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Cluster model study on GaAs epitaxial crystal growth by an arsenic molecular beam III. As_4 molecular beam

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Abstract

We examined the mechanism of GaAs epitaxial crystal growth with an As_4 cluster beam on the Ga-stabilized GaAs(100) surface using the cluster model and the Hartree–Fock and Møller–Plesset second-order perturbation methods. Our results indicate that when the surface is irradiated with the As_4 beam, the As_4 cluster is adsorbed at a ditch site of the GaAs surface and dissociated: two As atoms are dissociatively adsorbed onto the surface to give a new As-layer and the other two As atoms are released into vacuum as an As_2 molecule. Alternatively, two As_4 clusters can be coadsorbed on the surface and dissociated: four atoms of the two As_4 clusters are dissociatively adsorbed on the surface to give a new As-layer and the other four As atoms are released into vacuum as an As_4 cluster. Thus, the present results confirm a previously proposed reaction.

1. Introduction

In this series of articles, we have investigated the mechanism of GaAs epitaxial crystal growth by an ab-initio quantum chemical method based on the cluster model. In the first paper of this series, we studied the molecular and dissociative adsorption of As_2 on the surface of GaAs and clarified the site effect of the surface [1]. In the second paper, we studied the mechanism of crystal growth through the formation of an intermediate $GaAs_2$ cluster [2]. In these studies we considered an As_2 molecular beam, which has a different reaction mechanism from an As_4 molecular beam. Although many more defects are observed in GaAs crystal produced by an As_4 beam than in that produced using an As_2 beam, the causes and the types of these defects are unclear [3]. In the present study, we examined the mechanism of epitaxial crystal growth using an As_4 cluster beam, assuming either a single As_4 cluster or two As_4 clusters [4,5].

At temperatures of 300–450 K, As_4 is physically adsorbed with an adsorption energy of 0.38 $\pm$ 0.03 eV (8.8 kcal/mol), and a surface migration energy barrier of 0.24 eV (5.5 kcal/mol) [3,4]. At an active Ga site, the molecularly adsorbed species is dissociated and a new As layer grows on the surface. Above 600 K, As_2 is lost

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due to dissociation from the GaAs surface, but this loss is supplied by irradiation of the surface with an As_4 cluster beam. When two As_4 clusters migrating on the surface collide with each other, they may form a state of coadsorption. The coadsorption state is decomposed into four dissociatively adsorbed As atoms and an As_4 cluster which is released into vacuum. Since this mechanism involves two As_4 clusters, and only one survives in the reaction, the sticking coefficient is always less than 0.5.

Several reaction mechanisms have been proposed for GaAs crystal growth in addition to the reaction model Foxon and Joyce derived experimentally. For example, Frolov et al. [6] proposed that $(GaAs)_n$ cluster generation is an intermediate step in a gas phase, while Lays and Veenvliet [7], and Nishijima and Kurabayashi [8] have proposed that adsorbed As_4 reacts with a free Ga atom on the surface.

Although the structures of As_2, As_4 and small GaAs clusters have been studied by the ab-initio molecular orbital method [9–15], except for the As hydride, their reactivities have not yet been reported [16–18].

In this study, we first examine the energetics of the following dissociation combination reactions,

$$As_4(gas) \leftrightarrow 2\ As_2(gas), \quad (1)$$

to confirm that the mechanism involving the As_4 cluster beam studied here is different from that involving the As_2 molecular beam studied previously [1,2]. In the previous study [2], we showed that the As_2 cluster reacts with a free Ga atom on the surface to give a $GaAs_2$ cluster, which is an important intermediate for crystal growth. In this study, we examine the possibility of the following similar reaction involving the As_4 cluster:

$$As_4(gas) + Ga(gas) \rightarrow GaAs_4(gas). \quad (2)$$

We also investigated the role of the As_4 cluster in two types of crystal growth.

(i) The surface reaction involves a single As_4 cluster: an As_4 cluster reaches the Ga-stabilized GaAs surface and is molecularly adsorbed:

$$As_4(gas) + Ga(surface) \rightarrow As_4(adsorbed) + Ga(surface). \quad (3)$$

The molecularly adsorbed As_4 is then dissociated into two As atoms which are adsorbed on the

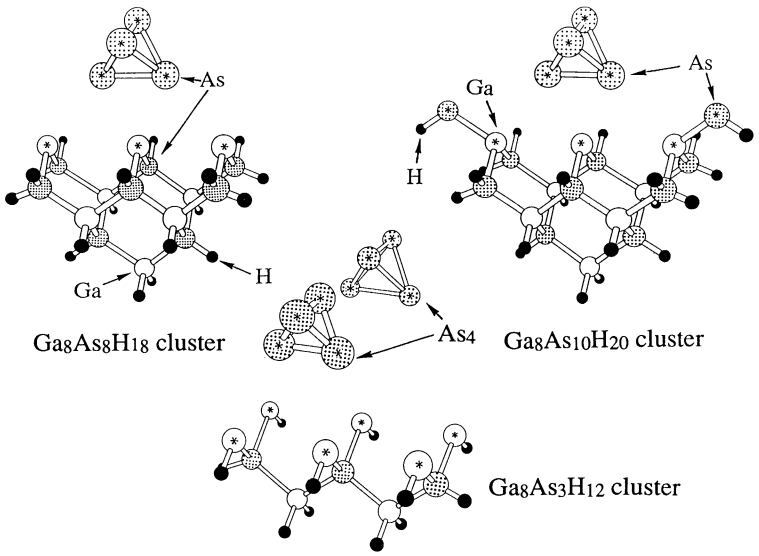

Fig. 1. $Ga_8As_8H_{18}$ and $Ga_8As_{10}H_{20}$ clusters interacting with As_4, and $Ga_8As_3H_{12}$ cluster interacting with two As_4 clusters. Th atoms marked by asterisks are treated with the SZP basis set while the others are treated with the minimal basis set.

surface to produce a new As layer, while the other two As atoms desorb from the surface as an As_2 molecule:

$$As_4(\text{adsorbed}) \rightarrow 2\ As(\text{surface}) + As_2(\text{gas}). \quad (4)$$

In this study, we examine the possibilities that the As_4 cluster reacts at either a flat surface or at a ditch site.

