

Cluster model study on GaAs epitaxial crystal growth by arsenic molecular beam

II. Mechanism involving a GaAs₂ intermediate cluster

Y. Fukunishi and H. Nakatsuji

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Sakyou-ku, 606 Kyoto, Japan

and

Institute for Fundamental Chemistry, 34-4 Takano-Nishihiraki-cho, Sakyou-ku, 606 Kyoto, Japan

Received 2 February 1993; accepted for publication 23 March 1993

The mechanisms of the GaAs epitaxial crystal growth by Ga atomic and As₂ molecular beams on Ga-stabilized and As-stabilized GaAs(100) surfaces are studied with the use of the cluster model and the Hartree–Fock method. We propose the mechanism involving the formation of the GaAs₂ cluster as an intermediate. When the As₂ beam is irradiated on the surface, the GaAs₂ cluster is generated from As₂ and a free Ga atom without energy barrier. This GaAs₂ is adsorbed on the As-stabilized surface and gives a new Ga-layer on the surface and the As₂ remains to the molecularly adsorbed on the new Ga layer without an activation energy. On the other hand, the adsorption of this GaAs₂ on the Ga-stabilized surface gives a new As layer and the remaining Ga atom migrates on the surface to make a new Ga layer. The mechanism involving the dissociative adsorption of As₂ studied previously and the presently proposed mechanism involving the GaAs₂ intermediate cluster are compared and it is concluded that the present mechanism is more favorable than the previous one. We summarize the overall reaction mechanism of the GaAs epitaxial crystal growth by the Ga atomic and As₂ molecular beams.

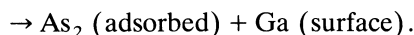
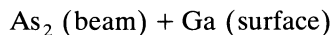
1. Introduction

The mechanism of GaAs crystal growth in molecular beam epitaxy (MBE) has been studied extensively by both experimental and theoretical methods. Arthur [1] and Foxon et al. [2,3] investigated the adsorption mechanisms of the As₂ and As₄ clusters on the GaAs surface. The mechanism of the As₂ adsorption they proposed is as follows: the As₂ molecule reaches the GaAs surface and is adsorbed and migrates as a precursor species. This precursor dissociates into two As atoms at an active Ga site, making the Ga–As bond with the surface Ga atom and the crystal grows. However, since this argument is based on the reaction rate theory and since this reaction has not been observed explicitly by an experimen-

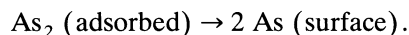
tal technique, the details of the actual crystal growth mechanism are not yet known. In particular, we have to clarify what is the precursor species and the role of the active Ga site. If molecularly adsorbed As₂ does not arrive at the active Ga site, it may be desorbed from the surface as an As₂ or As₄ cluster.

The crystal growth mechanism in the metal-organic MBE (MOMBE) has been studied theoretically using small cluster models, but there are very few reports about the growth mechanism of the GaAs crystal in MBE [4–9]. In our previous report, the reactions of the As₂ beam on the Ga-stabilized GaAs(100) surface have been studied by the cluster model combined with the ab-initio method [10]. It was clarified that the As₂ molecule irradiated on the surface is molecularly

adsorbed on a flat surface and at the step site with the energy barriers of 23.5 and 9.6 kcal/mol, respectively, and migrates on the surface.

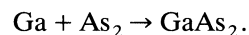


The dissociative adsorption does not occur on a flat surface but occurs on a step site with an energy barrier of 16.9 kcal/mol and with an appreciable stabilization energy.

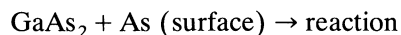


In MBE, the GaAs surface is heated up at about 600 K for generating a free Ga atom on the surface whose life time is about 0.1 s and it is said that this species plays an important role in the crystal growth, though the actual reaction of the free Ga atom and its product remain to be clarified. In the present study, we examine the role of the free Ga atom in the crystal growth mechanism, assuming the following reaction steps.

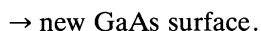
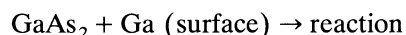
(step 1) The As₂ beam reaches on the surface, reacts with the free Ga atom on the surface and gives a GaAs₂ cluster.



(step 2) The GaAs₂ cluster thus generated reacts with the GaAs surface and leads to the crystal growth. There are two possibilities: the Ga site of the GaAs₂ cluster reacts with the As-stabilized surface or the As site of the GaAs₂ cluster reacts with the Ga-stabilized surface.



or



In the following section, we explain the details of the computational method. In section 3, the reaction of As₂ with a free Ga atom (step 1) is examined and in sections 4 and 5, the above two reactions of step 2 are studied. Throughout the calculations, the GaAs surface is simulated by the small cluster model.

