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Theoretical study of As_2 desorption from the Ga dangling-bond site

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The cluster model As_2-$(GaH_2)_4$ is used for *ab initio* complete active space self-consistent-field (CASSCF) molecular-orbital calculations, to investigate the electronic mechanism of As_2 desorption from the fourfold-hollow Ga dangling-bond (DB) site. The electronic state of the adsorbed As_2 is revealed to be the $\sigma_g^2\pi_u^2\pi_g^2$ doubly excited configuration, where the free As_2 molecule is characterized by $\sigma_g^2\pi_u^4$ with the triple bond. Namely, the four π orbitals of the As_2 unit are used to form the four Ga-As covalent bonds with the Ga-DB site and a weak σ bond remains between the two As atoms. The calculated CASSCF wave functions indicate that the desorption process could be just the chemical reaction of multiple bond conversions having strong electron correlations due to the near degeneracy. The single-configurational picture is completely invalid in understanding the As_2 desorption. The transition state is found to be of the "late-barrier" type, and from this the "cold" vibrational distribution of the desorbed As_2 is predicted.

I. INTRODUCTION

Very recently, a series of *ab initio* molecular-orbital (MO) calculations have been performed to investigate the Ga layer growth mechanism in the chloride atomic layer epitaxy (ALE) process.[1-3] In the chloride ALE, to grow the Ga monolayer, the GaCl molecules are supplied together with the carrier H_2 gas at the As dangling-bond (DB) site. The fundamental electronic mechanism of Ga layer growth has been revealed as follows: First, the GaCl is absorbed by forming Ga-As covalent bonds through configuration mixing.[1] Nondynamical electron correlations are essential to describe properly the GaCl/As-DB adsorption process because of the near degeneracy, as in the case of $SiCl_2$/Si-DB.[4] It is notable here that the electronic structure of the adsorbed GaCl does not correlate with the ground state $^1\Sigma^+$ but does correlate with the valence excited state $^3\Pi$. At the second stage, the H_2 removes the Cl atom from Ga as HCl by the concerted reaction.[2,3] The Cl removal should be followed by the formation of the Ga-Ga reactive "dimer." Cluster models have been used in Refs. 1–4 and the results show that the electrons concerned with surface reactions seem to be reasonably localized around the active reaction site. Therefore, the cluster approach can be a useful tool as long as discussions are focused on the nature of reaction mechanisms.

In this paper, the electronic mechanism of As_2 desorption from the Ga-DB site will be analyzed in detail by using the MO-cluster approach, taking electron correlations into account. Since the control of As stoichiometry during growth is very important to obtaining defectless GaAs crystals, the surface chemistry of As layers is of special interest for general epitaxial growth processes including ALE or molecular-beam epitaxy (MBE). Thus, there have been extensive experimental and theoretical studies on the As surface.[5-32] The loss of As atoms crucially affects the surface stoichiometry and this leads to a variety of reconstructions. In other words, the stable surface phase depends on the As coverage Θ_{As}. The most probable loss route is the As_2 desorption (or sublimation). The energetics of As_2 desorption are investigated mostly in the temperature-programmed desorption (TPD) experiments.[5-11] The stable structures of the As layer are measured by methods such as scanning tunneling microscopy (STM), reflection high-energy electron diffraction (RHEED), and x-ray diffraction.[12-24] The associated theoretical calculations are based on the density-functional (DF) and tight-binding schemes.[25-32] For example, in the case of the (100) surface of $\Theta_{As}=0.75$, the stable phase seems to be settled as 2×4-$c(2\times8)$ which contains the three As dimer rows and the one "missing-dimer" row in the unit cell. The experimental TPD values for this structure are reported to be 1.95,[5] 2.25,[8] and 2.42 eV.[9] Ohno has reported a corresponding estimate of 2.8 eV by using the DF-slab calculations.[32] This value compares reasonably with experimental values 1.95–2.42 eV (Refs. 5 and 8–9). However, to our knowledge, there have been no studies involving the electronic mechanism of the As_2 desorption process. The As dimer adsorbed on the fourfold-hollow Ga site of the (100) direction should have an As-As σ bond. Namely, each As atom of the dimer has two Ga-As bonds, one As-As σ bond, and one 4*s*-like lone pair. On the contrary, the free As dimer or the As_2 molecule has the triple bond of σ, $\pi\times2$, whose main configuration is isovalent with N_2 and is symbolically given by

$$X\,^1\Sigma_g^+ : \sigma_g^2\pi_u^4 \; . \tag{1}$$

Except for some changes of the hybridization, this formally predicts that all four π orbitals of As_2 should be

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used to form the four Ga-As bonds through the excitation of $\pi_u^2 \rightarrow \pi_g^2$. When the As_2 completely desorbs from the Ga-DB site, the Ga-Ga "dimerization" is also expected. This naturally suggests that the As_2 desorption process could be understood as a chemical reaction of multiple bond conversions, where the four Ga-As bonds are being broken and the two As-As π bonds of As_2 and the two Ga-Ga bonds of the DB site are being created. From the viewpoint of chemical reactions, such multiple bond conversions would be the common feature of As_2 desorption independent of various surface phases. Therefore, the present MO-cluster approach, which will illuminate desorption mechanisms such as configuration mixing, should be informative for understanding the As surface chemistry.