(ii) The surface reaction involves two As_4 clusters: either two As_4 clusters are adsorbed on the Ga-stabilized GaAs surface, or two adsorbed As_4 clusters migrate and form a coadsorption state:

$$2\ As_4(\text{adsorbed}) \rightarrow 2\ As_4(\text{coadsorbed}). \quad (5)$$

The two adsorbed As_4 then react to form an As_8 cluster, from which four As atoms are dissociatively adsorbed on the surface to produce a new As-layer, while the other four As atoms form an As_4 cluster and desorb from the surface:

$$2\ As_4(\text{coadsorbed}) \rightarrow 4\ As(\text{surface}) + As_4(\text{gas}). \quad (6)$$

In all of the following calculations, the GaAs surface is represented using the small cluster model.

2. Computational method

We used the Hartree–Fock (HF) optimization method followed by an energy calculation using the Møller–Plesset second-order perturbation (MP2) method. The calculations were performed using the HONDO7 software package [19]. For the open-shell system discussed in Section 4, we used a Roothaan-type open-shell HF method. Although it would have been preferable to perform geometric optimization using the MP2 method, our systems were too large to carry out such calculations.

Fig. 1 shows the $Ga_8As_8H_{18}$, $Ga_8As_{10}H_{20}$, and $Ga_8As_3H_{12}$ clusters which simulate the Ga-stabilized GaAs(100) surface, its ditch site for the adsorption of a single As_4 molecule and the Ga-stabilized GaAs(100) surface for the coadsorption of two As_4 molecules. Although these clusters may appear to be too small to represent the surface, cluster beam experiments using silicon clusters have shown that the cluster size effect converges with respect to the ionization potential and electron affinity, when the cluster is larger than 10 atoms [20,21].

In Fig. 1, a single As_4 molecule approaches and reacts with the $Ga_8As_8H_{18}$ and $Ga_8As_{10}H_{20}$ clusters, which represent a flat surface and a ditch site, respectively. The latter model may also represent the step effect, although the present cluster is small and the two edges are close to each other. These reactions are examined in Sections 5 and 6. The reaction of two As_4 molecules with the $Ga_8As_3H_{12}$ cluster is studied in Section 7. The lattice constant of the Ga and As atoms in these clusters is 5.654 Å, which is the value for the crystal [22]. The H atoms cover the artificial dangling bonds of the Ga_8As_8 and Ga_8As_3 clusters. Covalent bonding crystals can often be simulated by a cluster model in which dangling bonds are covered by hydrogen atoms [23–25], and our previous studies have shown the usefulness of this approach. The Ga–H and As–H bond lengths are fixed respectively at 1.663 and 1.511 Å, which are the bond lengths in free GaH and AsH_3 molecules, respectively [26].

Table 1
The accuracy of several basis sets

	SZ	DZ	SZP	DZP	Exp.
As_2 bond length	2.297	2.139	2.22	–	2.1026
As_4 bond length	2.7117	2.5795	2.5654	–	2.435
Heat of formation (kcal / mol) for $2\ As_2 \rightarrow As_4$					
Hartree–Fock	−35.93	−7.94	−60.10	−36.77	−54.1
MP2	−4.93	+3.55	−54.51	−46.38	

The Gaussian basis sets for the Ga and As atoms at the reaction center are the (3s3p)/[1s1p] minimal basis plus polarization d functions (ζ = 0.293 for As, ζ = 0.207 for Ga atom), and the (3s3p)/[1s1p] minimal basis sets for the other atoms. The STO-3G basis set is used for the capping H atoms [27]. The Ne cores of Ga and As atoms are replaced by the effective core potentials [28].

3. Dissociation of the As_4 cluster into two As_2 molecules

We will first verify the reliability of the basis set. The As_2 and As_4 clusters are optimized for the bond length using the HF method with several basis sets. The As_4 cluster retains Td symmetry. The results are summarized in Table 1. SZ represents (3s3p)/[1s1p] basis, DZ (3s3p)/[2s2p], DZP (3s3p)/[2s2p] plus polarization d functions (ζ = 0.293), and SZP represents SZ plus polarization d functions. All of the basis sets give bond lengths greater than the experimental values for both As_2 and As_4, and this tendency is remarkable for the minimal basis set. Although the DZ basis set gives a better value for the As_2 bond length, the heat of formation is not better than that with the minimal basis set. The SZP basis set gives the best As_4 bond length and reproduces the experimental heat of formation, but does not give a good As_2 bond length. Since the As_4 cluster shows Td symmetry, the As–As–As angle is only 60°. Therefore, polarization d functions are needed to represent the As–As bond in As_4. These results show that the SZP basis set represents the best compromise for the present calculation.