2. Computational method

Fig. 1 shows Ga₅As₄H₁₁ and Ga₈As₈H₁₈ clusters which simulate the As-stabilized and Ga-

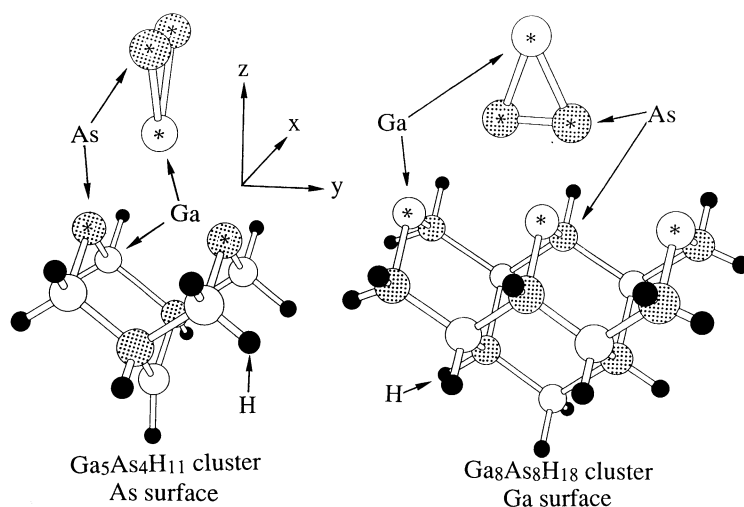


Fig. 1. Ga₅As₄H₁₁ and Ga₈As₈H₁₈ clusters interacting with GaAs₂. The atoms indicated by the asterisks are treated with the double zeta basis and the others are with minimal basis.

stabilized GaAs(100) surfaces, respectively. The GaAs₂ molecule approaches and reacts with the cluster in two alternative ways shown in fig. 1, which are discussed in sections 4 and 5, respectively. The Ga and As atoms are located at the crystal lattice whose lattice constant is 5.654 Å [11]. The H atoms cap the artificial dangling bonds of the Ga₅As₄ and Ga₈As₈ clusters except for the surfaces. The covalent bonding crystal has often been simulated by the cluster model whose dangling bonds are capped by hydrogen atoms [12–14]. The Ga–H and As–H lengths are fixed to 1.663 and 1.511 Å, respectively, which are the bond lengths of the free GaH and AsH₃ molecules, respectively [15].

The Gaussian basis sets for the Ga and As atoms are double zeta (3s3p)/[2s2p] sets for the important atoms and minimal (3s3p)/[1s1p] sets for the less important atoms [17]; the double zeta basis sets are used for the two As atoms and for the three Ga atoms located on the surface of the cluster and the other As and Ga atoms of the cluster are treated with the minimal basis sets. The atoms treated with the double zeta basis are indicated by the asterisks in fig. 1. The Ne cores are replaced by the effective core potential [17]. For the capping H atoms, the STO-3G basis is used [18].

All calculations are carried out by the Hartree–Fock (HF) method with the use of the HONDO7 program [16]. Since the systems simulating the reaction steps 1 and 2 include GaAs₂ whose ground state is doublet, the calculations are performed by the Roothaan open-shell HF method. The Møller–Plesset second order perturbation (MP2) method which was used in our previous study is useful for estimating the correlation energy of large cluster systems. This method is popular for calculating closed-shell singlet states well approximated by the HF wave function, but the use for doublet and triplet states is not general. The previous study showed that the HF method does not give identical results as the MP2 method, but the implications of the HF potential curves, like the positions of the minimum and maximum, are roughly equal to those of the MP2 potential curves. Furthermore, the results for the GaAs₂ cluster and As₂ calculated by

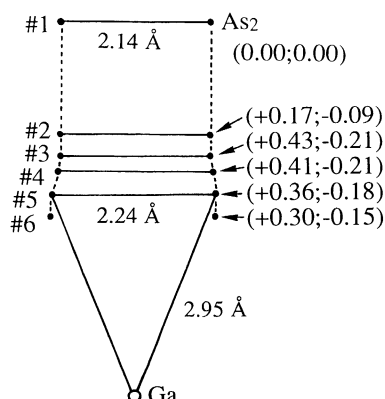


Fig. 2. Reaction path for the Ga + As₂ system, which is assumed to keep the C_{2v} symmetry. The values in the left- and right-hand sides in the parentheses show the gross charges of the Ga and As atoms, respectively.

the HF method are similar to the results of the multi-reference CI calculations [10,19]. Then, we perform only the ROHF method and further electron correlation effect is not considered in this study.

3. Reaction of an As₂ beam with a Ga atom

We calculate here the reaction of the As₂(¹Σ⁺) beam with the Ga(²P) atom as a beam or on the surface using the double zeta basis set for the Ga and As atoms. The reaction path, which is as-

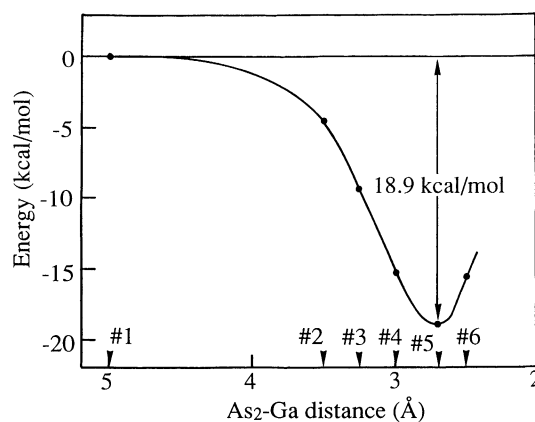


Fig. 3. Potential curve for the Ga + As₂ system along the reaction path shown in fig. 2.