The complete active space self-consistent-field[33] (CASSCF) scheme is applied in the present theoretical investigation, since the nondynamical correlation due to the near degeneracy of many electronic configurations is highly expected for the multiple bond conversions. In fact, the system will show strong configuration mixing. The CASSCF calculations are performed on the cluster model As_2-$(GaH_2)_4$ which mimics the As dimer on the fourfold-hollow Ga-DB site. According to previous studies,[1-4] although the present cluster is the simplest model, it is still sufficient to qualitatively understand the bond-conversion process during the As_2 desorption. The two-dimensional potential-energy surface (PES) is calculated, where the geometrical parameters are the distance between As_2 and the Ga-DB surface and the As-As distance. The structures of the stable surface As dimer and the transition state (TS) are determined, and the characterizations of the PES of desorption are also made.

II. COMPUTATIONAL DETAILS

A. Basis set

In the present calculations, the model potential (MP) technique[34] is applied to replace the 28 $1s$-$3d$ core atomic orbitals (AO's) of the Ga and As atoms. Namely, the $4s4p$ valence electrons of Ga and As are explicitly treated using the basis-set expansion. The valence *Gaussian* basis set is $5s5p$, whose functions are contracted to (4,1/3,1,1). The core AO potentials are also constructed by the *Gaussian* sets of $12s9p4d$. These numerical parameters were determined by two of the authors (Y.S. and E.M.).[35] For these Ga and As valence basis functions, the sets of diffuse-s and polarization-d functions are augmented. The exponents for Ga are 0.023 384 9 for diffuse s and 0.207 (Ref. 36) for polarization d. The corresponding values for As are 0.039 249 9 and 0.293.[36] The extra s exponent is derived from the two outermost exponents of $5s$ in the geometric mean manner. The contracted sets for Ga and As can be written as $[3s3p1d]$. For H in the GaH_2 unit, Van Duijneveldt's $5s$ primitives[37] are contracted to (4,1). The total number of basis functions is 118 for the cluster model.

B. Cluster model

The cluster model As_2-$(GaH_2)_4$ illustrated in Fig. 1 is used to calculate the CASSCF PES of the As_2 desorption.

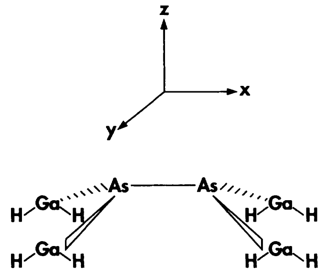

FIG. 1. Structure of the As_2-$(GaH_2)_4$ cluster.

This locally "extracts" the single As dimer unit on the fourfold-hollow Ga-DB site of the (100) surface. Since the symmetry of this cluster is C_{2v}, the MO's are classified into the four subgroups of C_{2v}, i.e., a_1, a_2, b_1 and b_2. The C_{2v} framework is kept throughout the calculations. Namely, the As_2 is imposed to be desorbing along the z axis without any tilting and twisting. The C_{2v} restriction could make the orbital phasings between As_2 and Ga-DB clearest. The lower symmetry cases will be considered in Sec. III B. Note that the As_2 ${}^1\Sigma_g^+$ state (1) of the $D_{\infty h}$ symmetry correlates with the ${}^1A_1$ state under the C_{2v} symmetry group currently used.