The dissociation of As_4 to two As_2 is examined assuming D_{2h} symmetry. Fig. 2 shows the schematic reaction path, and the explicit reaction path shown in Fig. 3 is optimized by the HF calculation with an accuracy of within 0.1 Å. The geometries are summarized in Table 2. The potential curve along the path is shown in Fig. 4, where the solid and broken lines represent the results with the MP2 and HF methods, respectively. Although the potential curves with the MP2 and HF methods are similar, the As–As bond length with the MP2 method is shorter than that with the HF method.

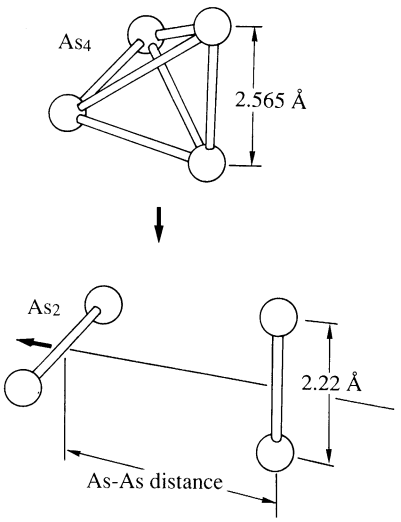

Fig. 2. Schematic representation of the dissociative reaction of As_4 to two As_2. The system retains D_{2h} symmetry.

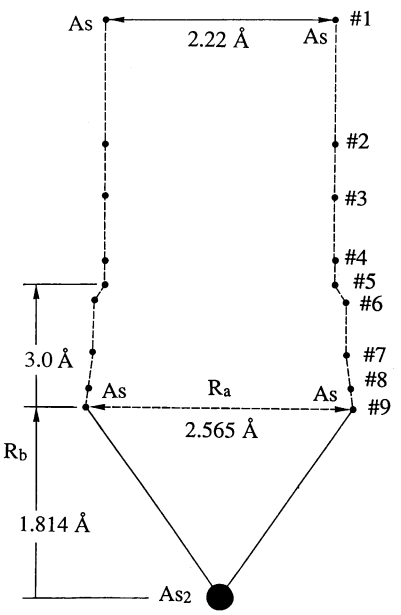

Fig. 3. Reaction path for the dissociation of As_4 to two As_2 molecules. This reaction path retains C_{2v} symmetry. R_a represents the distance between the two As atoms and R_b represents the distance between the two As_2 molecules.

Table 2
Geometry of As atoms along the reaction path shown in Fig. 3

Position	R_a (Å)	R_b(Å)
1	2.22	6.814
2	2.22	4.314
3	2.22	3.814
4	2.22	3.2
5	2.22	3.0
6	2.4	2.814
7	2.4	2.314
8	2.5	2.0
9	2.565	1.814

R_a and R_b are defined in Fig. 3.

The As_4 cluster at the equilibrium Td symmetry is at point 8 and the two isolated As_2 molecules are at point 1. The As_4 molecule is 67.0 kcal/mol more stable than the two As_2 molecules. The energy barrier for the dissociation from As_4 to As_2 is 140.4 kcal/mol and the energy barrier for the combination of two As_2 to As_4 is 73.4 kcal/mol. This result shows that the As_4 cluster is sufficiently stable on a surface heated at 600 K. Furthermore, the dissociation of As_4 to As_2 does not occur in vacuum, and the As_2 beam does not give As_4 cluster in vacuum. Therefore, the mechanism of GaAs crystal growth by As_4 beam and that previously reported for As_2 beam should be studied separately.

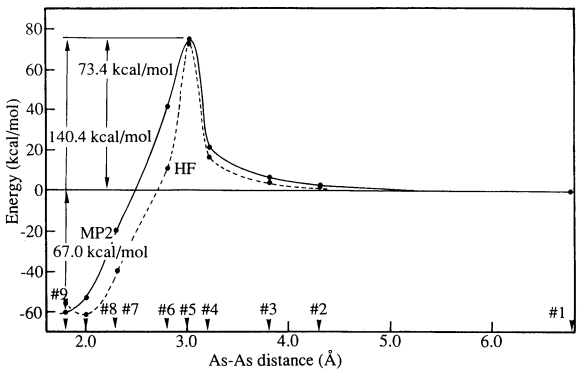

Fig. 4. Potential curves for the dissociation of As_4 to two As_2 molecules. Solid line represents the result with the MP2 method and the broken line represents the result with the HF method.

4. Reaction of an As_4 cluster with a Ga atom

We first study the reaction between a Ga atom and an As_4 cluster. The As_4 cluster retains Td symmetry, and we examine the three reaction paths shown in Fig. 5, which correspond to Ga adsorptions at the on-top, bridge and three-fold hollow sites of the As_4 cluster. Throughout these reactions, the system is assumed to show C_3, C_{2v}, or C_3 symmetry, respectively, and other lower symmetry paths are not examined. Since this is an open-shell system, the calculations are performed using the Roothaan open-shell HF method and further electron correlations are not considered. The geometries of all the Ga and As atoms are optimized within an accuracy of 0.1 Å. Fig. 6 shows the potential curves along the three paths depicted in Fig. 5. At point 1, the As_4 cluster shows Td symmetry and the As–As bond length is 2.565 Å, which is the value in the free As_4 molecule. Since all of the potential curves are repulsive and do not give a bound state, the Ga atom and the As_4 cluster do not react to form a $GaAs_4$ cluster. This result differs from that previously obtained with As_2 cluster: i.e. As_2 cluster reacts with Ga atom without activation energy and forms a $GaAs_2$ cluster which plays an important role as an intermediate species in crystal growth with an As_2 molecular beam.