sumed to keep the C_{2v} symmetry, and the Mulliken gross charge of the Ga and As atoms are shown in fig. 2. At point 1, the As–As bond length is kept to 2.14 Å which is the optimized value for the free As₂ molecule. The potential curve along the reaction path is shown in fig. 3. The As₂ cluster approaches the Ga atom without energy barrier and reaches the equilibrium at point 5. The calculated heat of formation of the GaAs₂ cluster is 18.9 kcal/mol. The optimized As–As length is 2.24 Å, which is slightly longer than 2.14 Å of free As₂, and the optimized Ga–As length is 2.95 Å. These values are very similar to the values reported by Balasubramanian: the As–As length 2.2 Å, the Ga–As length 2.85 Å, and the heat of formation, 30.3 kcal/mol [19]. At point 5, the charges of the Ga and As atoms are +0.36 and –0.18, respectively; 0.36 electron is transferred from the Ga atom to As₂.

Since the potential curve is attractive and the potential minimum is deep enough to keep the GaAs₂ cluster, the As₂ beam reacts with the Ga atom on the GaAs surface heated at 600 K to give the GaAs₂ cluster on the surface and this cluster does not dissociate on the surface.

The orbital correlation diagram is shown in fig. 4. The electron donation from the singly occupied p_y orbital of the Ga atom to the π_z^* anti-bonding

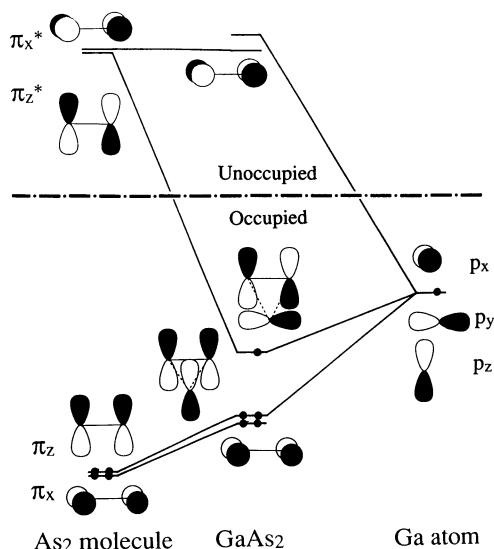


Fig. 4. Orbital correlation diagram for the Ga + As₂ system.

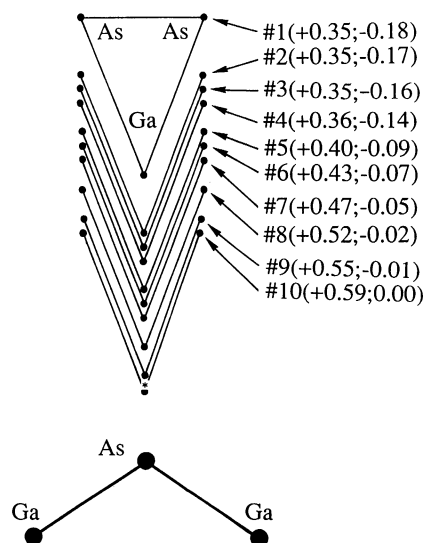


Fig. 5. Reaction path for the GaAs₂ adsorption on an As-stabilized GaAs(100) surface with keeping the C_{2v} symmetry. The values in the left- and right-hand sides of the parentheses are the charges of the Ga and As atoms, respectively. The asterisk indicates the position of the Ga atom in the GaAs crystal lattice without surface relaxation.

orbital of As₂ and the back donation from the π_z bonding orbital of As₂ to the p_z orbital of the Ga atom are important to make the Ga–As bond. The doubly occupied π_x bonding orbital of the As₂ does not react and keeps the As–As bond. The electron donation from the Ga atom to the As₂ molecule causes the polarization of the GaAs₂ cluster as the reaction proceeds.

4. Adsorption of the GaAs₂ cluster on an As-stabilized GaAs surface

The approach of the GaAs₂ cluster onto the As-stabilized GaAs surface is simulated by the cluster model shown on the left-hand side of fig. 1. Fig. 5 shows the different views of the reaction path and the electronic charges of the Ga and two As atoms. Throughout the reaction, the system is kept in C_{2v} symmetry and only the Ga and As atoms belonging to the GaAs₂ cluster are optimized with the Ga₅As₄H₁₁ cluster fixed. The geometry of the optimized reaction path is shown

Table 1
Geometries of the Ga and As atoms of the GaAs₂ cluster along the reaction path shown in fig. 5^{a)}

Position	Cartesian coordinate (Å)		
	As		Ga
	x	z	z
1	1.122	7.729	5.0
2	1.122	6.729	4.0
3	1.122	6.229	3.5
4	1.122	5.729	3.0
5	1.122	5.479	2.75
6	1.122	5.229	2.5
7	1.122	4.729	2.0
8	1.122	4.429	1.7
9 (minimum)	1.122	4.0	1.5
10	1.122	3.65	1.3

^{a)} Point (0, 0, 0) is on the center of the surface two As atoms. The z-axis is vertical to the surface, the x-axis is parallel to the As-As bond of the GaAs₂ cluster and the y-axis is parallel to the two surface As atoms shown in fig. 1.

in table 1: the accuracy is within 0.1 Å. The potential curve along the path is shown in fig. 6.

