

Quantum-Chemical Study on the Mechanism of Atomic Layer Epitaxy of GaAs Using Arsine and Trimethylgallium

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The mechanism of atomic layer epitaxy of GaAs using arsine and trimethylgallium was studied in terms of quantum chemistry, using the calculation results of LEAF molecular orbital method. Some large GaAs clusters (~ 200 atoms) were adopted as models for the GaAs (001) surfaces and its electronic states were calculated and discussed. The total-energy changes with reactions of gas-phase molecules (H_2 , AsH_3 , and $Ga(CH_3)_3$) on surfaces were calculated by the LEAF method, considering the charge distribution in a system. The surface-localized occupied orbitals near HOMO and the pronounced stability of hydrogen adsorption on the As surface are pointed out as clues which could reveal the mechanism of atomic layer epitaxy of GaAs.

1. INTRODUCTION

The atomic layer epitaxy (ALE) [e.g., 1-5] is a key technology which could realize the atomistic fabrication of semiconductor devices. It is helpful to the design of ALE processes to understand the elementary reaction processes in the epitaxial growth in terms of quantum chemistry. Such a study was already tried for the epitaxial growth mechanism of a Ga layer on the (001) As surface of GaAs crystal [6]. We are now interested in the self-limiting processes and the selective epitaxial growth on surfaces of GaAs crystal.

In this paper, we adopt some large clusters as models of surfaces of GaAs crystal, and calculate the electronic structures and the total-energy changes of the systems involved with the surface reactions in ALE using arsine (AsH_3) and trimethylgallium (TMG). Using the calculation results, the self-limiting mechanism and the selective epitaxial growth are discussed.

2. THEORY AND CALCULATION

The electronic structure calculations are done by LEAF molecular orbital method [7] using

the parameters derived from spectra and ab-initio calculations of free atoms only [8].

The total-energy formula in the LEAF theory is

$$E = \sum_i v_i \varepsilon_i + \text{const.} + \sum_{\alpha} (1/2) Q_{\alpha} (Q_{\alpha} - 1) \gamma_{\alpha} + \sum_{\alpha < \beta} \sum Q_{\alpha} Q_{\beta} e^2 / |\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|, \quad (1)$$

where ε_i denotes the i -th one-electron (noniterative) orbital energy, v_i the occupation number of the orbital, 'const.' the constant term against variations of atomic and electronic configurations, Q_{α} the zeroth order charge of the α th atom, and $\mathbf{R}_{\alpha}$ the position vector of the α th atom. In Eq.(1), the first sum plus the constant term corresponds to the zeroth order term and the second sum plus the third sum corresponds to the first-order correction in the many-body perturbation formalism. In actual calculations, we adopt the Mulliken charge as Q_{α} .

In order to check the accuracy of the LEAF method for GaAs system, we calculated the equilibrium internuclear distances and the dissociation energies of AsH , GaH , and H_2 . The calculation results reproduce the experimental internuclear distances in the accuracy of 0.1 Å and the relative magnitudes of the experimental

dissociation energies.

3. MODEL FOR GaAs SURFACE

The pyramid-shaped clusters as shown in Fig. 1 are adopted as the (001) surfaces of GaAs crystal. The configurations of Ga and As atoms in these clusters are identical with those in GaAs crystal. The bottom of the pyramid corresponds to the (001) surface. All other boundary atoms of the cluster are capped with hydrogen (H) atoms where the distance between a boundary atom and the cap atom is 1.5Å and the direction of cap bond is identical with the Ga-As bond direction in the crystal.

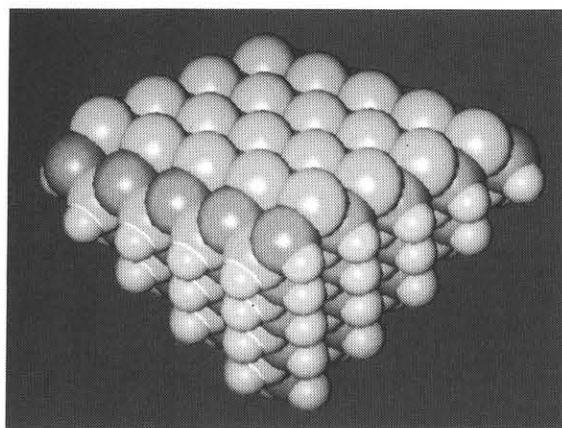


Fig.1 A Model for the Ga (001) Surface of GaAs Crystal

The radius of each sphere is the van der Waals radius of the atom. This cluster has 20 Ga atoms at the surface.