5. Adsorption of As_4 on a Ga-stabilized flat GaAs surface

In this section we examine the adsorption of an As_4 cluster on a Ga-stabilized flat GaAs sur-

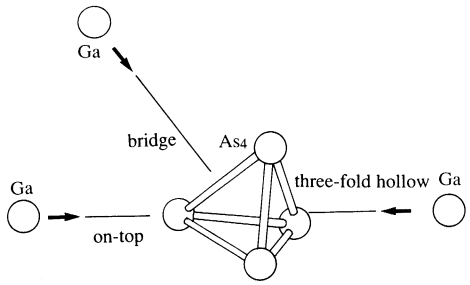

Fig. 5. Schematic representation of three reaction paths for the Ga + As_4 system: attacking the on-top, bridge, and three-fold hollow sites.

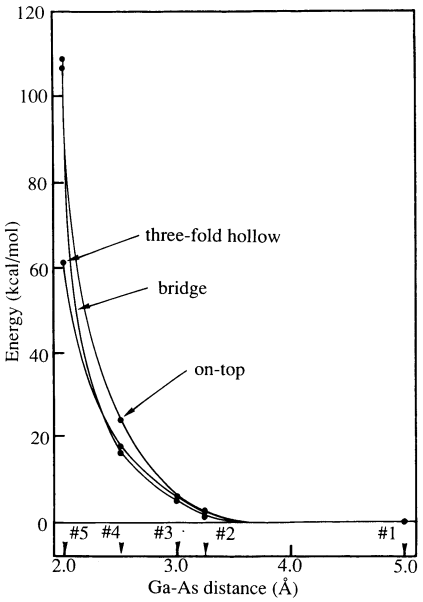

Fig. 6. Potential curves calculated by the ROHF method for the $Ga + As_4$ systems shown in Fig. 5.

face. The reaction path is schematically represented in Fig. 7: from point 1 to 7 the As_4 cluster approaches the cluster and is adsorbed, and from point 7 to 10 two As atoms in direct contact with the surface remain on the surface while the other two As atoms combine to form an As_2 cluster

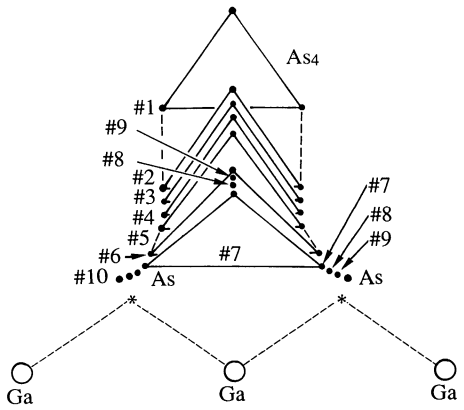

Fig. 8. Reaction path for the adsorption of As_4 on a flat GaAs(100) surface. This reaction path retains C_{2v} symmetry. Two asterisks indicate the positions of the As atoms in the GaAs crystal lattice without surface relaxation.

which desorbs from the surface. Fig. 8 shows the reaction path optimized by the HF calculation assuming C_{2v} symmetry. Table 3 gives the geometry of the approaching As_4 cluster with an accuracy of 0.1 Å. Only the four As atoms of the approaching As_4 cluster are optimized, with the $Ga_8As_8H_{18}$ cluster fixed. The electronic charges of two different As atoms of the As_4 cluster are summarized in Table 4, and Fig. 9 shows the calculated potential curve along the reaction path.

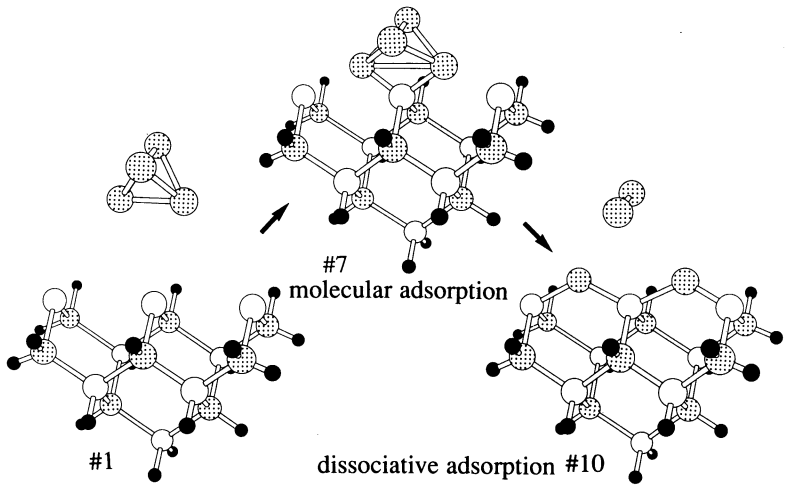

Fig. 7. Schematic representation of the adsorption of As_4. As_4 is adsorbed on the cluster. Two As atoms are dissociatively adsorbed on the surface while the other two As atoms are released into vacuum as an As_2 molecule.