At point 1, GaAs₂ is kept at the geometry of the free GaAs₂ molecule optimized in section 3. The GaAs₂ cluster approaches the surface and is adsorbed without an energy barrier. The mini-

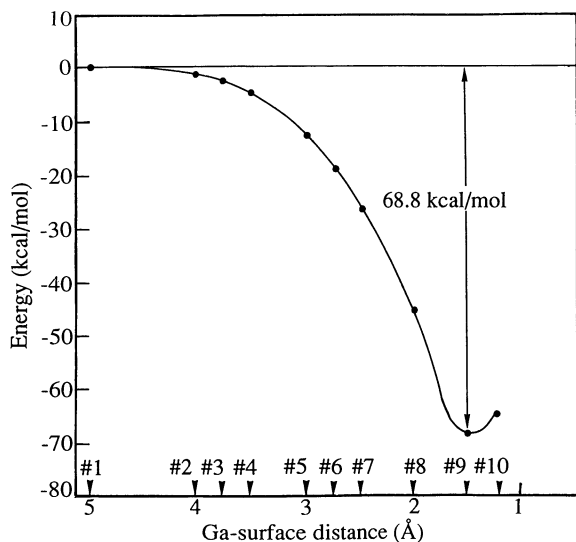
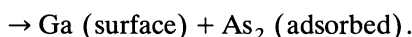


Fig. 6. Potential curve for the GaAs₂ adsorption on an As-stabilized GaAs surface along the reaction path shown in fig. 5.

um of the molecular adsorption is found at point 9 with a calculated adsorption energy of 68.8 kcal/mol. At this point, the GaAs₂ cluster becomes smaller than the free one, that is, the Ga-As bond length is 2.55 Å which is shorter than 2.95 Å of the free GaAs₂ cluster and the As-As bond length is 2.22 Å which is slightly longer than 2.24 Å of free GaAs₂. This geometry is similar to molecularly adsorbed As₂ on the Ga-stabilized GaAs(100) surface for which the Ga-As length is 2.55 Å and the As-As bond length is 2.4 Å as reported in our previous study [10].

The asterisk in fig. 5 shows the position of the Ga atom in the GaAs crystal lattice without surface relaxation: the difference from the Ga atom at the equilibrium position 9 is only 0.1 Å. Since the distance between the Ga atom of the GaAs₂ cluster and the As atom of the surface is only 2.50 Å which is close to the Ga-As distance in the crystal, 2.45 Å, the Ga atom of the GaAs₂ cluster makes a bond with the surface As atoms. The gross charges of the Ga and As atoms in the GaAs₂ cluster change monotonously and uniformly. The As atoms become neutral as the reaction proceeds and the Ga atomic charge increases up to +0.55. The total charge of the GaAs₂ cluster changes from +0.0 at point 1 to +0.53 at point 9. This shows the occurrence of the electron donation from GaAs₂ to the surface in the course of the adsorption.

The GaAs₂ cluster is adsorbed on the GaAs surface without energy barrier. The Ga-As bond of the GaAs₂ cluster becomes weak and the Ga atom is put onto the lattice site of the GaAs crystal: the two As atoms of the GaAs₂ cluster become molecularly adsorbed As₂ on the surface. Namely, the GaAs₂ adsorption gives a new Ga surface on the As-stabilized surface and a molecularly adsorbed As₂ species.



This reaction has no energy barrier and therefore this mechanism is more favorable than the direct adsorption of As₂ whose energy barrier is 23.5 kcal/mol for a flat GaAs surface and 9.6 kcal/mol

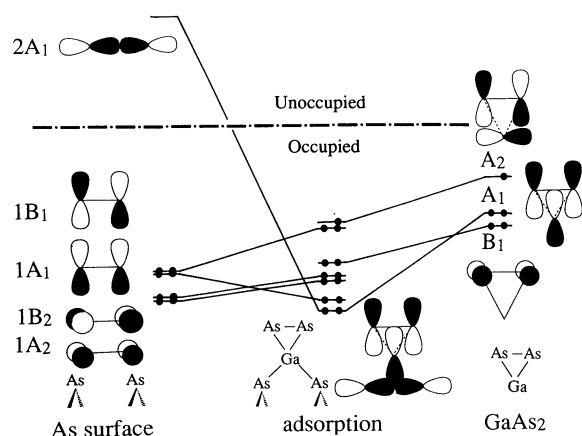
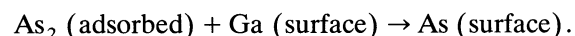