When the desorption is completed, the free Ga-DB site should be dimerized with some reconstructions. However, the reconstruction at the dimerized Ga site is neglected in the present model, and all the Ga-Ga distances are fixed at 4 Å (=7.55 a.u.) of the GaAs bulk value throughout the calculations, as done in the previous studies.[1,4] The effect of this constraint will be discussed in Sec. III B. The inner Ga-As bonds, which are directed toward the As sublayer under the Ga-DB site, are simply replaced by the isopolar Ga-H bonds, where the positive polarity is on the Ga atom.[2,3] Thus, the fourfold-hollow Ga-DB site is mimicked by the $(GaH_2)_4$ cluster in the current simulation. The local symmetry of the GaH_2 fragment is also the C_{2v} point group and the ground state is ${}^2A_1$ with the one open-shell MO (a_1 symmetry). The bond angle of H-Ga-H is set at 109.5° by assuming sp^3 hybridization. With the fixed angle of 109.5°, the Ga-H bond length is optimized to be 1.55 Å (=2.93 a.u.) by using the five-electron SCF calculations because of the MP replacement. The GaH_2 unit has an empty Ga $4p(b_1)$ orbital which is perpendicular to the H-Ga-H plane. The Ga sp^3 lobe to be connected with the As dimer should be formed by mixing the open-shell a_1 MO and the empty b_1 MO of each GaH_2 and the four open-shell electrons are active, or are concerned with, the Ga-As bonds. At the desorption limit, the dimerized Ga-DB site with the two Ga-Ga bonds is formally represented by the lowest ${}^1A_1$ state of $(GaH_2)_4$, although there is the multiconfigurational character, as pointed out in Refs. 1 and 4. Note that the other Ga sp^3 lobes, where are directed away from the As_2 side, are kept vacant throughout the present computational scheme.

C. CASSCF calculations

When the MP is used to replace the 28 $1s$-$3d$ core electrons, the total number of electrons of the As_2 unit is 10.

In the free As_2 case, the six electrons are actively involved in the triple bond of configuration (1) and the remaining four electrons are of the semicore 4*s* type. Similarly, for $(GaH_2)_4$, the total number of electrons is 20 ($=5\times4$), where the four electrons are of the active DB type and the other 16 electrons belong to the terminating Ga-H bonds. thus, the total number of electrons is 30 for the As_2-$(GaH_2)_4$ cluster.

According to the prediction in Sec. I the four Ga-As bonding MO's could be schematically decomposed into components of As_2 and Ga-DB, as illustrated in Fig. 2. Note that a similar figure was used by Panas, Siegbahn, and Wahlgren who analyzed the O_2 adsorption onto the fourfold-hollow Ni (100) surface by using the MO-cluster approach.[38] Hoffmann's "isolobal analogy" concept[39] relates the present MO decomposition of As_2/Ga-DB with that of O_2/Ni. The *z* and *y* components of π orbitals of As_2 fragments are perpendicular and parallel to the Ga surface, respectively. The As_2 π orbitals are labeled by a_1 for π_{uz}, b_2 for π_{uy}, b_1 for π_{gz}, and a_2 for π_{gy}, under the present C_{2v} coordinate system. The four possible combinations of active sp^3 lobes of each GaH_2 also present symmetric orbitals, DBa_1, DBa_2, and DBb_1, and DBb_2. Therefore, as shown in Fig. 2, the four Ga-As bonding orbitals result from the in-phase mixings between As_2 and Ga-DB sides.

In the stable As dimer structure, the single closed-shell $^1A_1$ configuration

$$^1A_1{:}(1a_1-5a_1)^{10}(1a_2-3a_2)^{5}(1b_1-4b_1)^{8}(1b_2-3b_2)^{6} \tag{2}$$

dominates the CASSCF wave function of the cluster system, where its weight will be shown to be 86% in Sec. III B. The $5a_1$ MO, which consists of As $4p_x$ AO's, describes the As-As σ bonding orbital. The $4a_1$, $3b_2$, $4b_1$, and $3a_2$ of the MO correspond, respectively, to the Ga-As bonding MO's illustrated in Fig. 2, $\pi_{uz}+\mathrm{DB}a_1$, $\pi_{uy}+\mathrm{DB}b_2$, $\pi_{gz}+\mathrm{DB}b_1$, and $\pi_{gy}+\mathrm{DB}a_2$. However, if the system even slightly proceeds to the desorption from the stable dimer structure, the single-configurational description immediately becomes a poor approximation. Namely, the multiconfigurational description is needed because of the near degeneracy among excited configurations. Such multiconfigurational characters should decrease the occupations of Ga-As bonding MO's and increase those of antibonding MO's that have the out-of-phase combinations between As_2 and Ga-DB. Finally, at the desorption limit, the total of eight bonding and antibonding Ga-As MO's have to separate into the four As_2 π and four Ga-DB fragmental orbitals, where the state of free As_2 is $^1\Sigma_g^+$ ($={}^1A_1$) and that of dimerized $(GaH_2)_4$ is $^1A_1$. The changes of π-electron configurations should affect the σ bond length of the As_2 unit, and the proper description of σ space requires the pairing of $\sigma_g(a_1)$ and $\sigma_u(b_1)$. Therefore, the CASSCF active orbital space consists of the σ_g, π_u, π_g, and σ_u of As_2 and the DBa_1, DBa_2, DBb_1, and DBb_2 of $(GaH_2)_4$. These ten orbitals correlate with the MO's of $4a_1$-$6a_1$, $3a_2$-$4a_2$, $4b_1$-$6b_1$, and $3b_2$-$4b_2$ in the As_2-$(GaH_2)_4$ cluster. Under the constraint of the $^1A_1$ total symmetry, the ten [six from As_2 and the remaining from $(GaH_2)_4$] active electrons are distributed among the ten active MO's in all possible ways. Thus, the complete active space configuration-interaction (CASCI) dimension is 4936. The remaining ten occupied MO's are defined as inactive and are composed of two 4*s*-like MO's of As_2 and the eight Ga-H bonding orbitals. Note that the two lone pairs of the stable As dimer could be described by the As 4*s* inactive MO's through some hybridizations with 4*p*.