Table 3
Geometry of As atoms along the reaction path shown in Fig. 8[a]

Position	Distance (Å)			
	R_{Ga-As} [b]	$R_{As1-As1}$ [c]	$R_{As1-As2}$ [d]	$R_{As2-As2}$
1	5.0	2.565	2.565	2.565
2	3.5	2.565	2.565	2.565
3	3.25	2.565	2.565	2.565
4	3.0	2.565	2.565	2.565
5	2.75	2.6	2.528	2.56
6	2.25	3.2	2.513	2.50
7	2.0	3.3	2.513	2.44
8	1.9	3.74	2.860	2.40
9	1.8	4.16	2.981	2.30
10	1.77	4.3	5.555	2.22

[a] The reaction path retains C_{2v} symmetry.
[b] Distance from the As atom in contact with the surface to the Ga surface.
[c] As1 represents the As atom in contact with the surface.
[d] As2 represents the As atom in the top position of the adsorbed As_4 cluster.

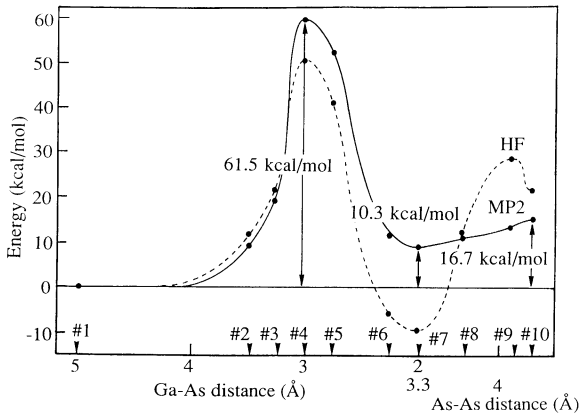

Fig. 9. Potential curves for the adsorption of As_4 on a GaAs surface. Solid line represents the result with the MP2 method and the broken line represents the result with the HF method. From point 1 to 7, the horizontal axis shows the Ga–As distance From 7 to 10, this axis shows the As–As distance.

The broken line represents the HF result and the solid line represents the MP2 result. From point 1 to 7, the horizontal axis shows the Ga–As distance, i.e., the vertical distance from the As of the As_4 cluster to the surface Ga of the $Ga_8As_8H_{18}$ cluster. From point 7 to 10, this axis shows the vertical As–As distance from the As of the desorbed As_2 to the two adsorbed As atoms.

The potential curve has a single minimum at point 7 and two maxima at points 4 and 10:

Table 4
Mulliken gross charges of the As atoms in the As_4 cluster along the reaction path shown in Fig. 8

Position	$Ga_8As_8H_{18}$ cluster		$Ga_8As_{10}H_{20}$ cluster	
	As [a]	As [b]	As [a]	As [b]
1	+0.04	−0.04	+0.01	−0.01
2	+0.06	−0.07	+0.02	−0.00
3	+0.07	−0.07	+0.04	+0.07
4	+0.04	−0.01	+0.04	+0.07
5	+0.03	−0.03	+0.03	+0.06
6	−0.12	−0.08	−0.18	+0.04
7	−0.20	−0.05	−0.22	+0.07
8	−0.26	−0.06	−0.25	+0.12
9	−0.37	−0.07	−0.30	+0.12
10	−0.56	0.00	−0.24	0.00

[a] As atoms in direct contact with the surface.
[b] Other As atoms which are eventually released into vacuum.

passing through the initial barrier at point 4, the As_4 attains the molecular adsorption geometry at point 7 and the dissociatively adsorbed geometry at point 10. At point 1, the optimized As–As bond length is 2.565 Å, which is the same as that in the free As_4 cluster. The barrier height at point 4 is 61.5 kcal/mol. After passing this barrier, the As atoms show a slight negative charge and the As_4 cluster is adsorbed while retaining its tetrahedral form. This molecular adsorption corresponds to the geometry at point 7. By the HF method, the molecular adsorption state of As_4 is calculated to be stable relative to the initial state. However, consideration of electron correlation reveals that the molecular adsorption energy is −10.3 kcal/mol, and therefore less stable than the initial state. The geometry is shown in Fig. 8: the Ga–As length is 2.0 Å and the As–As length close to the surface is 3.3 Å, which is longer than that in the free As_4 (2.565 Å). The two As atoms in contact with the surface are charged to −0.20 and the other two As atoms are charged to −0.05. Thus, the As_4 cluster has a charge of −0.5. As the reaction proceeds, the length of the As_2 in contact with the surface increases, which indicates that this As–As bond is dissociated on the surface and the associated charges suddenly increase; from −0.20 at point 7 to −0.56 at point

10. Finally, these two As atoms attain dissociated adsorption at point 10, which is 16.7 kcal/mol less stable than the initial state. The optimized As–As distance of the adsorbed As atoms is 4.3 Å, which is slightly longer than that in the GaAs crystal (asterisks in Fig. 8). The optimized As–Ga distance on the surface is 2.71 Å, which is slightly shorter than the experimental As–Ga distance for the crystal (2.827 Å). The charge of these As atoms (−0.56) is similar to the average value for the inner As atoms of the cluster (−0.48). In contrast, the two As atoms which are more distant from the surface remain almost neutral throughout this reaction. They are repelled from the surface, especially at the final stage (points 9 and 10) of the reaction.

Since the dissociative adsorption state necessary for crystal growth is less stable than the molecular adsorption state or the initial state, and the energy barrier for molecular adsorption (61.5 kcal/mol) is too high to cross at 600 K, an As_4 cluster irradiated on the surface will be desorbed back to the vacuum and crystal growth will be difficult to maintain by this mechanism.