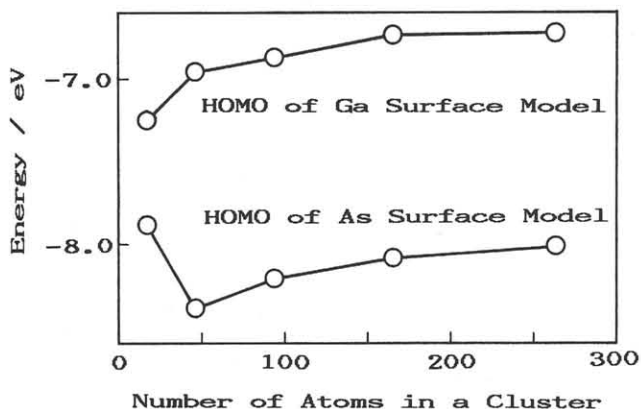


Fig.2 Energy Levels of HOMOs of Models for Ga and As (001) Surface of GaAs Crystal as Functions of the Cluster Size

In Fig.2, the calculated energies of the heighest occupied molecular orbitals (HOMOs) of the Ga and As surface models are described as functions of the size of the models. The HOMO energy levels of the Ga and As surface models converge to -6.72eV and -8.02eV, respectively, as the the cluster size increases. In this work, we take the clusters at the size of 165 atoms, $\text{Ga}_{80}\text{As}_{85}\text{H}_{50}$ and $\text{As}_{80}\text{Ga}_{85}\text{H}_{50}$, as the Ga and As surface models, respectively.

4. KEY ORBITALS IN REACTIONS AT SURFACE

The distribution of surface-localized one-electron states (SLSs) near HOMO is shown in Table 1. The Ga surface has more vacant SLSs near HOMO than the As surface, and the As surface has more occupied SLSs near HOMO than the Ga surface. Thus the Ga surface could behave as a Lewis acid and the As surface as a Lewis base. However, the Ga surface has 6 occupied SLSs around -7.1 eV and their energy levels are heigher than the levels of the occupied SLSs of the As surface. Accordingly, the electron donation from the occupied SLSs of the Ga surface should be considered in the surface reactions as well as that of the As surface.

The one-electron states (or orbitals) around the HOMOs and the lowest unoccupied molecular orbitals (LUMOs) of TMG and AsH_3 are described in Table 2. The table shows that the LUMO of TMG represents the Lewis acidity and the HOMO of AsH_3 represents the Lewis basicity. However, both the naked Ga and As surfaces more or less have the Lewis basicity and acidity at the same time according to the distribution of SLSs near HOMO (Table 1). If this argument is true, both the AsH_3 and TMG are expected to be easily adsorped on the naked Ga and As surfaces. In addition to it, both the As-H anti-bonding orbitals in AsH_3 and the Ga-C anti-bonding orbitals in TMG are vulnerable to the electron donation from the occupied SLSs near HOMO at the Ga and As surfaces and drive the decomposition of AsH_3 and TMG on the naked

surfaces.

