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

## I. $As_2$ adsorption on a GaAs surface

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We study the chemisorption of an $As_2$ cluster on a flat GaAs(100) surface and at the step site of this surface with the Hartree–Fock geometry optimization method followed by the energy calculation with the second-order Møller–Plesset perturbation method. On the flat surface, the activation energies for both molecular and dissociative adsorption are high and the molecular adsorption is more favorable than the dissociative one, so that the $As_2$ cluster is hardly adsorbed and dissociated. At the step site, on the other hand, the dissociative adsorption occurs smoothly: the dissociative adsorption becomes more favorable than the molecular one and the activation energy for the molecular adsorption is only 9.6 kcal/mol. Therefore, the $As_2$ cluster arriving at the step site is easily adsorbed and dissociated and thus one As layer is added on a Ga surface. We explain the mechanism of this reaction and the difference in the reactivity between the flat surface and the step site.

## 1. Introduction

Gallium arsenide, an artificial material which does not exist in nature, is a typical compound semiconductor and shows many nice behaviors. Because of the difference between the vapor pressures of gallium and arsenic, the GaAs crystal is difficult to produce and it is made by a special technique, namely by the so-called epitaxial method. In molecular beam epitaxial (MBE) growth, a gallium atomic beam and an arsenic cluster beam composed of $As_4$ or $As_2$ are irradiated onto a GaAs surface which is kept at about 600 K in a vacuum chamber, and Ga and As atomic layers grow alternatively. Though the surface morphology has been observed by LEED, RHEED, photoemission and so on, it was difficult to identify the species existing on the surface and to clarify the mechanism of the crystal growth.

Arthur [1] and Foxon et al. [2,3] studied the reaction mechanisms of MBE by the reaction rate theory and showed that the mechanisms of the adsorption of the $As_2$ and $As_4$ clusters are different to each other. In the case of the $As_2$ beam, the $As_2$ cluster migrates on the Ga-stabilized surface terminated by Ga atoms and shows the dissociative adsorption there. Thus, the As layer grows with making an As-island region on a Ga surface. The sticking coefficient for the $As_2$ cluster is close to unity so that even a single $As_2$ molecule can react. On the other hand, the sticking coefficient for $As_4$ is smaller than 0.5 and the reaction is more complicated than the $As_2$ adsorption.

The crystal growth in metal-organic MBE has been studied theoretically using small cluster models, but there are very few reports on the growth mechanism in MBE and about the difference due to the size of the cluster included in the beam [4–9]. Though Foxon et al. [2,3] proposed a reaction mechanism of MBE, they adopted several assumptions on the reaction rate and there-

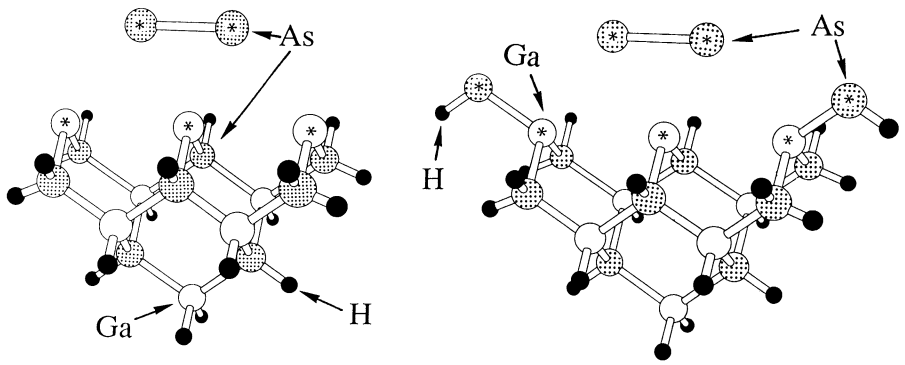
fore the explicit geometry of the adsorbate, the reaction path, and the reason of the smooth epitaxial growth remain to be clarified.

We study the mechanism of the GaAs crystal growth in the $As_2$ beam epitaxy by an ab-initio theoretical method using the cluster model. In this study, the adsorption and the dissociative reaction of a single $As_2$ are studied. We simulate the Ga-stabilized GaAs(100) surface by the $Ga_8As_8H_{18}$ cluster and its step site by the $Ga_8As_{10}H_{20}$ cluster. In section 2, the method of calculations is briefly explained. In section 3, the reaction of the $As_2$ cluster on a flat GaAs surface is studied. The equilibrium structure and transition state are given and the reaction mechanism is explained qualitatively using the orbital correlation diagram. In section 4, the adsorption of $As_2$ on a step site is studied similarly to section 3 and the adsorption mechanisms on the flat surface and at the step site are compared. Conclusions are given in the last section.