6. Adsorption of As_4 at a ditch site on the GaAs surface

The ditch site of the Ga-stabilized GaAs(100) surface is simulated by the $Ga_8As_{10}H_{20}$ cluster shown in Fig. 1. Two As atoms which represent two As atoms around the ditch site are added at the edge of the $Ga_8As_8H_{18}$ cluster discussed in the preceding section. We use the same reaction path as that calculated in Section 5. The electronic charges of the four As atoms along the path are summarized on the right-hand side of Table 4. The calculated potential surface along the reaction path is shown in Fig. 10. The broken line represents the result with the HF method and the solid line represents the result with the MP2 method. The horizontal axis in Fig. 10 is defined as in the previous section.

The potential curve has two minima at points 7 and 10 and two maxima at points 3 and 9: passing through the initial barrier at point 3, As_4 reaches the molecular adsorption state at point 7, and as

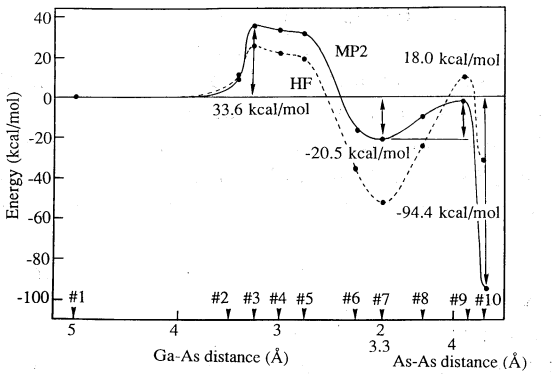

Fig. 10. Potential curves for As_4 adsorption at a ditch site of the GaAs surface. Solid line represents the result with the MP2 method and the broken line represents the result with the HF method. From point 1 to 7, the horizontal axis shows the Ga–As distance. From 7 to 10, this axis shows the As–As distance.

it passes beyond the barrier at point 9, it is dissociatively adsorbed at point 10. The height of the barrier at point 3 is 33.6 kcal/mol. After passing this barrier, the As atoms show a slight negative charge and the adsorbed As_4 is almost in a tetrahedral form. Molecular adsorption occurs at point 7 with an adsorption energy of 20.5 kcal/mol, and the As atoms are suddenly charged around this point: the charge of the As atoms in contact with the surface increases from 0.03 at point 5 to −0.22 at point 7. The calculated energy barrier of 33.6 kcal/mol is about a half of that for the flat surface in Section 5 (61.5 kcal/mol). After passing this point, the As–As length of the As_2 in contact with the surface increases and the cluster reaches the second barrier at point 9. This energy barrier is 18.0 kcal/mol higher than the molecular adsorption state. Finally, dissociative adsorption occurs at point 10, with an adsorption energy of 94.4 kcal/mol. Although the HF calculation shows that the final state is less stable than the molecular adsorption state, the correlated MP2 calculation indicates that the reaction does proceed. Throughout the reaction, the charge of the As atoms in contact with the surface changes dramatically, while the other As atoms remain almost neutral. The first barrier is due to electron transfer from the surface to the As_4 cluster, and

the second barrier is due to dissociation of the adsorbed As_4 cluster. The charge of the adsorbed As atom is almost equal to the charge of the surface As atom (−0.21) in our previous study [1]. However, the calculated molecular adsorption energy of 20.5 kcal/mol is larger than the previously observed experimental value of 8.8 kcal/mol [4].

Since the dissociative adsorption necessary for crystal growth occurs more readily than molecular adsorption, with an energy barrier of about 34 kcal/mol, the As_4 cluster is likely to be adsorbed and dissociated at a ditch site on the GaAs surface. This result is in sharp contrast to that obtained using a flat surface. Therefore, using an As_4 molecular beam, the As layer may grow at a ditch site of the GaAs surface by the desorption of As_2 from the surface.

7. Coadsorption of two As_4 on a Ga-stabilized GaAs surface

Finally, we examine the possibility of coadsorption of two As_4 clusters on a Ga-stabilized GaAs surface. The Ga-stabilized flat GaAs(100) surface is simulated by the $Ga_8As_3H_{12}$ cluster shown in Fig. 1. The reaction path is depicted in Fig. 11: from point 1 to 2 the two As_4 clusters are coadsorbed on the GaAs surface, from 2 to 4, the two coadsorbed As_4 clusters couple, and from point 4 to 6 the four As atoms which directly interact with the surface are adsorbed on the surface while the other four As atoms rearrange to form an As_4 cluster which desorbs from the surface. The reaction path is shown in more detail in Fig. 12: from point 2 to 3, the As atoms which are in direct contact with the surface are fixed at the molecularly adsorbed position (i.e. point 7 in Fig. 7) calculated in Section 5; and from point 4 to 6 they are fixed at the dissociatively adsorbed position (i.e. point 10 in Fig. 7) calculated in Section 5. The other four As atoms are optimized by the HF calculation within an accuracy of 0.1 Å by assuming C_{2v} symmetry, with the $Ga_8As_3H_{12}$ cluster fixed. The geometries and electronic charges of these As atoms along the reaction path are summarized in Tables 5 and 6, respectively, and the calculated potential curve is shown in Fig. 13. The broken line represents the