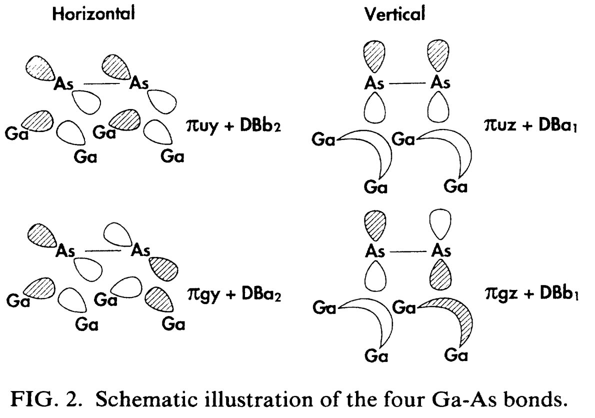

FIG. 2. Schematic illustration of the four Ga-As bonds.

Unfortunately, the further expansion of the active orbital space, e.g., inclusion of the four vacant Ga sp^3 lobes, is impossible due to the dimensional explosion. The successive multireference singly and doubly excited CI (MRSDCI) calculations, which incorporate dynamical correlations in the system, are definitely desired but are similarly intractable on the current computational resources. In other words, only nondynamical correlations are taken into account by CASSCF in the present computational scheme.

By changing the two geometrical parameters, the distance between As_2 and the Ga surface and the As-As distance, more than 100 grid points are calculated. The stable structure of the As dimer is determined by the global fitting into the sixth-order polynomial. In contrast, the TS structure is obtained by second-order local fitting.

III. RESULTS AND DISCUSSION

A. Electronic structure of As_2

The electronic structure of the As_2 unit must be changing during the desorption process. Therefore, before discussing the mechanism of As_2 desorption, the electronic structure of As_2 itself should be reviewed and the reliability of the present computational scheme should be proved. Table I summarizes the CASSCF spectroscopic constants and important configurations for the $X\,^1\Sigma_g^+$ As_2 molecule. To assess the present results, the Table also contains the experimental data[40] and the other theoretical estimates[41-43] published previously. In Refs. 41 and 42, the effective core potential (ECP) technique was used to replace the 1*s*-3*d* AO's, as in the present MP calculations. The quality of the valence basis could be virtually the same for the calculations listed in Table I.

First, Table I shows that the noncorrelated SCF

TABLE I. CASSCF results for the $X\,^1\Sigma_g^+$ As_2.

Experimental	R_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
Experimental Ref. 37	3.97	430	4.01
Theoretical, present MP [3s3p1d]/CASSCF[a]	4.10	393	2.74
Theoretical, Ref. 41, ECP [3s3p1d]/MRSCI	4.09	394	2.71
Theoretical, Ref. 42, ECP [3s3p1d]/SCF	3.95	508	−0.72
/MRSDCI	4.11	429	2.54
Theoretical, Ref. 43, all-electron [7s5p2d]/SCF	3.91	514	0.43
/CCSD	4.05	437	2.67

Configuration	Excitation	Weight (%)[b]
$\sigma_g^2\pi_u^4$		87.17
$\sigma_g^2\pi_u^2\pi_g^2$	$\pi_u^2 \rightarrow \pi_g^2$	9.30
$\sigma_g\pi_u^3\pi_g\sigma_u$	$\sigma_g\pi_u \rightarrow \pi_g\sigma_u$	2.03

[a] The R_e is determined by the fourth-order polynomial fitting. The total energy at R_e is −12.1509 a.u.