## 2. Computational method

We use the Hartree–Fock (HF) method followed by the second-order Møller–Plesset perturbation (MP2) method. The HF and MP2 calculations are performed with the use of the HONDO7 program [10]. Fig. 1 shows the $Ga_8As_8H_{18}$ and $Ga_8As_{10}H_{20}$ clusters which simulate the GaAs(100) surface and its step site, respectively. We assume that the $As_2$ molecule approaches the cluster and reacts with it as shown in fig. 1. The lattice constant of the Ga and As atoms located in the crystal lattice is 5.654 Å [11]. The H atoms cover the artificial dangling bonds of the $Ga_8As_8$ and $Ga_8As_{10}$ clusters. A covalent bonding crystal is often simulated by the cluster model whose dangling bonds are covered by hydrogen atoms [12–14]. The Ga–H and As–H bond lengths are fixed to the values of 1.663 and 1.511 Å which are the bond lengths in free GaH and $AsH_3$ molecules, respectively [15].

The Gaussian basis sets for the Ga and As atoms at the reaction center are (3s3p)/[2s2p] double zeta contracted Gaussian type orbitals (CGTO's) and for the other atoms are the (3s3p)/[1s1p] minimal basis sets and the Ne cores are replaced by the effective core potential [16]. For an H atom, the STO-3G basis is used [17]. The double zeta basis sets are used for the two As atoms of the $As_2$ cluster and the three Ga atoms located on the surface of the cluster: they are indicated by the asterisks in fig. 1. Other As, Ga and H atoms are treated with the minimal basis sets. For the $Ga_8As_{10}H_{20}$ cluster, two fur-




$Ga_8As_8H_{18}$ cluster $Ga_8As_{10}H_{20}$ cluster

Fig. 1. $Ga_8As_8H_{18}$ and $Ga_8As_{10}H_{20}$ clusters interacting with $As_2$. The atoms indicated by the asterisks are treated with the double zeta basis and the others are with minimal basis.

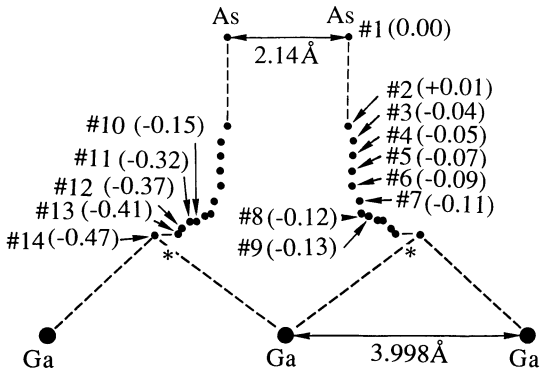



Fig. 2. Reaction path for the $As_2$ adsorption on a GaAs(100) flat surface. This reaction path keeps the $C_{2v}$ symmetry. Values in parentheses shows the gross charge of the adsorbed As atom. Two asterisks indicate the positions of the As atoms in the GaAs crystal lattice without surface relaxation.

ther As atoms which are located on the surface are treated with the double zeta basis.

## 3. Adsorption of $As_2$ on a flat GaAs surface

We show in fig. 2 the reaction path optimized by the HF calculations assuming $C_{2v}$ symmetry. The values in parentheses are the electronic charges of the two As atoms. Table 1 gives the geometries of the approaching $As_2$ whose accuracy is within 0.1 Å. Only the two As atoms of the approaching $As_2$ cluster are optimized with the $Ga_8As_8H_{18}$ cluster fixed. We show the calculated potential curve along the reaction path in fig. 3. The dashed line represents the result of the HF method and the solid line the MP2 method. From points 1 to 8, the horizontal axis stands for the Ga–As distance, that is the distance from the As of the $As_2$ cluster and the surface Ga of the $Ga_8As_8H_{18}$ cluster, and from points 8 to 14, the axis stands for the As–As distance of the adsorbing $As_2$ cluster.