Fig. 7. Orbital correlation diagram for the reaction of the Ga₅As₄H₁₁ + GaAs₂ system. Since the orbitals of the Ga₅As₄H₁₁ cluster localize on the surface As atoms, only the two As atoms are displayed.

for a step site as shown in the previous paper [10]. Through the formation of the intermediate GaAs₂ cluster, the As₂ beam gives molecular adsorption of As₂ without activation energy. Furthermore, as shown in the previous paper [10], this molecularly adsorbed As₂ on a Ga surface is dissociated with 16.9 kcal/mol at its step site: thus a new As surface is generated again on the Ga surface, and the reaction cycle is closed.



This cyclic generation of similar As (surface) as in the above equation is an essential aspect of the crystal growth.

The adsorption mechanism of the GaAs₂ cluster is qualitatively explained by the orbital correlation diagram shown in fig. 7. Orbitals playing a role in the reaction are the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and their neighboring orbitals which correspond to the dangling bonds localized on the two surface As atoms. Only two surface As atoms and the orbitals localized on them are displayed in fig. 7. The electron donation from the A₁ orbital of the GaAs₂ cluster to the LUMO of the GaAs surface facilitates the adsorption and makes the Ga–As bond of the GaAs₂ cluster weak, causing the total charge of the adsorbed GaAs₂ cluster to increase from

+0.0 to +0.53. The other B₁ and A₂ orbitals of the GaAs₂ cluster are not active in this reaction and keep the Ga–As and As–As bond of the GaAs₂ cluster. The occupied orbitals, B₂, A₂, B₁, and A₁ orbitals of the surface are also not activated. The electron donation from GaAs₂ to the surface occurs smoothly, so that this reaction does not require any activation energy. The gross charge of the As atom of the adsorbed GaAs₂ cluster is –0.01 which is similar to the values of the molecularly adsorbed As₂ which are previously reported to be –0.11 for the adsorption on a flat Ga-stabilized surface and –0.03 for the adsorption on a step site of the GaAs crystal [10].

5. Adsorption of the GaAs₂ cluster on a Ga-stabilized GaAs surface

The As-stabilized GaAs(100) surface is simulated by the Ga₈As₈H₁₈ cluster shown on the right-hand side of fig. 1. Throughout the reaction, the system is kept to C_{2v} symmetry and only the Ga and As atoms belonging to the GaAs₂ cluster are optimized with the Ga₈As₈H₁₈ cluster fixed. Fig. 8 and table 2 show the optimized reaction path: the accuracy is within 0.1 Å. The gross

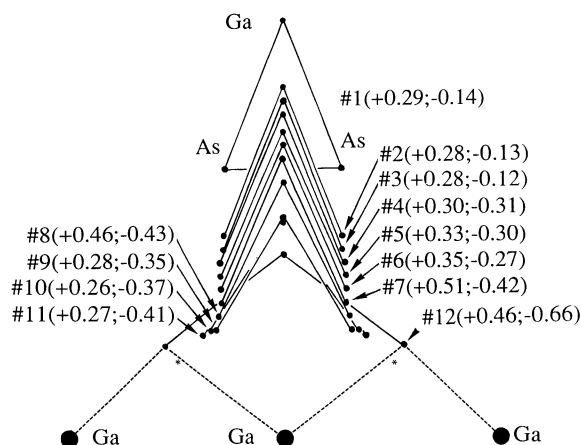


Fig. 8. Reaction path for the GaAs₂ adsorption on a Ga-stabilized GaAs(100) surface with keeping the C_{2v} symmetry. The values in the left- and right-hand sides of the parentheses are the charges of the Ga and As atoms, respectively. The two asterisks indicate the positions of the As atom in the GaAs crystal lattice without surface relaxation.

Table 2
Geometries of the Ga and As atoms of the GaAs₂ cluster along the reaction path shown in fig. 8^{a)}

Position	Cartesian coordinate (Å)		
	As		Ga
	y	z	z
1	1.122	5.0	7.729
2	1.122	3.75	6.479
3	1.122	3.5	6.229
4 (maximum)	1.15	3.25	5.979
5	1.15	3.0	5.729
6	1.15	2.75	5.479
7	1.15	2.5	5.229
8 (minimum)	1.2	2.25	4.77
9 (maximum)	1.25	2.0	4.12
10	1.35	2.0	4.1
11	1.5	1.9	4.0
12 (minimum)	2.2	1.7	3.429

^{a)} Point (0, 0, 0) is on the surface center Ga atom. The z-axis is vertical to the surface and the y-axis is parallel to the As-As bond of the GaAs₂ cluster shown in fig. 1.

charges of the Ga and As atoms of the GaAs₂ cluster are shown at the left and right-hand sides, respectively, in the parentheses of fig. 8. The calculated potential curve along the path is shown in fig. 9.

