Extended Abstracts of the 2016 International Conference on Solid State Devices and Materials, Tsukuba, 2016, pp203-204

D-4-02

First Principle and Thermodynamic Analysis of MOVPE Growth of GaN and AlN

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Abstract

We analyzed metal organic vapor phase epitaxy (MOVPE) growth mechanism of GaN and AlN based on first principles calculations and thermodynamic analysis. Our calculated results clearly show that $(CH_3)_2GaNH_2$ adduct cannot be formed in the gas phase reaction in MOVPE. Whereas, $(CH_3)_2AlNH_2$ adduct can be produced in gas phase. In case of GaN MOVPE, trimethylgallium (TMG) decomposes into $Ga(CH_3)$ by the assistance of H_2 carrier gas instead of $(CH_3)_2GaNH_2$ adduct formation. On the other hand, in case of AlN MOVPE, trimethylaluminum (TMA) reacts with NH_3 forming $(CH_3)_2AlNH_2$ adducts. For high quality AlN fabrication, it is necessary to inhibit TMA and NH_3 reaction near the nozzle during MOVPE.

1. Introduction

GaN and AlN are expected as materials for future power devices as well as conventional optical devices. To develop these devices, it is crucial to fabricate high-quality GaN and AlN by epitaxial growth. However, theoretical knowledge about epitaxial growth of GaN and AlN are quite limited. In particular, the detailed growth mechanisms of metal organic vapor phase epitaxy (MOVPE) are not clarified. In case of GaN MOVPE, gas phase reaction of $(CH_3)_2GaNH_2$ adduct formation is reported [1], and they think that GaN nanoparticles are formed from the $(CH_3)_2GaNH_2$ adduct in the gas phase reaction near the surface. On the other hand, it is also believed that Ga is incorporated as atomic Ga gas on GaN growth surfaces and Ga atoms migrate on the surfaces [2]. In this paper, we theoretically investigate the MOVPE growth process of GaN and AlN, and propose a recipe to fabricate high-quality nitride semiconductors. In this study, we performed first principles calculation and thermodynamic analysis to investigate whether $(CH_3)_2GaNH_2$ and $(CH_3)_2AlNH_2$ adducts can be formed in gas phase reaction under realistic MOVPE conditions.

2. Calculation Method

Molecule total energies are calculated by first principles calculations based on density functional approximations. In this study, we used VASP code [3].

We calculated Gibbs free energies of each molecule as a function of temperature based on Kangawa formalism [4]. Gibbs free energy can be computed using quantum statistical mechanics and be expressed in the sum of total energy (E_{tot}) and chemical potential (μ_{gas}). E_{tot} can be obtained using ab initio calculations. The μ_{gas} for the ideal gas is given by [4]:

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

where ζ_{trans}, ζ_{rot} and ζ_{vibr} are the partition functions for the translation motion, the rotational motion and the vibrational motion, respectively. Here, 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_l is the moment of inertia, n is the degree of freedom of the rotation, N is the number of atoms in the particle, i is the degree of freedom for the vibration, and v is the frequency. We interpreted the reaction occurs when Gibbs free energies of the molecules after reaction are lower than those before reaction and the lower the difference is, the more easily reaction occurs. In the calculations, each partial pressure of TMG and TMA is 10^{-4} atm and V/III ratio is 1000, H_2 is 1 percent inside the carrier gases and the total pressure is 1 atm.

3. Results and discussions

First, we investigated the decomposition process of TMG during GaN MOVPE. We considered following four possible reaction paths.