The potential curve has two minimum points 7 and 14 and two maximum points 3 and 11: passing though the initial barrier at point 3, $As_2$ reaches the molecular adsorption at point 7 and then going beyond the barrier at point 11, it is dissociatively adsorbed at point 14. At point 1, the optimized As–As bond length and the force constant are 2.14 Å and 456 $cm^{-1}$ which are almost equal to the experimental values of the free $As_2$ of 2.10 Å and 430 $cm^{-1}$, respectively. The barrier height at point 3 is 23.5 kcal/mol and the As–As distance becomes a bit longer. After passing this barrier, the As atoms become slightly negatively charged and the $As_2$ is adsorbed keeping the As–As length almost constant. The

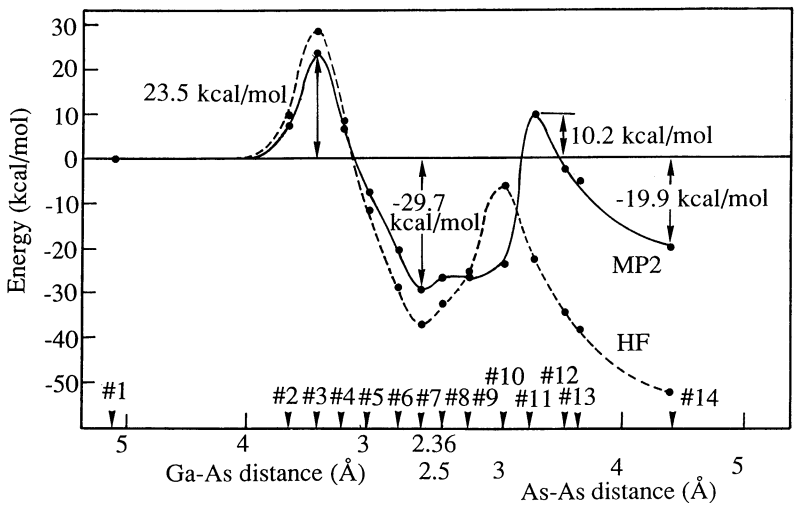



Fig. 3. Potential curves for the $As_2$ adsorption on a GaAs(100) surface. The solid line represents the result of the MP2 method and the broken line the HF method. From point 1 to 8, the coordinate shows the Ga–As distance and from 8 to 14, it shows the As–As distance.

Table 1
Geometries of $As_2$ along the reaction path shown in fig. 2

| Position | Distance (Å) | |
|---|---|---|
| | $R_{As-As}$ | $R_{Ga-As}$ [a] |
| 1 | 2.14 | 5.11 |
| 2 | 2.14 | 3.66 |
| 3 (barrier) | 2.30 | 3.45 |
| 4 | 2.30 | 3.21 |
| 5 | 2.30 | 2.98 |
| 6 | 2.30 | 2.75 |
| 7 (minimum) | 2.40 | 2.55 |
| 8 | 2.50 | 2.38 |
| 9 | 2.70 | 2.41 |
| 10 | 3.00 | 2.42 |
| 11 (barrier) | 3.20 | 2.48 |
| 12 | 3.50 | 2.51 |
| 13 | 3.60 | 2.48 |
| 14 (minimum) | 4.40 | 2.78 |

[a] Distance to the nearest Ga atom.

molecular adsorption is found at point 7 with the adsorption energy of 29.7 kcal/mol: the Ga–As length is 2.55 Å and the As–As length is 2.4 Å, slightly longer than that of the free $As_2$, and the As net charge is −0.11. These results are similar to the result of the previous study on the $GaAs_2$ system [18]: the Ga–As and As–As lengths were reported to be 2.85 and 2.2 Å, respectively, and the stabilization energy relative to the $Ga + As_2$ system to be 30.3 kcal/mol. This result indicates the locality of the interaction between $As_2$ and the surface in the molecular adsorption state.

Beyond this point, the As–As length becomes longer indicating that the As–As bond is broken by the adsorption and the As atoms reach the second barrier at point 11. The As atoms are suddenly charged at this point; the charge of −0.15 at point 10 becomes the value of −0.32 at point 11. The energy barrier is 10.2 kcal/mol higher than the free system and 39.9 kcal/mol higher than the molecular adsorption state. Finally, the dissociative adsorption occurs at point 14 with the adsorption energy of 19.9 kcal/mol. There, the optimized As–As distance is 4.40 Å which is slightly longer than that in the GaAs crystal which is indicated by the asterisks in fig. 2. The optimized As–Ga distance on the surface is 2.78 Å which is slightly shorter than 2.827 Å, the experimental AsGa distance for the crystal. The charge of these As atoms −0.47 is similar to the value −0.48 which is the average for the inner eight As atoms in the cluster. Since the dissociative adsorption state necessary for the crystal growth is less stable than the molecular adsorption state, the crystal growth is hard to occur and we expect that the molecularly adsorbed $As_2$ cluster migrates on the surface.