The potential curve has two minima at points 8 and 12 and two maxima at points 4 and 9: passing through the initial barrier at point 4, GaAs₂ reaches the molecular adsorption state at point 8 and then going over the barrier at point 9, it is dissociatively adsorbed at point 12. At point 1, the GaAs₂ cluster is kept to the geometry of the free GaAs₂ molecule. The GaAs₂ cluster is let to approach the surface horizontally and reach the first transition state at point 4 whose energy barrier is 4.8 kcal/mol. The molecular adsorption is found at point 8 with an adsorption energy of 48.4 kcal/mol. At this point, the As-As length is 2.4 Å, slightly longer than 2.24 Å of free As₂, and the charges of the Ga and As atoms are +0.46 and -0.43, respectively. Beyond this point, the system reaches the second transition state at point 9: the energy barrier from the molecular adsorption state is only 3.3 kcal/mol. Finally, the As-As bond is dissociated completely and is adsorbed at point 12 with an adsorption energy of 86.8 kcal/mol. The optimized structure at point 12 is not identical with the GaAs lattice structure at point 12 which is indicated by the asterisks in fig. 6. The charges of the adsorbed Ga and As atoms are +0.46 and -0.66, respectively, and the latter

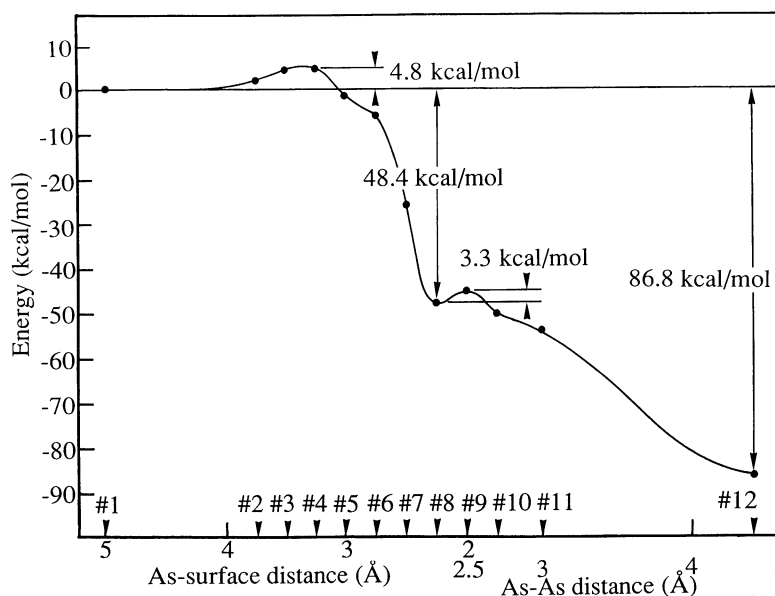


Fig. 9. Potential curve for the GaAs₂ adsorption on the Ga-stabilized GaAs surface along the reaction path shown in fig. 8.

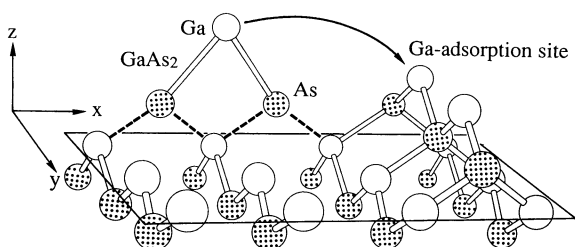


Fig. 10. Adsorbed GaAs₂ cluster (left-hand side) and Ga-adsorption site (right-hand side) on a GaAs surface. The filled and empty circles represent As and Ga atoms, respectively. The adsorbed GaAs₂ is located at the optimized geometry (point 12) of fig. 8 and the arrow represents a migration path of the Ga atom.

is smaller than -0.48 , the charge of the inner As atom of the crystal.

We show in fig. 10 the dissociatively adsorbed GaAs₂ cluster at point 12 on the left-hand side and the Ga adsorption site on a GaAs surface on the right-hand side. Since the Ga atom is adsorbed at the bridge site of the As-stabilized surface, the alignment of the As atoms along the y -axis gives the Ga adsorption site. On the other hand, the alignment of the As atoms along the x -axis does not give the Ga adsorption site. Comparing fig. 10 with the Ga₈As₈H₁₈ cluster shown in fig. 1, it is shown that the Ga₈As₈H₁₈ cluster is too small as a surface to give the Ga adsorption

site. Since the adsorbed As atoms originating from the GaAs₂ cluster aligns along the x -axis, the Ga atom on them is not at the most stable Ga-adsorption site. Therefore, after the adsorption of the GaAs₂ cluster, the Ga atom migrates on the surface as indicated by an arrow in fig. 10 and occupies the most stable Ga adsorption site. Another possibility is the coadsorptions of many GaAs₂ clusters along the y -axis and the shift of the Ga atom at the bridge site of the two As atoms along the x -axis, giving another empty Ga site opposite to it. Anyway, the cluster model representing this reaction is too large to make the calculation feasible. Furthermore since the present model cluster is restricted to satisfy the C_{2v} symmetry, the Ga atom of GaAs₂ must be located on the C₂ axis and therefore cannot reach the Ga site of the GaAs crystal lattice. The calculated energy barrier for the dissociation, i.e. 3.3 kcal/mol, would therefore be larger than the true value.