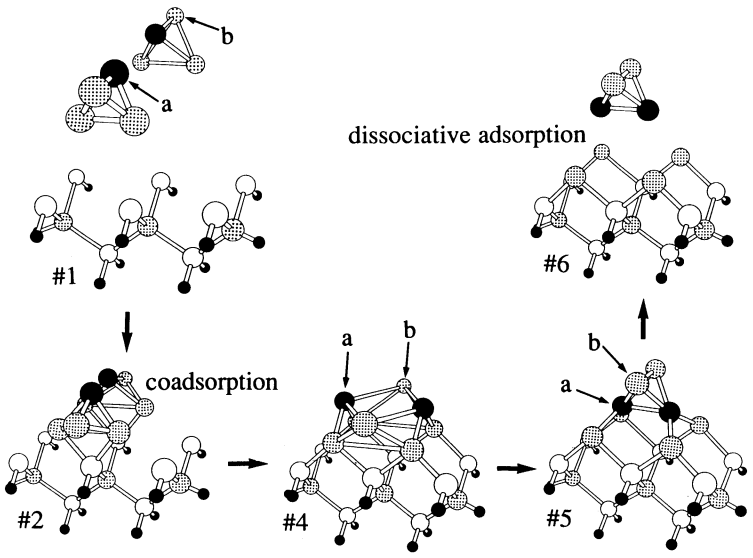

Fig. 11. Schematic representation of the dissociation of the two coadsorbed As_4 clusters. From these two As_4, four As atoms are dissociatively adsorbed on the surface and the other four As atoms are released into vacuum as an As_4 cluster. The filled circles are provided to distinguish the two As atoms.

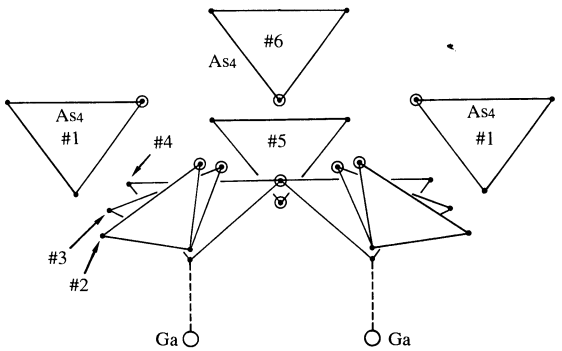

Fig. 12. Reaction path for the coadsorption of two As_4 clusters on a GaAs(100) surface. This reaction path retains C_{2v} symmetry. Double circles represent the same As atom.

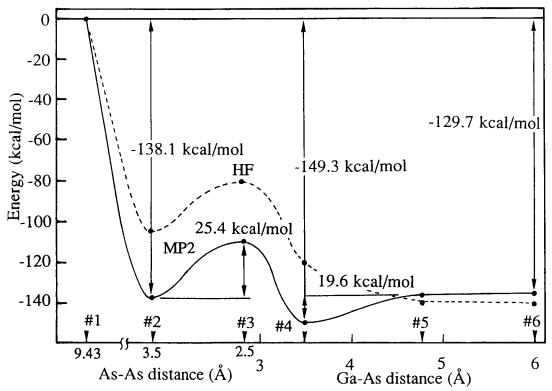

Fig. 13. Potential curves for the dissociation of the two coadsorbed As_4 on a GaAs surface. Solid line represents the result with the MP2 method and the broken line represents the result with the HF method. From point 1 to 4, the horizontal axis shows the As–As distance (Raa in Table 5). From 4 to 6, this axis shows the Ga–As distance (R_{As-Ga} in Table 5).

result with the HF method and the solid line represents the result with the MP2 method. From point 1 to 4, the horizontal axis shows the As–As distance, i.e., the distance between the As atoms indicated by the filled circles in Fig. 11. From point 4 to 6, this axis shows the Ga–As distance, i.e., the distance from an As atom of the desorbing As_4 molecule to the surface Ga atom.

The potential curve has two minima at points 2 and 4, and two maxima at points 3 and 6: As_4 is molecularly coadsorbed at point 2 and then dissociatively adsorbed at point 6. At point 1, the optimized As–As bond length is 2.565 Å, which is the same as that in the free As_4 molecule. Molecular adsorption occurs at point 2 with an adsorption energy of 138.1 kcal/mol, and the As_4 cluster then collapses with a barrier of 25.4 kcal/mol, indicating that the two As_4 clusters repel each other. The four As atoms in contact with the surface are charged to −0.18 and the other four As atoms are charged to only +0.03 and −0.01. Beyond this point, the two As_4 clusters come closer to each other and the four As atoms on top

Table 5
Geometry of As atoms along the reaction path shown in Figs. 11 and 12

Position	Adsorbed As distance (Å)			Dissociated As distance (Å)			
	R_{Ga-As} [a]	R_{As-As} [b]	R_{As-As} [c]	R_{As-Ga} [d]	Raa [e]	Rab [f]	Rbb
1	5.0	2.565	12.0	7.0	9.43	12.00	14.57
2	2.0	3.3	3.998	2.28	3.5	5.66	7.8
3	2.0	3.3	3.998	2.85	2.5	4.94	7.5
4	1.77	4.3	3.998	3.48	4.3	4.19	7.2
5	1.77	4.3	3.998	4.79	2.565	2.7	2.6
6	1.77	4.3	3.998	6.0	2.565	2.565	2.565

[a] Distance between the four equivalent As atoms adsorbed on the surface and the surface Ga atom.
[b] Distance between the adsorbed As atoms from the same As_4 cluster.
[c] Distance between the adsorbed As atoms from different As_4 clusters.
[d] Distance between the As atoms indicated by "a" (filled circle in Fig. 11) and the surface Ga atom.
[e] As atoms indicated by "a"; filled circle in Fig 11.
[f] As atoms indicated by "b"; shaded circle in Fig 11.