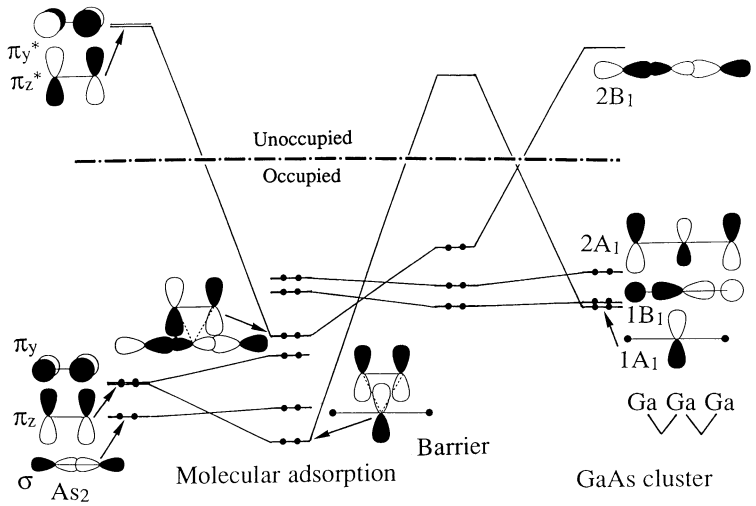



Fig. 4. Orbital correlation diagram of the $Ga_8As_8H_{18} + As_2$ system from point 1 to 8. Since the dangling bonds of the GaAs surface localize on the surface Ga atoms, only three Ga atoms are shown.

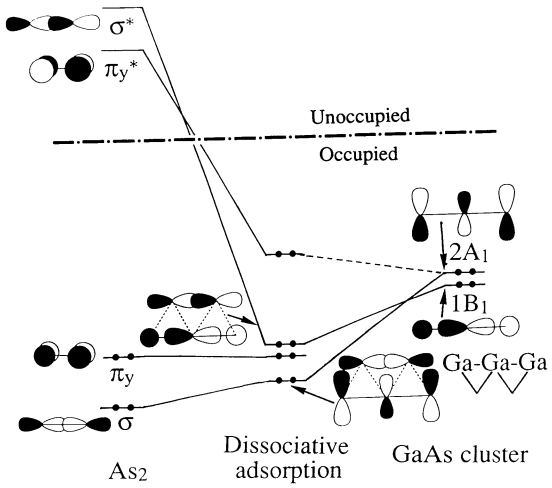



Fig. 5. Orbital correlation diagram of the $Ga_8As_8H_{18} + As_2$ system from point 8 to 14. Only these orbitals which do not have full participation in fig. 4 are shown. The broken line represents a charge transfer from the surface to $As_2$.

The mechanisms of the molecular and dissociative adsorption are qualitatively explained by the orbital correlation diagrams shown in figs. 4 and 5. Fig. 4 is for the first stage of the reaction from the free system at point 1 to the molecular adsorption at point 7, and fig. 5 is for the second stage of the reaction from the molecular adsorption at point 7 to the dissociative adsorption at point 14. Orbitals playing a role in the reaction are the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and their neighboring orbitals. The surface dangling bonds are localized on the three surface Ga atoms. We therefore show only three surface Ga atoms in figs. 4 and 5.

First, the origin of the initial energy barrier and the nature of the interaction in the molecular adsorption are explained with reference to fig. 4. The orbitals of the free $As_2$ and the free GaAs cluster are displayed in the left- and right-hand sides, respectively, and the orbitals at "barrier" and "molecular adsorption" represent the orbitals at points 3 and 7, respectively. The approach of the $As_2$ cluster to the Ga surface leads to the electron excitation from the $1A_1$ orbital to the $2B_1$ orbital of the GaAs cluster. This is the excitation within the surface dangling bonds and causes the energy barrier to the molecular adsorption at point 3. The next step is an electron donation from the $2B_1$ orbital to the $\pi_z^*$ anti-bonding orbital of $As_2$ and the back donation from the $\pi_z$ bonding orbital of $As_2$ to the $1A_1$ orbital. This step creates the two bonding orbitals which give an attractive interaction for the molecular adsorption at point 7. The As–As bonding orbitals of $As_2$ remain and keep the As–As bond length constant.