[b] Configurations whose weights are greater than 0.8% are shown.

values[42,43] for ω_e and D_e are quite poor even for the free As_2 molecule. The reason for this is apparently the near degeneracy, which is demonstrated by the weights in the present CASSCF wave function. Its artificially enhanced single-configurational character is responsible for the seemingly close correspondence between the SCR R_e of Ref. 42 and the experimental value of 3.97 a.u. Hereafter, our discussions will focus on the correlated results.

The types of CI calculations used in Refs. 41 and 42 are MRSCI [or first-order CI (FOCI)] and MRSDCI, respectively. Note that the MRSCI hardly takes dynamical correlations into account. In contrast, the coupled-cluster single and double excitations (CCSD) theory[44] in Ref. 43 is started on the SCF single reference, but the multireference nature is partly introduced by the incorporation of higher-order multiple (more than two-body) excitations. Thus, the CCSD method is applicable for a system having some near degeneracies[45] such as As_2 around R_e.

The As-As equilibrium distance R_e is currently calculated to be 4.10 a.u. which is appreciably longer than the experimental length of 3.97 a.u. The other theoretical R_e's show the same trend. In Ref. 43, Scuseria also reported the very accurate CCSD value of 3.98 a.u. which was obtained by using the more extended basis of [7s6p4d1f] and by further correlating the outer-core 3d electrons. Namely, the extensively correlated treatment, which takes the higher-order excitations, the up-to-f polarizations, and the additional correlations from outer-core electrons into account, should be required to quantitatively estimate the R_e of As_2. Such calculation is unable to perform the As_2-$(GaH_2)_4$ cluster system. Therefore, a certain correction should be considered, if the calculated As-As bond length for the stable As dimer on the Ga-DB site is compared with the experimental data in Sec. III B.

The present ω_e of 393 cm^{-1} is in reasonable agreement with the experiment (430 cm^{-1}). The D_e of 2.74 eV is similar with the other theoretical values,[41−43] although there is still an error more of than 1 eV in comparison with the experimental data of 4.01 eV.[40] As a whole, the present CASSCF procedure is expected to have an acceptable reliability for the purpose of investigating the electronic mechanism of As_2 desorption from the Ga-DB site.

The near degeneracy in the π space is notable for the As_2 molecule, as seen in Table I. Namely, the nondynamical correlation is important even at the R_e. The $\pi_u^2 \rightarrow \pi_g^2$ doubly excited configuration $\sigma_g^2\pi_u^2\pi_g^2$ should describe the left-right correlation of the π electrons, where its weight in the CASSCF wave function is 9.3%. Balasubramanian also pointed out the importance of the $\pi_u^2 \rightarrow \pi_g^2$ excited configuration[41] for the As_2 molecule. The mixing of $\sigma_g^2\pi_u^2\pi_g^2$ substantially reduces the formal bond order of 3 given by the $\sigma_g^2\pi_u^4$ ground configuration (1). The effective configuration of $X\,^1\Sigma_g^+$ As_2 at R_e can be represented as

$$\sigma_g^{1.96}\pi_u^{3.76}\pi_g^{0.24}\sigma_u^{0.04} \qquad (3)$$

by the occupation numbers of present CASSCF active orbitals.

In Sec. I of this paper, the configuration of the stable As dimer on surface was formally predicted to be $\sigma_g^2\pi_u^2\pi_g^2$, which results from the double excitation and has the single σ bond. Thus, the excited states should be of interest. Balasubramanian already surveyed the singlet and triplet excited states.[41] The lowest one was calculated to be the singly excited $c\,^3\Sigma_u^+$ state whose main configuration is $\sigma_g^2\pi_u^3\pi_g$, where the estimated excitation energy of 1.47 eV is comparable to the experimental value of 1.80 eV. Balasubramanian[41] also showed that the doubly excited states, which are characterized by $\sigma_g^2\pi_u^2\pi_g^2$, are quasibound relative to the ground-state dissociation, but are low lying, where the excitation energies are 4.06 eV for $^1\Sigma_g^+$(II) and 3.80 eV for $^3\Delta_g$. The quintet excited state $^5\Sigma_g^+$, which was not calculated in Ref. 41, would be lower than these singlet and triplet states, due to the exchange interaction. According to the intramolecular Hund's rule, the contribution of the quintet $\sigma_g^2\pi_u^2\pi_g^2$ might be mostly favored to form the four Ga-As bonds with the fourfold-hollow Ga-DB site, as seen in the previous study of GaCl/As-DB.[1] The CASSCF results for the doubly excited ${}^5\Sigma_g^+$ will be shown in Sec. III B, and compared with the character of the stable As dimer on the Ga surface.

