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Thermodynamic Analysis of the Surface Reactions in GaN MOVPE

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Abstract

We analyzed the mechanism for the growth of GaN by metal organic vapor phase epitaxy (MOVPE) based on first-principles calculations and a thermodynamic analysis. In our previous study, based on calculations of the formation and activation energies, it was clarified that TMG decomposes into GaH, which is then adsorbed on the GaN surface. In this paper, we discuss growth on a GaN(0001) surface.

1. Introduction

The crystal growth of high quality GaN is crucial for the practical realization of GaN power devices, with which significant energy savings can be achieved. Among the various crystal growth techniques, metal-organic vapor phase epitaxy (MOVPE) is a well established method for the growth of crystalline GaN; however, there is little known about the detailed mechanism of the growth of GaN using this technique. In particular, it is unclear how trimethylgallium (TMG, [$Ga(CH_3)_3$]), which is used as the Ga source, reacts and decomposes in the gas phase. Clarification of the TMG decomposition process is key to obtaining high quality GaN crystals. In our previous study, we clarified that formation of the $(CH_3)_2GaNH_2$ adduct only occurs at low temperature and it is not the main reaction during GaN MOVPE [1]. Moreover, we analyzed the TMG decomposition process by calculating the formation energy based on the Kangawa formalism [2] and the activation energy based on the nudged elastic band (NEB) method [3]. It was found that TMG decomposes as follows by reacting with the H_2 carrier gas in the vapor phase during GaN MOVPE; $(CH_3)_2GaH$ → $(CH_3)GaH_2$ → GaH_3 → GaH [4]. These results, in which TMG loses methyl groups one by one, are consistent with recent high resolution mass spectrometry experiments by Nagamatsu et al. [5]. Therefore, TMG finally decomposes into GaH beyond the activation barriers shown in Fig. 1, and GaH is adsorbed on the GaN surface. In this paper, we theoretically investigate the reactions of GaH adsorbed on the GaN(0001) surface.

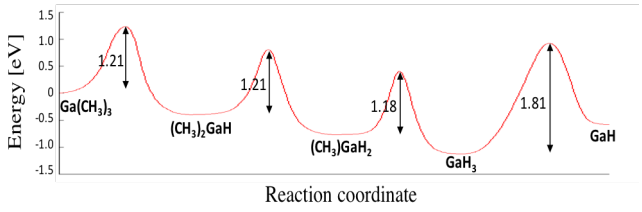

Fig. 1. Activation energy of the main reaction path of TMG at absolute zero.

2. Calculation Method

In analyzing the surface phenomenon, calculations of the formation energy, which is the difference in energy between the initial and final states of the reaction, were made. For the analysis, we calculated the Gibbs free energy (G) of the gas molecule as a function of temperature and partial pressure based on the Kangawa formalism [2]. This is expressed by the sum of the chemical potential (μ_{gas}) and the total energy (E_{tot}). μ_{gas} for the ideal gas is given as follows:

$$\mu_{gas} = -k_B T \ln(g k_B T/p \times \zeta_{trans}\zeta_{rot}\zeta_{vibr}) \quad (1)$$
$$\zeta_{trans} = (2\pi m k_B T/h^2)^{3/2} \quad (2)$$
$$\zeta_{rot} = 1/(\pi\sigma)\{8\pi^3(I_A I_B \cdots)^{1/n} k_B T/h^2\}^{n/2} \quad (3)$$
$$\zeta_{vibr} = \prod_i^{3N-3-n}\{1-\exp(-h\nu_i/k_B T)\}^{-1} \quad (4)$$

where ζ_{trans}, ζ_{rot} and ζ_{vibr} are the partition functions for the translational, rotational, and vibrational motions, respectively. k_B is Boltzmann's constant, T is the temperature, g is the degree of degeneracy of the electron energy level, p is the partial pressure of the particles, m is the mass of one particle, h is Planck's constant, σ is the symmetric factor, I_I is the moment of inertia, n is the degrees of freedom of the rotation, N is the number of atoms in the particle, i is the degrees of freedom for the vibration, and v is the frequency. The total energy at absolute zero can be obtained by first principles calculations. We performed the calculations using the VASP code based on density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [6]. For the calculations, we assumed the following growth conditions; the partial pressure of the TMG is 10^{-4} atm, the V/III ratio is 1000, the carrier gas contains 1 percent H_2, and the total pressure is 1 atm.