Since the calculated energy barriers for the molecular and dissociative adsorption are less than 5 kcal/mol, the GaAs₂ cluster would be easily adsorbed and dissociated on the Ga-stabilized surface and gives a new As layer.

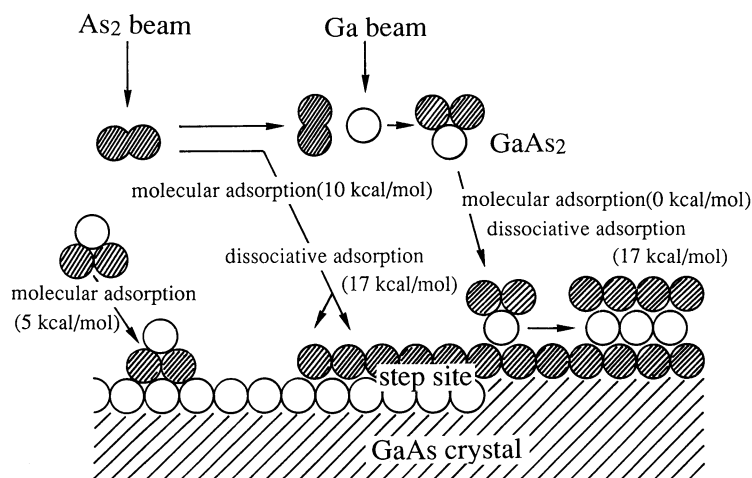
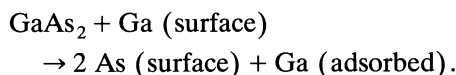
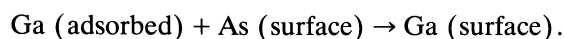


Fig. 11. Schematic representation of the crystal growth mechanisms by the As₂ beam epitaxy method. Only the most probable reactions are displayed. The hatched and empty circles represent As and Ga atoms, respectively. The value in the parentheses shows the energy barrier for each reaction.

The Ga atom is adsorbed on the As-stabilized GaAs surface without activation energy [4]. The adsorbed Ga atom migrates and gives a new Ga layer: the Ga-stabilized surface is again generated and the reaction cycle is closed.



Thus, the crystal grows continuously.

6. Conclusion and remarks

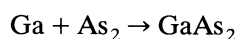
The activation energies calculated here are less than 5 kcal/mol and the reactions examined are all allowed. Without the restriction of the C_{2v} symmetry, we may expect lower activation energies, but the orbital correlation diagram indicates the preference of the C_{2v} symmetry. We therefore expect that the relaxation of the C_{2v} restriction would not much change the calculated results.

We propose in this paper the GaAs crystal growth mechanism involving the GaAs₂ cluster as an intermediate. The cluster GaAs₂ is easily formed from molecular As₂ and atomic Ga beams, and it is stable enough on a heated GaAs surface. The reaction of the GaAs₂ cluster on the As-stabilized surface occurs easily and the Ga atom is put into the crystal lattice and a new Ga layer grows on the As-stabilized surface. The As₂ of the GaAs₂ cluster is molecularly adsorbed on this new Ga surface without energy barrier. Likewise, the reaction of the GaAs₂ cluster on the Ga-stabilized surface occurs easily too and a new As layer grows on the Ga-stabilized surface. The Ga atom migrates on the surface and a new Ga layer grows on the As-stabilized surface.

This mechanism is more favorable than the previously studied direct adsorption mechanism of As₂ on a GaAs surface [10]. Previously, we have shown that As₂ is hardly adsorbed on the Ga-stabilized surface and the dissociative adsorption is less stable than the molecular adsorption. On the other hand, at the step site, the As₂ molecular adsorption can occur with an activation energy of 9.6 kcal/mol and the molecularly adsorbed As₂ cluster dissociates with an activation energy of 16.9 kcal/mol.

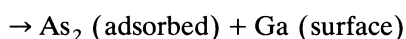
Based on the present and previous studies, the mechanism of the GaAs crystal growth using the Ga atomic and As₂ molecular beams may be summarized as follows and a qualitative illustration is given in fig. 11.

(1) The As₂ molecular beam reaches the GaAs surface and reacts with the free Ga atom or atomic beam to create a GaAs₂ cluster without activation energy. This species is stable on the surface.



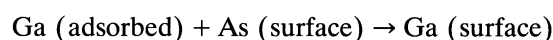
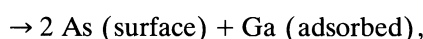
(activation energy = 0 kcal/mol).

(2) The GaAs₂ cluster is molecularly adsorbed on the As-stabilized surface without energy barrier and a new Ga layer grows: the Ga atom of the GaAs₂ is put onto the crystal lattice and the As₂ of the GaAs₂ is molecularly adsorbed on it.