Table 6
Mulliken gross charges of the As atoms of the As_4 cluster along the reaction path shown in Figs. 11 and 12

Position	Adsorbed As [a]	Asa [b]	Asb [c]
1	−0.02	+0.03	−0.00
2	−0.18	+0.03	−0.01
3	−0.22	+0.06	−0.02
4	−0.21	+0.05	+0.02
5	−0.19	+0.04	−0.04
6	−0.18	+0.02	−0.02

[a] As atoms in direct contact with the surface.
[b] As atoms indicated by "a", filled circle in Fig 11.
[c] As atoms indicated by "b", shaded circle in Fig 11.

of the As_4 clusters combine at point 4. Finally, the As atoms reach a state of dissociative adsorption at point 6 with an energy barrier of 19.6 kcal/mol, which is 129.7 kcal/mol more stable than the initial state and 8.4 kcal/mol less stable than the coadsorption state. At this point, four As atoms combine and desorb as a As_4 cluster from the surface and the other four As atoms are adsorbed on the Ga-stabilized surface. Throughout the reaction, the charges of the As atoms remain fairly constant; the charge of the adsorbed As remains in the range of −0.18 to −0.22 and that of the desorbed As is almost neutral (−0.04 to +0.06). The charge of the adsorbed As at point 6 (−0.18) is similar to that of the adsorbed As atom at the ditch site in Section 5 (−0.24). The MP2 result shows a minimum at point 4. Since the actual surface is heated to 600 K, the As atoms would be able to reach points 5 and 6. However, since the minimum lies near point 4, there is a strong possibility of finding an As_4 molecule near that point.

This reaction path retains C_{2v} symmetry, even though the movement of the As atom from point 3 to 4 requires a lower symmetry of at least C_2. Therefore, the exact transition state is not necessarily at point 4 and a higher barrier is expected.

This result shows that if the adsorbed As_4 is able to migrate on the surface, the coupling of two As_4 is preferable and the energy barrier for the reaction

$$2\ As_4(\text{coadsorbed}) \rightarrow As_4(\text{gas}) + 4\ As(\text{adsorbed})$$

is only 25.4 kcal/mol. Therefore, we conclude that this reaction occurs and a new As-layer grows on the surface with the desorption of an As_4 molecule.

8. Concluding remarks

These results indicate that two adsorbed As_4 clusters give a coadsorption state which produces a new As-layer while releasing an As_4 cluster into vacuum. The reaction which involves only a single As_4 cluster is also possible. These energy profiles are summarized as follows and a qualitative representation is given in Fig. 14.

(1) An As_4 cluster of the beam is molecularly adsorbed at a ditch site of the Ga-stabilized GaAs surface with an energy barrier of 33.6 kcal/mol:

$$As_4(\text{gas}) + Ga(\text{surface}) \rightarrow As_4(\text{adsorbed}) + Ga(\text{surface})\ (33.6\ \text{kcal/mol}).$$

(2) Two As_4 clusters adsorbed on the Ga-stabilized GaAs surface may migrate and collide with each other to produce a coadsorption state:

$$2\ As_4(\text{gas}) + Ga(\text{surface}) \rightarrow 2\ As_4(\text{coadsorbed}) + Ga(\text{surface}).$$

(3) The coadsorbed As_4 clusters are reconstructed to give four As atoms that are dissociatively adsorbed on the surface to make a new As-layer and four As atoms that form an As_4

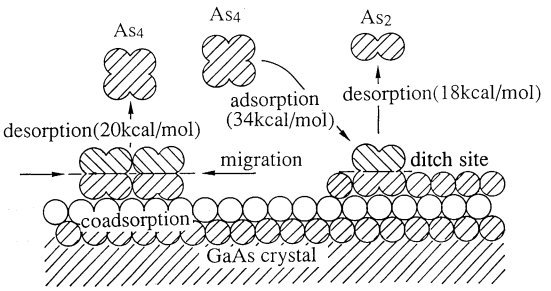

Fig. 14. Schematic representation of GaAs epitaxial crystal growth using an As_4 cluster beam.

cluster and desorb from the surface with an energy barrier of 25.4 kcal/mol:

$$2\ As_4(\text{coadsorbed}) \rightarrow As_4(\text{gas}) + 4\ As(\text{surface})$$

(25.4 kcal/mol).

The energy barrier for the reaction involving only a single As_4 cluster is 18.0 kcal/mol, as discussed in Section 6. This energy barrier is lower than that in Section 7 (25.4 kcal/mol) and the sticking coefficient of this reaction (equal to 0.5) is consistent with the experimental value (< 0.5). Therefore, we suggest that the following reaction step may occur.

(4) The molecularly adsorbed As_4 in (1) above is dissociated thermally and a new As layer grows on the Ga-stabilized surface with an energy barrier of 18.0 kcal/mol:

$$As_4(\text{adsorbed}) \rightarrow As_2(\text{gas}) + 2\ As(\text{surface})$$

(18.0 kcal/mol).

Thus, the present results confirm the reaction involving two As_4 clusters, i.e., steps 2 and 3, which was experimentally proposed previously. Furthermore, we can very roughly estimate the magnitude of the reaction probability by using the calculated reaction barrier for dissociation of the adsorbed As cluster: i.e., the reaction which involves a single As_4 cluster should occur more easily than that involving two As_4 clusters. Bonapasta et al. showed that the Ga atom is adsorbed on an As-stabilized surface without an energy barrier [16]. Therefore, irradiation with As_4 cluster and Ga atom beams forms alternating As and Ga layers, and the GaAs crystal grows. Finally, it is noted that the reaction steps examined here are certainly only part of the possible reactions on the surface and other reactions may be possible.

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