In this study, we analyzed the surface phenomena using an ideal GaN(0001) surface. The GaN slab model was a (3 × 3) surface slab model comprising a vacuum layer of more than 15 Å and eight bilayers. The bottom layer was fixed and passivated with imaginary hydrogen atoms.

3. Results and discussions

Table I. Analyzed Reactions on GaN(0001) Surface

	Adsorbed molecule		Reaction gas		Adsorbed molecule		Product gas
1.	GaH			→	(bulk)	+	GaH
2.	GaH	+	GaH	→	2GaH		
3.	GaH	+	GaH	→	2Ga	+	H_2

Table I shows the reactions we analyzed in this study. Reaction 1 is one in which GaH desorbs from the GaN surface. Reaction 2 is where another GaH molecule is adsorbed on the surface, and reaction 3 is where another Ga molecule adsorbs on the surface and H_2 is released in the vapor phase. Fig. 2 shows the slab model optimized by placing molecules on the (0001) surface. Model (a) is the initial state for each of the three reactions, and models (b) and (c) are the final states for reactions 2 and 3, respectively. Fig. 3 shows the results of calculations of the formation energy for the three reactions shown in Table I. Comparing these energies at 1300 K, which is the GaN substrate temperature, the formation energy of reaction 1 is -0.62 eV, that of reaction 2 is -0.23 eV, and that of reaction 3 is -1.43 eV. As the results show, of these three, reaction 3 is the most likely for the growth of MOVPE GaN. Therefore, only Ga remains on the substrate and H_2 is released into the vapor phase.

4. Conclusions

In the case of an ideal GaN(0001) surface, TMG decomposes into GaH. A molecule of this is adsorbed on the surface, followed by adsorption of another GaH molecule and release of a H_2 molecule. Therefore, a Ga-rich layer is formed on the GaN(0001) surface. Kusaba et al. clarified that in the case of (0001) growth using H_2 as a carrier gas, an ideal surface was observed at high temperatures, but a Ga adatom reconstructed surface or a hydrogen-terminated surface with 3Ga-H structure appeared depending on the V/III ratio around the substrate temperature [7]. We also investigate the surface phenomena on Ga adatom and 3Ga-H reconstructed surfaces.

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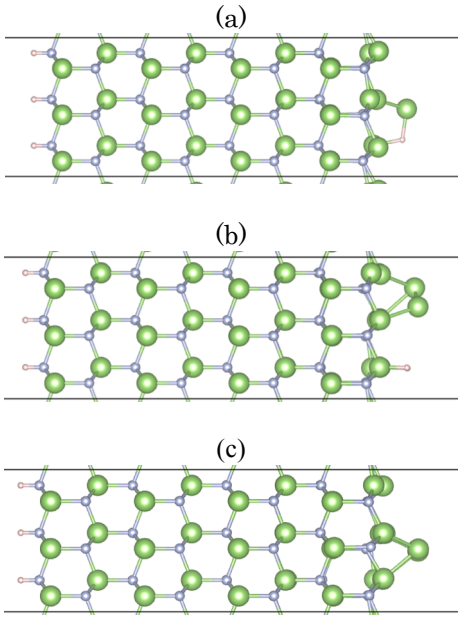

Fig. 2. Slab models where molecules are adsorbed on the (0001) surface. (a), (b) and (c) are the models where one GaH molecule, two GaH molecules and two Ga atoms are absorbed on the surface, respectively. The green, blue and orange circles show Ga, N and H atoms, respectively.

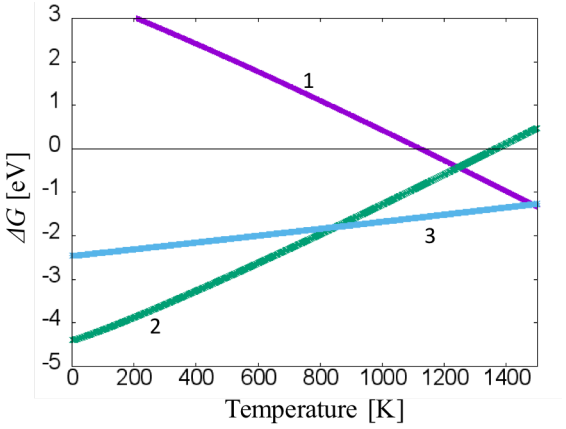

Fig. 3. Calculated formation energy for the three reactions shown in Table I. The purple, green and blue lines are for reactions 1, 2 and 3, respectively.