B. Nature of As_2 desorption from Ga-DB

Figure 3 illustrates the schematic view of CASSCF PES for the As_2 desorption of the ${}^1A_1$ state. The energetic summary of PES is given in Table II. Prior to focusing the discussions on the electronic mechanism of desorption, the calculated energetics and the stable dimer length are compared with the available experimental data, checking the reliability of the present investigation.

First, the TPD value is considered. Since the TS exists during the desorption, the theoretical TPD energy is estimated to be 2.65 eV by summing up the well depth (2.19 eV) and the barrier height of TS (0.46 eV). The value of 2.65 eV compares with the experimental TPD values of 1.95–2.42 eV.[5,8,9] However, some problematic concerns should be pointed out for this direct comparison, as mentioned in Ref. 1. The first is the so-called "cluster size" problem which has been extensively studied in the adsorption energies on the transition-metal surfaces.[46–51] Namely, the computational energetics depends on the sizes of model clusters, where their deviations are roughly 0.5–1.0 eV. A similar situation could also take place for semiconductor surfaces such as GaAs. To see the convergence trend for quantitative discussions, a series of systematically enlarged cluster models should be employed. The other two concerns, which should have some effects on the energetics, are the geometrical constraint noted in Sec. II B and the missing of dynamical correlations caused by the impossible execution of MRSDCI (Sec. II C). Recall that, in the present investigation, the CASSCF calculations are performed on the simplest cluster As_2-$(GaH_2)_4$ only to investigate the electronic mechanism of As_2 desorption such as configuration mixing. Although we mention above three problematic concerns, the first estimate by the *ab initio* MO-cluster approach was 2.65 eV, which is qualitatively acceptable for the present purpose. Definitely, future extensive *ab initio* MO calculations, in which the size dependence, the geometrical freedom, and the dynamical correlation are all taken into account, are required to quantitatively compare the theoretical As_2 TPD energies with the experimental value of 1.95–2.42 eV.[5,8,9]

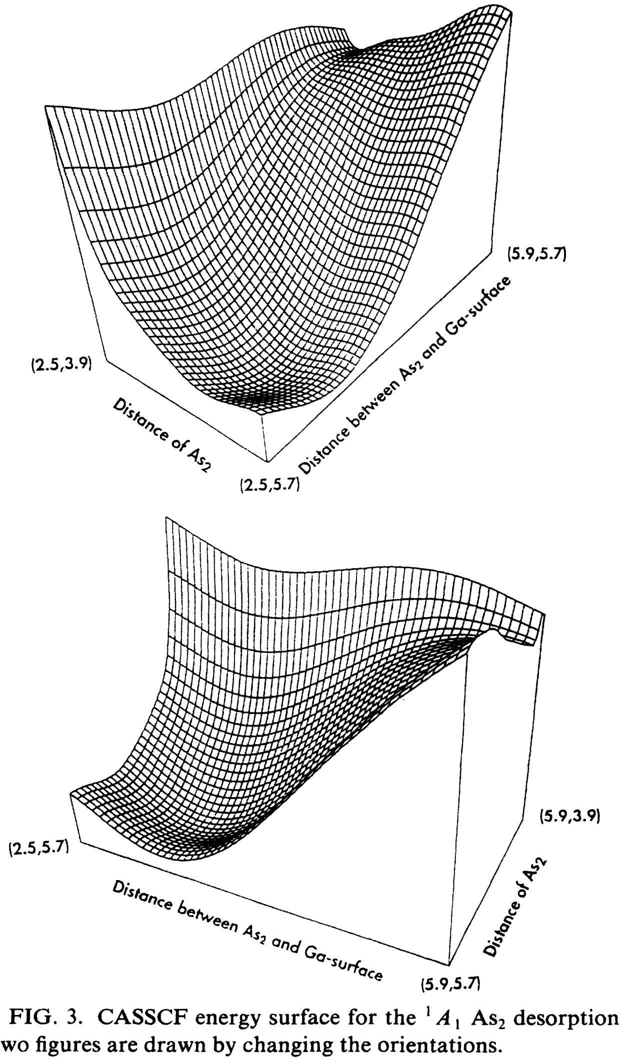

FIG. 3. CASSCF energy surface for the ${}^1A_1$ As_2 desorption. Two figures are drawn by changing the orientations.

TABLE II. Distance parameters and energies (relative energies to the desorption limit; the total energy at the desorption limit is -24.5582 a.u., where the As-As distance is 4.10 a.u. in Table I) for the stable surface dimer and the TS of desorption.