The second stage of the reaction is shown in fig. 5. Only the four orbitals of the $As_2$ and GaAs cluster are shown on the left- and right-hand side of fig. 5. The origin of the second energy barrier at point 11 and the nature of the interaction in the dissociative adsorption are explained. The orbitals at point 14 are shown as "dissociative adsorption". The electron transfer from the $2A_1$ orbital to the $\pi_y^*$ anti-bonding orbital of $As_2$, which is indicated by a dashed line in fig. 5 and which is the electron transfer from the surface to the adsorbate at point 11, causes the second energy barrier. At the last stage, the electron donation from the $1B_1$ orbital to the $\sigma^*$ anti-bonding orbital of $As_2$ and the back donation from the $\sigma$ bonding orbital of $As_2$ to the $2A_1$ orbital are important for the occurrence of the dissociative adsorption at point 14. The $\pi_y^*$ orbital corresponds to the dangling bond of the newly created As surface and it does not interact with the underground Ga atoms.

The mechanisms shown in figs. 4 and 5 explain the change of the charge on the As atoms shown in fig. 2. From point 1 to 10, the As charge is less than $-0.11$. From point 11 to 14, when $As_2$ begins to dissociate, it becomes $-0.47$ due to the charge transfer from the surface to the adsorbate. The orbital correlation diagram indicates that both the molecular and dissociative adsorption states are stabilized in the geometries of $C_{2v}$ symmetry, so that the $C_{2v}$ symmetry assumption on the reaction path would not much change the results.

## 4. Adsorption of $As_2$ at a step site of the GaAs surface

The step 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 the As atoms at the step site are added at the edge of the $Ga_8As_8H_{18}$ cluster dealt with in the preceding section. We show in fig. 6 the reaction path optimized by the HF calculations assuming $C_{2v}$ symmetry. The values in parentheses are the electronic charges of the two As atoms. Table 2 gives the geometries of the approaching As, and the accuracy is within 0.1 Å. Only the two As atoms of the approaching $As_2$ cluster are optimized with the $Ga_8As_{10}H_{20}$ cluster fixed. The optimized reaction path is almost the same as the one given in section 3 for the flat surface. The calculated potential curve along the reaction path is depicted in fig. 7. The dashed line represents the result of the HF method and the solid line the MP2 method. From points 1 to 9, the horizontal axis stands for the Ga–As distance, that is the distance from the As of the $As_2$ cluster to the surface Ga of the $Ga_8As_{10}H_{20}$ cluster, and from point 9 to 14, the axis stands for the As–As distance of the adsorbing $As_2$ cluster.

The potential curve is roughly similar to the one given in section 3, that is, it has two minimum at points 8 and 14 and two maximum at points 3 and 9: after passing the barrier at point 3, $As_2$ reaches the molecular adsorption state at point 8, and then it is dissociatively adsorbed at point 14. At point 1, the $As_2$ cluster has the same bond length as in section 3. The first barrier height at point 3 is only 9.6 kcal/mol, which is almost one half of the barrier for the flat surface and the As–As distance becomes a little longer. After passing this barrier, the As atoms become slightly charged and the $As_2$ is adsorbed keeping the As–As length constant. The molecular adsorption is found at point 9 with an adsorption energy of 49.2 kcal/mol: the Ga–As length is 2.50 Å and the As–As length is 2.36 Å, slightly longer than free $As_2$, and the charge of the As

Table 2
Geometries of $As_2$ along the reaction path shown in fig. 6

| Position | Distance (Å) | |
|---|---|---|
| | $R_{As-As}$ | $R_{Ga-As}$ [a] |
| 1 | 2.14 | 5.11 |
| 2 | 2.14 | 3.90 |
| 3 (barrier) | 2.14 | 3.66 |
| 4 | 2.30 | 3.45 |
| 5 | 2.30 | 3.21 |
| 6 | 2.30 | 2.98 |
| 7 | 2.30 | 2.75 |
| 8 (minimum) | 2.40 | 2.55 |
| 9 (barrier) | 2.50 | 2.36 |
| 10 | 2.70 | 2.41 |
| 11 | 3.00 | 2.42 |
| 12 | 3.20 | 2.45 |
| 13 | 3.60 | 2.48 |
| 14 (minimum) | 4.20 | 2.58 |

[a] Distance to the nearest Ga atom.

