically facile. The subsequent dissociation of NH(ad) experiences a significant activation barrier of 57.2 kcal/mol (see Fig. 3b). Considering GaN MOCVD undergoes a very high temperature (900–1100 °C), the NH_3(ad) dissociation all the way through N(ad) is still kinetically viable, but at least it is safe to say that the NH_3(ad) breakdown to NH (ad) occurs virtually without kinetic limit in that condition. In Fig. 3b, another pathway is proposed in which NH(ad) on H_3 site (**3-i1**) moves to T_4 site (**3-i2**) by surface diffusion and proceeds on the pathway with a lower activation energy of 44.0 kcal/mol winding up with N(ad) on stable H_3 site (**3-p2**). The existence of two local minima for the positions of NH(ad) and N(ad) thus demands an analysis combined with surface diffusion of adatoms.

Surface diffusion of Ga(ad), NH(ad), and N(ad) on the Ga-terminated GaN (0001) surface: The surface diffusion was considered for three reactant species; Ga(ad), NH(ad), and N(ad). The adsorp-

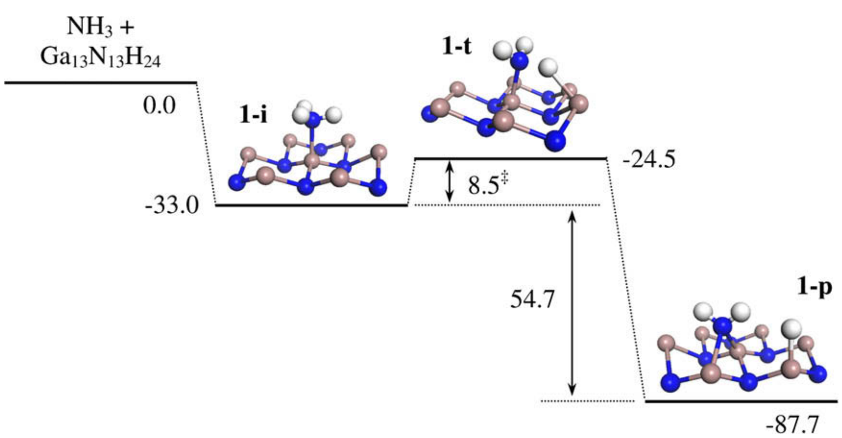

Fig. 2. Calculated energetics of NH_3(ad) adsorption and dissociation on the Ga-terminated GaN (0001) surface. Hydrogen edge atoms and the third/fourth (Ga/N) layers in the $Ga_{13}N_{13}H_{24}$ cluster were omitted for simplicity. Energies are in kcal/mol. The **1-i** shows the optimized geometry of an NH_3(ad) on the Ga-terminated GaN (0001) surface and the **1-t** is the transition state for the NH_3(ad) dissociation on the surface. The **1-p** indicates NH_2(ad) + H(ad) on the same surface, resulted from the NH_3(ad) dissociation.