Table 1 Distribution of Surface-Localized One-Electron States near HOMO in the Models for the Ga and As (001) Surfaces of GaAs Crystal

(a) Ga surface model (HOMO: -6.73eV)		
energy/eV	N	Nocc
-6.65 ~ -6.55	6	0
-6.75 ~ -6.65	6	1
....		
-7.05 ~ -6.95	4	4
....		
-7.25 ~ -7.15	2	2
(b) As surface model (HOMO: -8.08eV)		
energy/eV	N	Nocc
-8.05 ~ -7.95	6	0
....		
-8.45 ~ -8.35	6	6
-8.55 ~ -8.45	6	6

Table 2 Orbitals around the HOMOs and the LUMOs of AsH₃ and TMG

(a) AsH ₃			
Energy/eV	N	Nocc	Character
-3.68 (LUMO)	4	0	As-H anti-bonding
-10.25 (HOMO)	2	2	As-localized
(b) TMG			
Energy/eV	N	Nocc	Character
-3.06	6	0	Ga-C anti-bonding
-4.14 (LUMO)	2	0	Ga-localized
-10.75 (HOMO)	4	4	Ga-C bonding

N: Number of one-electron states.

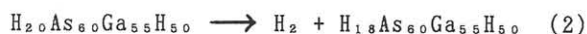
Nocc: Number of occupied states.

5. INERT COATING ON SURFACE

If the resultant adsorbed species after the decomposition on the surfaces have no ligands (H in AsH₃, CH₃ in TMG), the epitaxial growth on the GaAs cannot be stopped at one atomic layer because there are the reactive occupied orbitals at the (Ga or As) surface. Here we assume the ligand-capped (As/Ga) atomic layer after the decomposition of (AsH₃/TMG) source molecules on the naked (Ga/As) surface

(see Fig.3). According to the electronic structure calculations of the H-coated As layer (H₂₀As₆₀Ga₅₅H₅₀) and the CH₃-coated Ga layer ((CH₃)₂₀Ga₆₀As₅₅H₅₀), there is no reactive orbitals localized at the surface, i.e., at the ligand coating while there still exist the electron-donating reactive orbitals localized at the (As/Ga) atomic layer beneath the coating.

The formation of CH₃-coating on the Ga atomic layer has been already proposed to interpret the experimental data in ALE [9]. We calculated the stability of the models for H-coatings on As and Ga atomic layer (H₂₀As₆₀Ga₅₅H₅₀ and H₂₀Ga₆₀As₅₅H₅₀; H-As, H-Ga ⊥ surface, H-As=H-Ga=1.5 Å). The dissociation of an H₂ molecule from the H-coated surfaces represented as



have the calculated dissociation energy of +11.90eV and -4.33eV, respectively. Thus the H-coating on the As layer is very stable in contrast with the H-coating on the Ga layer.

6. SELECTIVITY IN SURFACE REACTIONS

Certainly, the self-limiting mechanism could be explained by the the inert ligand-coating, but it cannot explain the layer-by-layer epitaxial growth, i.e., the reaction of AsH₃ on the CH₃-coated Ga layer and the reaction of TMG on the H-coated As layer.

According to the zeroth order calculation of the charge distribution, the surfaces of AsH₃ and the H-coated As layer are negatively charged (Q_H = -0.14e and -0.11e, respectively), and the surfaces of TMG and the CH₃-coated Ga layer are positively charged (Q_H = +0.07e and +0.08e, respectively). Thus, by the attractive electrostatic interactions, it can be expected that TMG stays on the H-coated As layer longer than AsH₃, and that AsH₃ stays on the CH₃-coated Ga layer than TMG. During the longer stay on the coating, TMG/AsH₃ may have the opportunity to interact with the reactive