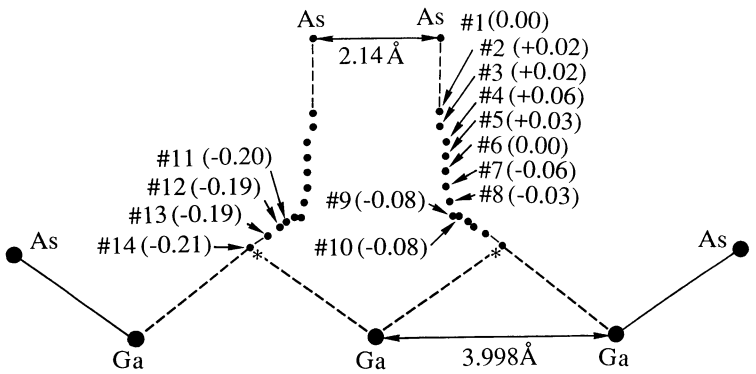



Fig. 6. Reaction path for the $As_2$ adsorption at the step site of a GaAs(100) surface. This reaction path keeps the $C_{2v}$ symmetry. Values in palentheses shows the gross charge of the adsorbed As atom. Two asterisks indicate the positions of the As atoms in the GaAs crystal lattice without surface relaxation.

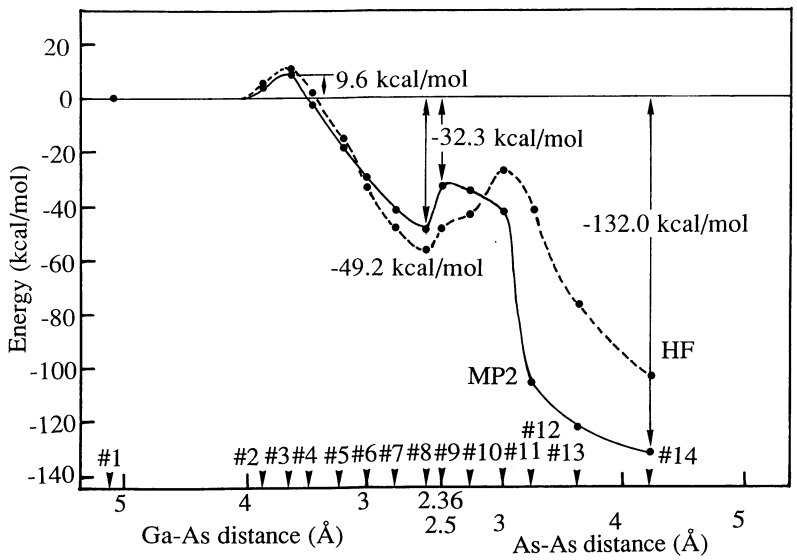



Fig. 7. Potential curve for the $As_2$ adsorption on a GaAs surface. The solid line represents the result of the MP2 method and the broken line the HF method. From point 1 to 9, the coordinate shows the Ga–As distance and from 9 to 14, it shows the As–As distance.

atom is only −0.03. The calculated activation energy for the desorption is 58.8 kcal/mol which is compared with the experimental value of 45 kcal/mol [1]. This result is similar to the result of the previous study on the $GaAs_2$ system [18] and the molecular adsorption discussed in section 3.

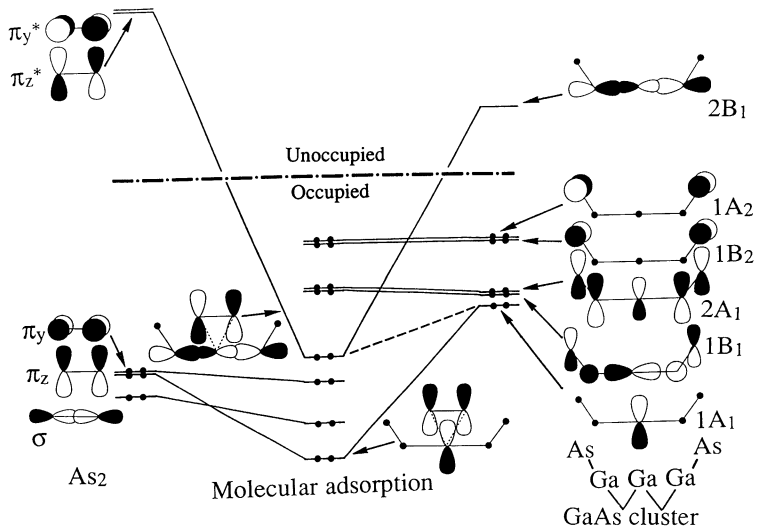



Fig. 8. Orbital correlation diagram for the $Ga_8As_{10}H_{20} + As_2$ system from point 1 to 8. Since the dangling bonds of the GaAs surface localize on the surface Ga and As atoms, only these atoms are shown. The broken line represents an excitation of surface dangling bond.