	As_2-Ga surface (a.u.)	As-As (a.u.)	Energies (eV)
Stable dimer	3.34	5.14	−2.19
TS	5.71	4.22	0.46

The second comparison with the experiment concerns the As-As distance of the stable dimer. The experimental dimer distance has been measured to be 2.56–2.62 Å (=4.84–4.95 a.u.) for the $c(4\times4)$ structure by the x-ray diffraction.[17] Even considering some geometrical constraints imposed on the present model cluster, the estimated value of 5.14 a.u. in Table II is appreciably longer than the experiment. The most probable reason for this disagreement could be the basis-set flexibility and the dynamical correlation effect involving further 3*d* electrons, as seen in Sec. III A for the free As_2 molecule. The calculated R_e for As_2 was longer than the experimental value[40] by 0.13 a.u. (see Table I). If the correction of 0.13 a.u. is adapted for the surface dimer, the corrected estimate of 5.01 a.u. (= 2.65 Å) seems to be acceptable relative to the experiment.[17] This again implies that the present calculations are reliable enough to qualitatively reveal the electronic mechanism of desorption.

Now, we will discuss the nature of As_2 desorption. Figure 3 shows that the TS of desorption is located far from the stable As dimer structure. Namely, the TS is characterized to be of Polanyi's "late-barrier" type,[52] which is generally known for endothermic reactions as in the present case. The As-As distance of 4.22 a.u. at the TS is considerably shortened from that of the stable structure of 5.14 a.u. The close correspondence between 4.22 a.u. of TS and 4.10 a.u. of the free As_2 molecule is consistent with the "lateness." This suggests that the As_2 π bond is "slowly" reproduced during the desorption.

Polanyi's rule[52] could predict that the vibrational distributions of the products as "cold" for the reactions of the "late-barrier" type. Therefore, the vibrational distributions of the desorbed As_2 from the Ga-DB site are expected to be "cold." Recently, using the laser-induced-fluorescence (LIF) spectroscopy, Alstrin *et al.* have measured the vibrational distributions of the As_2 molecules which have just desorbed from the Si (100) and (111) surfaces.[53] They actually reported the "cold" vibrational distributions of As_2 for both (100) and (111) orientations and speculated that the desorption process, in which the Si-As covalent bonds should be broken, has a localized nature. Alstrin *et al.*[53] also pointed out that the covalent bonding to the Si surface would make the well depth of the As dimer bond more shallow. Although there should be some quantitative differences between the cases of Ga/As_2 and Si/As_2, their results are in accord with the present investigation. Reference 53 did not treat the rotational distributions. Note that the "cold" rotational distributions have been known for the recombinatively desorbed H_2 from Si surfaces.[54,55] In the present study, to illustrate clearly the orbital interactions between As_2 and Ga-DB during the desorption, the C_{2v} symmetry restriction is imposed. Namely, the motion of As_2 is forced to be in the concerted manner and there is no torque to rotate the desorbing As_2 molecule. When the system has an As_2 tilting in the xz plane, the symmetry is lowered to C_s. The two Ga-As bonds associated with the one As atom should break first in the C_s desorption. In contrast, the desorption system belongs to the lowest C_1 symmetry, if the As_2 is twisted in the xy plane. The C_1 desorption may favor the first breaking of the two diagonal Ga-As bonds. Thus, the rotational motions could be induced for the routes of C_s (vertical to the surface) and C_1 (horizontal). According to the Woodward-Hoffmann rules, the C_1 desorption is expected to be the lowest route. Unfortunately, due to more geometrical parameters, the correlated calculations for the lower symmetry PES's are much more demanding than the present C_{2v} case. The experiments on rotational distributions will make the nature of As_2 desorption more clear. The rovibrational distributions should be experimentally measured for the Ga/As_2 system.

The four Ga-As bonds in Fig. 2 are symbolically described in the completely covalent fashion. However, as expected by the difference of electronegativities, a polarity of $Ga^{\delta+}$-$As^{\delta-}$ should exist due to the contributions of ionic or dative types. In fact, the active bonding MO's have the larger components on the As_2 side than on the Ga-DB side. At the stable dimer structure, the Mulliken analyses on the active orbitals show that the weights of each As_2 component for a_1, b_2, b_1, and a_2 bonding MO's are 63% (π_{uz}), 56% (π_{uy}), 54% (π_{gz}), and 50% (π_{gy}), respectively. The corresponding antibonding active MO's which are weakly occupied at the stable structure must result from the countermixings.