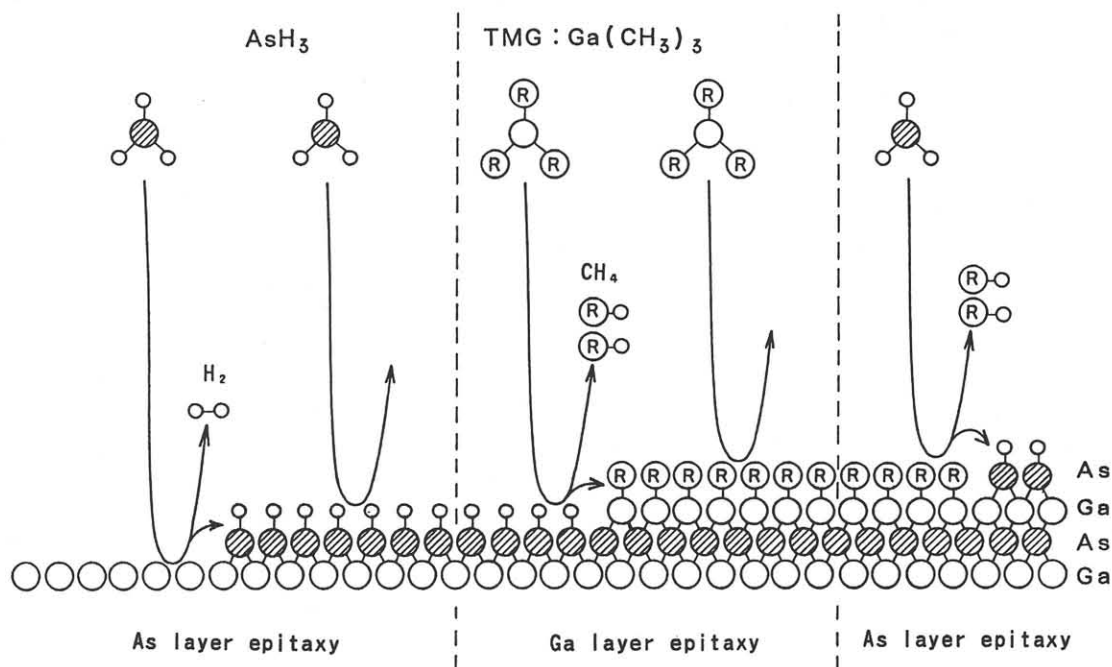
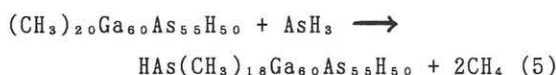
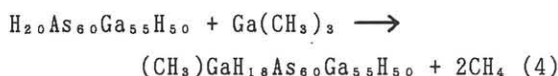


Fig.3 A Model for ALE growth of GaAs crystal

orbitals of the As/Ga layer beneath the coating by the thermal fluctuation of the coating ligands. On the other hand, AsH₃ and TMG would be eventually excluded from the H-coating and the CH₃-coating, respectively (see Fig.3). In addition to it, the above surface reactions represented as



are exothermic according to the calculation of the total-energy change with reactions ($\Delta E = -1.16\text{eV}$ and -8.21eV respectively).

7. CONCLUSION

The mechanism of ALE of GaAs crystal using AsH₃ and TMG was quantum-chemically studied using LEAF molecular orbital method. The Ga₆₀As₅₅H₅₀ and As₆₀Ga₅₅H₅₀ pyramid-shaped clusters were adopted as models for the Ga and As (001) surfaces. The self-limiting and the layer-by-layer processes in the ALE were discussed in terms of the SLSs near HOMO and the inert ligand coatings. Especially, we pointed out the importance of the stable

H-coating on As layer in the ALE.

ACKNOWLEDGMENT

The authors would like to thank Dr. Y. Fujisaki for valuable discussions.

REFERENCES

- [1] J. Nishizawa et al., J. Electrochem. Soc. 132 (1985) 1197.
- [2] S. M. Bedair et al., Appl. Phys. Lett. 47 (1985) 51.
- [3] A. Doi et al., Appl. Phys. Lett. 49 (1986) 785.
- [4] M. Ozeki et al., Appl. Phys. Lett. 53 (1988) 1509.
- [5] H. Ohno et al., Appl. Phys. Lett. 54 (1989) 2000.
- [6] M. Tsuda et al., Jpn. J. Appl. Phys. 27 (1988) 1960.
- [7] R. Irie, Theor. Chim. Acta 70 (1986) 239; R. Irie, PACIFICHEM'89, INFO-54, 1989; R. Irie, JCPE Newsletter, vol. 1, no. 4, p. 24 (March 1990); R. Irie, Theor. Chim. Acta, in press.
- [8] C. E. Moore, Atomic Energy Levels, Circular of the National Bureau of Standards 467, 1949, 1952; E. Clementi et al., Atomic Data and Nuclear Data Tables 14 (1974) 177.
- [9] J. Nishizawa et al., Surface Science 185 (1987) 249.