It indicates the locality of the interaction between $As_2$ and the surface in the molecular adsorption state.

After passing the molecular adsorption state, the As–As length becomes longer indicating that the As–As bond is broken by the adsorption, and the As atoms reach the second barrier at point 9. The As atoms are rapidly charged near this point; the charge is −0.08 at point 9 and −0.20 at point 11. The energy barrier is 32.3 kcal/mol lower than the free system and 16.9 kcal/mol higher than the molecular adsorption state. Finally, $As_2$ is dissociated and adsorbed at point 14 with an adsorption energy of 132.0 kcal/mol which overestimates the experimental value of 45.9 kcal/mol for a complete monolayer of As on a GaAs surface [1]. This optimized structure is very similar to the GaAs lattice structure which is indicated by the asterisks in fig. 6, but the charge of the adsorbed As atom is −0.21 which is smaller than −0.48 which is the charge of the inner As atoms of the GaAs cluster. Since the dissociative adsorption necessary for the crystal growth is more stable than the molecular adsorption and the energy barrier is not more than 17 kcal/mol, the adsorbed $As_2$ cluster is likely to be dissociated and the crystal will grow. This result is in a sharp contrast to the result for a flat surface. We therefore conclude that the As layer grows at the step site of the GaAs surface. The step site model simulated here is a model of a groove on the As-stabilized surface rather than a real step site. Since the present model has two step sites, the site effect may be overestimated and the activation energy on a real step site would be larger than the calculated one.

The mechanisms of the molecular and dissociative adsorption are qualitatively explained by the orbital correlation diagrams shown in figs. 8 and 9. Fig. 8 is for the first stage of the reaction from the free system to the molecular adsorption state at point 8, and fig. 9 is for the second stage of the reaction from the molecular adsorption state at point 8 to the dissociative adsorption state at point 14. Orbitals important in the reaction localize on the three surface Ga atoms and two additional As atoms at the step site. We therefore display only three surface Ga atoms and two surface As atoms. We explain the origin of the energy barrier for molecular adsorption and the nature of the interaction in the molecular adsorption state. The orbitals of the free $As_2$ and the free GaAs cluster are displayed, respectively, in the left- and right-hand sides of fig. 4 and the orbitals at "barrier" and "molecular adsorption" represent the orbitals at points 3 and 8, respec-

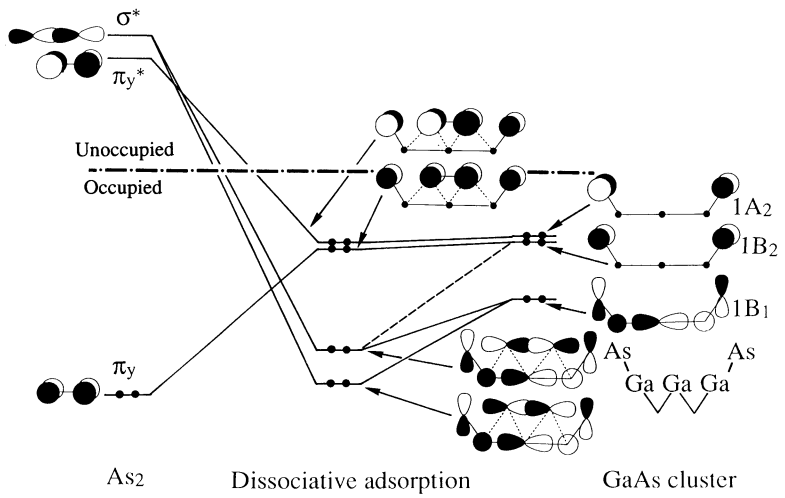



Fig. 9. Orbital correlation diagram for the $Ga_8As_{10}H_{20} + As_2$ system from point 9 to 14. Only these orbitals which do not have full participation in fig. 8 are shown. The broken line shows a charge transfer from the surface to $As_2$.

tively. The approach of $As_2$ to the Ga surface leads to the electron excitation from the $1A_1$ orbital to the $2B_1$ orbital of the GaAs cluster which is indicated by the broken line in fig. 8. This excitation causes the first energy barrier at point 3. The next step is an electron donation from the $2B_1$ orbital to the $\pi_z^*$ anti-bonding orbital of $As_2$ and the back donation from the $\pi_z$ bonding orbital of $As_2$ to the $1A_1$ orbital. This step creates the two bonding orbitals which give an attractive interaction at point 8. Two As atoms representing the step site do not take part in this stage of the reaction, so that the mechanism of this stage is essentially equal to the same stage of the reaction on a flat surface studied in the previous section.