(a) $Ga(CH_3)_3 + 1/2H_2 \rightarrow Ga(CH_3)_2 + CH_4$
(b) $Ga(CH_3)_3 + H_2 \rightarrow Ga(CH_3) + 2CH_4$
(c) $Ga(CH_3)_3 + 3/2H_2 \rightarrow Ga(gas) + 3CH_4$
(d) $Ga(CH_3)_3 + NH_3 \rightarrow (CH_3)_2GaNH_2 + CH_4$

The calculated results indicated that TMG can reacts with NH_3 forming $(CH_3)_2GaNH_2$ adducts only when temperature is lower than 260 K under realistic MOVPE condition as shown in Fig. 1(a). This result clearly shows that TMG hardly reacts with NH_3. In case of GaN MOVPE, $(CH_3)_2GaNH_2$ adduct formation cannot occur contrary to the previous report [1]. In Fig. 1(a), we considered TMG decomposes into $Ga(CH_3)$ when temperature is between 260 K

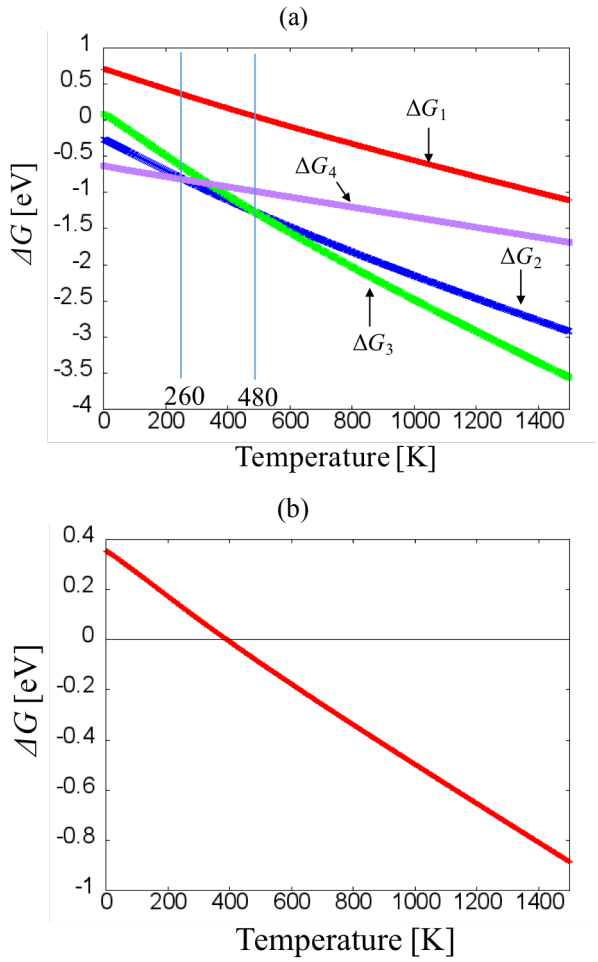

Fig. 1. Calculated Gibbs free energy difference.
(a)$\Delta G_1 = G(\mathrm{Ga(CH_3)_2} + \mathrm{CH_4}) - G(\mathrm{Ga(CH_3)_3} + 1/2\mathrm{H_2})$.
$\Delta G_2 = G(\mathrm{Ga(CH_3)} + 2\mathrm{CH_4}) - G(\mathrm{Ga(CH_3)_3} + \mathrm{H_2})$.
$\Delta G_3 = G(\mathrm{Ga(gas)} + 3\mathrm{CH_4}) - G(\mathrm{Ga(CH_3)_3} + 3/2\mathrm{H_2})$.
$\Delta G_4 = G(\mathrm{(CH_3)_2GaNH_2} + \mathrm{CH_4}) - G(\mathrm{Ga(CH_3)_3} + \mathrm{NH_3})$.
The red, blue, green and purple lines show ΔG_1, ΔG_2, ΔG_3 and ΔG_4 respectively.
(b) $\Delta G = G(\mathrm{Ga(gas)} + \mathrm{CH_4}) - G(\mathrm{Ga(CH_3)} + 1/2\mathrm{H_2})$.

and 480 K and Ga(gas) when it is higher than 480 K. Actually, the temperature around the inflow gases is near room temperature. Therefore, most of TMG decomposes into $Ga(CH_3)$ under the existence of H_2 carrier gas. In addition, $Ga(CH_3)$ decomposes into Ga(gas) when temperature is higher than 390 K as shown in Fig 1(b).

Next, we investigated the reaction and decomposition process of TMA during AlN MOVPE. We also considered following four possible reaction paths based on first principles calculations and thermodynamic analysis.