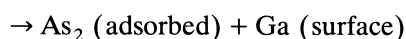
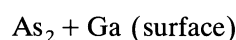
(activation energy = 0 kcal/mol).

(3) The GaAs₂ cluster is molecularly adsorbed on the Ga-stabilized surface with the energy barrier of 4.8 kcal/mol and a new As layer grows. The Ga atom of the GaAs₂ migrates on the surface and is adsorbed on the As-stabilized surface.



(activation energy = 4.8 kcal/mol).

(4) On the other hand, the direct adsorption path also exists, though it is less favorable than the above ones. Namely the As₂ cluster of the beam is molecularly adsorbed directly on the flat surface or at the step site of the Ga-stabilized surface with the activation energy of 23.5 or 9.6 kcal/mol, respectively.



(activation energy = 9.6 kcal/mol for step site, 23.5 kcal/mol for flat surface).

(5) Molecularly adsorbed As₂ given in steps (2) and (4) dissociates thermally with the activation energy of 16.9 kcal/mol, and a new As layer grows on the Ga-stabilized surface.

As₂ (adsorbed) → 2 As (surface)

(activation energy = 16.9 kcal/mol).

This step is the rate-determining step in the crystal growth reactions.

The reaction cycles (1) → (2) → (5) and (1) → (3) are closed, giving new As-stabilized and Ga-stabilized GaAs surfaces, respectively. Since the previous study showed that the Ga atom is adsorbed on the As stabilized GaAs surface without energy barrier and gives a new Ga layer on the surface [4], the reaction cycle (4) → (5) and the following Ga beam radiation is also closed and gives the As-stabilized and Ga-stabilized GaAs surface alternatively. However, the last cycle is less favorable because it involves step (4). In conclusion, we propose the reaction cycles (1) → (2) → (5) and (1) → (3) as the crystal growth mechanism of the GaAs crystal.

Finally, it must be noted that the reaction steps examined in the present and previous studies represent only one possibility for the reactions on the GaAs surface and other reactions may also be assumed; e.g. coadsorption is not examined in this study. However, the coadsorption of two As₄ clusters is believed to occur when the As₄ cluster beam is irradiated on the GaAs surface. This is the subject of our forth-coming article.

Acknowledgements

The calculations have been carried out with the FACOM M-1800 computer at the Data Pro-

cessing Center of Kyoto University and the HITAC M-680H computer at the Institute for Molecular Science. The authors thank the IMS computer center for the grant of computing time. Part of this study has been supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture.

References

- [1] J.R. Arthur, *Surf. Sci.* 43 (1974) 449.
- [2] C.T. Foxon, M.R. Boudry and B.A. Joyce, *Surf. Sci.* 44 (1974) 69.
- [3] C.T. Foxon and B.A. Joyce, *Surf. Sci.* 50 (1975) 434; 64 (1977) 293.
- [4] A.A. Bonapasta, M.R. Bruni, A. Lapicciarella, P. Nota, G. Scavia and N. Tomassini, *Surf. Sci.* 204 (1988) 273.
- [5] M. Tsuda, S. Oikawa, M. Morishita and M. Mashita, *Jpn. J. Appl. Phys.* 26 (1987) L564.
- [6] A. Doi, Y. Aoyagi and S. Namba, *Appl. Phys. Lett.* 48 (1986) 1787; 49 (1986) 785.
- [7] T. Ohno, *Phys. Rev. B* 44 (1991) 6306.
- [8] R.M. Graves and G.E. Scuseria, *J. Chem. Phys.* 95 (1991) 6602.
- [9] K. Balasubramanian, *J. Chem. Phys.* 87 (1987) 3518.
- [10] Y. Fukunishi and H. Nakatsuji, *Surf. Sci.* 291 (1993) 281.
- [11] K.H. Hellwege, W. Pies and A. Weiss, *Crystal Structure Data of Inorganic Compounds, Landolt-Börnstein, New Series, Group m, Vol. 7* (Springer, Berlin, 1979).
- [12] L.C. Snyder and Z. Wasserman, *Surf. Sci.* 71 (1978) 407; 77 (1987) 52.
- [13] A.C. Kenton and M.W. Ribarsky, *Phys. Rev. B* 23 (1981) 2897.
- [14] K. Hermann and P.S. Bagus, *Phys. Rev. B* 20 (1979) 1603.
- [15] J.H. Callomon, E. Hirota, K. Kuchitsu, W.J. Lafferty, A.G. Maki and C.S. Pote, *Structure Data of Free Polyatomic Molecules, Landolt-Börnstein, New Series, Group II, Vol 7* (Springer, Berlin, 1976).
- [16] M. Dupuis, J.D. Watts, H.O. Villar and G.H.B. Hurst, *Program Library No. 1501, Computer Center of the Institute for Molecular Science* (1987).
- [17] W.R. Wadt and P.J. Hay, *J. Chem. Phys.* 82 (1985) 284.
- [18] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* 51 (1969) 2567.
- [19] K. Balasubramanian, *J. Chem. Phys.* 86 (1987) 3410.