We next study the mechanism in the second stage of the reaction using fig. 9. Only the six orbitals of the $As_2$ and GaAs cluster are shown on the left- and right-hand sides of fig. 6. The orbitals at point 14 are shown as "dissociative adsorption". The difference from the second stage discussed in the previous section is the existence of the two orbitals belonging to the surface As atoms, namely $1A_2$ and $1B_2$ orbitals. The electron transfer from the $1B_2$ orbital to the $\pi_y^*$ anti-bonding orbital of $As_2$, which is indicated by the broken line in fig. 9, causes the second energy barrier at point 9. The electron donation from the $1A_2$ orbital to the $\sigma^*$ orbital of $As_2$ and the back donation from the $\pi_y$ orbital of $As_2$ to the $1B_2$ orbital are important for the dissociative adsorption. The $\pi_y$ and $\pi_y^*$ orbitals become the dangling bonds of the newly created As surface, but at the same time, they contribute to the bonds with the neighboring surface As atoms. These mechanisms explain the change of the charge on the As atoms shown in fig. 6. From point 1 to 8, the charge of As is less than $-0.06$. At point 9 to 14, it becomes $-0.21$ due to the charge transfer. On a flat surface, the $\pi_y$ bonding orbital of $As_2$ is filled and does not interact with any other orbital, but the electron donation from the $\pi_y$ orbital to the $1B_2$ orbital occurs and makes a bond with neighboring As atoms. Because of this electron donation, the charge of the adsorbed As atoms of $-0.48$ on a flat surface is reduced to $-0.21$ on a step site and the bonding with the surface As atoms makes the adsorption energy of 19 kcal/mol on a flat surface to the value of 132.0 kcal/mol at the step site.

## 5. Conclusion

The $As_2$ cluster beam on a Ga-stabilized GaAs surface is molecularly adsorbed and migrates on a flat surface, and then it is dissociated at a step site, giving a new As layer growing on the Ga surface. The calculated energy barrier for the $As_2$ adsorption is 23.5 kcal/mol on a flat surface and 9.6 kcal/mol at a step site, and the energy barrier for the dissociative adsorption at a step site is 16.9 kcal/mol.

The molecular adsorption state at a step site is similar to that on a flat surface and the adsorption energies are 29.7 kcal/mol on a flat surface and 49.2 kcal/mol at a step site. The adsorbed $As_2$ cluster is almost neutral and the As–As length is slightly longer than that of free $As_2$. The energy barrier for the molecular adsorption is due to the orbital reorganization within the dangling bonds of the Ga surface. At the molecular adsorption, the electron transfer from the dangling bond of the surface to the $As_2\,\pi^*$ orbital and the back donation from the $As_2\,\pi$ orbital to the dangling bond break the $\pi$ bonding of the $As_2$ and make a bond between the $As_2$ and the surface Ga atom.

The geometry of the dissociative adsorption state at a step site is similar to that on a flat surface and shows a good agreement with the crystal lattice structure, but the adsorption energy on a flat surface, 49.2 kcal/mol is much different from the value of 132.0 kcal/mol at a step site showing that the dissociative adsorption at a step site is more favorable. The charge of the adsorbed As atom is $-0.48$ on a flat surface and $-0.21$ at a step site. The energy barrier between the molecular and dissociative adsorption is due to the electron transfer from the dangling bond of the surface Ga atom to the $As_2$ cluster. At the dissociative adsorption, the electron transfers from the dangling bond to the $\sigma^*$ orbital of $As_2$ and from the $\sigma$ orbital of $As_2$ to the dangling bond of the surface work to break the $\sigma$ bond of

the $As_2$ and make a bond between the As atom and the surface Ga atom. The bonding between the adsorbed As atom and the neighboring As atom at the step site makes the adsorption energy and the atomic charges to be site-dependent.

Experimentally, a free gallium atom is shown to exist on a GaAs surface and expected to play an important role in the crystal growth mechanism. In our succeeding paper, we will study the epitaxial growth reaction by the participation of the free Ga atom.

## Acknowledgements

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