(e) $\mathrm{Al(CH_3)_3} + 1/2\mathrm{H_2} \rightarrow \mathrm{Al(CH_3)_2} + \mathrm{CH_4}$
(f) $\mathrm{Al(CH_3)_3} + \mathrm{H_2} \rightarrow \mathrm{Al(CH_3)} + 2\mathrm{CH_4}$
(g) $\mathrm{Al(CH_3)_3} + 3/2\mathrm{H_2} \rightarrow \mathrm{Al(gas)} + 3\mathrm{CH_4}$
(h) $\mathrm{Al(CH_3)_3} + \mathrm{NH_3} \rightarrow \mathrm{(CH_3)_2AlNH_2} + \mathrm{CH_4}$

The calculated results indicated that TMA can react with NH_3 forming $(CH_3)_2AlNH_2$ when temperature is lower than 1220 K. It is noted that Al(gas) can be formed when temperature is higher than 1220 K as shown in Fig. 2. In AlN MOVPE, $(CH_3)_2AlNH_2$ adduct can be formed easily. This is in good agreement with the experimental finding that AlN growth is observed near the nozzle [5]. To realize high quality AlN MOVPE growth, the design of nozzle which inhibits the reaction of TMA and NH_3 is very crucial. TMA will decompose into pure Al(gas) and high quality AlN crystal can be produced if it is developed such the new AlN MOVPE growth equipment.

As discussed above, adducts are not formed in the gas phase reaction during GaN MOVPE. Whereas adducts are produced during AlN MOVPE. To avoid the $(CH_3)_2AlNH_2$ adduct formation, we have to develop growth chamber in which we should avoid the $(CH_3)_2AlNH_2$ adduct formation near the nozzle.

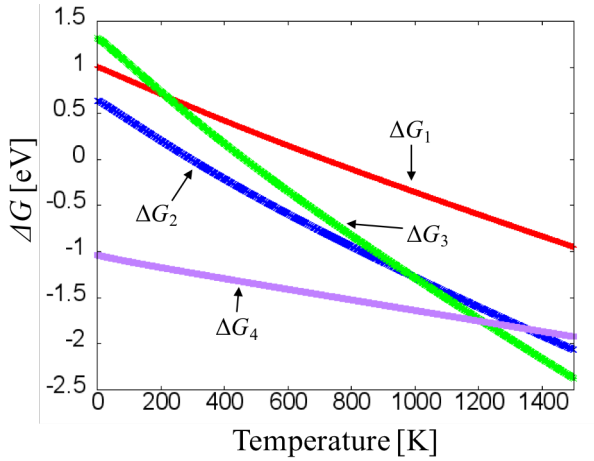

Fig. 2 Calculated Gibbs free energy difference.
$\Delta G_1 = G(\mathrm{Al(CH_3)_2} + \mathrm{CH_4}) - G(\mathrm{Al(CH_3)_3} + 1/2\mathrm{H_2})$.
$\Delta G_2 = G(\mathrm{Al(CH_3)} + 2\mathrm{CH_4}) - G(\mathrm{Al(CH_3)_3} + \mathrm{H_2})$.
$\Delta G_3 = G(\mathrm{Al(gas)} + 3\mathrm{CH_4}) - G(\mathrm{Al(CH_3)_3} + 3/2\mathrm{H_2})$.
$\Delta G_4 = G(\mathrm{(CH_3)_2AlNH_2} + \mathrm{CH_4}) - G(\mathrm{Al(CH_3)_3} + \mathrm{NH_3})$.
The red, blue, green and purple lines show ΔG_1, ΔG_2, ΔG_3 and ΔG_4 respectively.

4. Conclusions

In case of GaN MOVPE, TMG reacts with H_2 and $(CH_3)_2GaNH_2$ adduct is not produced. On the other hand, in case of AlN MOVPE, TMA reacts with NH_3 and $(CH_3)_2AlNH_2$ adduct is produced near the nozzle. For high quality AlN synthesis, AlN MOVPE growth equipment should be designed to inhibit $(CH_3)_2AlNH_2$ adduct production near the nozzle.

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