Table III shows the important configurations of the CASSCF wave functions and Table IV lists the resulting occupation numbers of active MO's. These tables impressively demonstrate that the significant multiconfigurational character appears when the system goes to desorption. The main configuration given by (2) dominates the CASSCF wave function by a weight of 86% at the stable dimer structure. However, the single-configurational picture is valid only around the bottom of PES. Toward the desorption, various excited configurations must mix to describe the multiple bond-conversion reaction in which the four Ga-As bonds are being broken and the two As_2 π bonds and the two Ga-Ga bonds are being created. In other words, nondynamical correlations are essential to trace properly the PES of the As_2 desorption. Reference 1 has also shown the multiconfigurational character during the GaCl adsorption onto the twofold-hollow As-DB site, but its degree is less significant than the present system, As_2/Ga-DB. The reason for this may be the difference of the number of bonds to be converted [currently four versus two previously (Ref. 1)].

The characteristics of active orbitals, which are sorted according to the occupation numbers in Table IV, are being changed by the progress of desorption. For example, the $4a_1$ active MO corresponds to the $\pi_{uz}+\mathrm{DB}a_1$ bonding orbital and the $5a_1$ MO is of the As-As σ_g bonding type, at the stable As dimer structure. But the relation is reversed at the sample point of intermediate 1. The $3a_2$ MO also changes from the $\pi_{gy}+\mathrm{DB}a_2$ type (stable point) to essentially $\mathrm{DB}a_2$ (TS). If one wishes to watch the effective configurations of the As_2 unit during the desorption process, this situation of active MO's is inconvenient. Thus, by the use of Mulliken populations of the active MO's, the effective occupation numbers of σ_g, π_u, π_g, and σ_u are estimated for the above object and the resulting numerical values are summarized in Table V. Note that the similar analysis was used by Panas, Siegbahn, and Wahlgren who calculated the O_2/Ni adsorption system.[38] The effective configuration of the As_2 fragment is shown to be

$$\sigma_g^{1.83}\pi_u^{2.41}\pi_g^{2.07}\sigma_u^{0.08} \tag{4}$$

at the stable structure. This is considered to essentially be the doubly excited configuration $\sigma_g^2\pi_u^2\pi_g^2$, being in exact agreement with the formal prediction in Sec. I. The π_u occupation increase of 0.4 should be attributed to the polarized Ga-As bonds in a_1 and b_2 symmetries, as discussed before. Intramolecular Hund's rule suggests that the quintet contribution of $\sigma_g^2\pi_u^2\pi_g^2$ doubly excited configuration could be mostly favored in the Ga-As bond formation, although the singlet and triplet contributions are also possible. To date, no quintet states have been calculated for As_2. Therefore, the CASSCF calculations are performed on the ${}^5\Sigma_g^+$ state of $\sigma_g^2\pi_u^2\pi_g^2$. The calculations show that this state is bound with a very shallow well of 0.16 eV relative to the dissociation limit. The calculated spectroscopic constants for ${}^5\Sigma_g^+$ are 5.16 a.u. for R_e, 166 cm^{-1} for ω_e, and 2.58 eV for T_e. These values indicate that the remaining σ_g bond is weak. The ${}^1\Sigma_g^+ \rightarrow {}^5\Sigma_g^+$ excitation energy of 2.58 eV is actually lower than 4.06 eV for ${}^1\Sigma_g^+$(II) and 3.80 eV for ${}^3\Delta_g$, which were calculated by Balasubramanian.[41] Thus, the highest-spin

TABLE III. Important configurations (configurations with weights greater than 0.8% are listed) of the CASSCF wave functions of the As_2-$(GaH_2)_4$ cluster.

Sample[a]	$4a_1$	$5a_1$	$6a_1$	$3a_2$	$4a_2$	$4b_1$	$5b_1$	$6b_1$	$3b_2$	$4b_2$	Weight (%)[c]
Stable dimer (3.34,5.14)	2	2	0	2	0	2	0	0	2	0	86.32
	2	0	0	2	0	2	2	0	2	0	1.48
	2	2	0	1	1	2	0	0	1	1	0.94
	2	0	0	2	0	2	1	1	2	0	0.82
											Sum 89.56
Intermediate 1 (4.00,4.90)	2	2	0	2	0	2	0	0	2	0	78.65
	2	2	0	1	1	2	0	0	1	1	1.72
	2	2	1	1	0	1	0	0	2	1	1.61
	2	1	1	2	0	1	1	0	2	0	1.49
	0	2	0	2	0	2	0	2	2	0	1.13
	2	2	0	2	0	1	1	0	1	1	0.93
	2	2	0	1	1	1	1	0	2	0	0.91
	2	1	1	1	1	2	0	0	2	0	0.85
	2	1	1	2	0	2	0	0	1	1	0.82
	2	2	1	2	1	1	0	0	1	0	0.80
											Sum 88.91
Intermediate 2 (4.50,4.60)	2	2	0	2	0	2	0	0	2	0	69.01
	2	2	1	1	0	1	0	0	2	1	4.09
	2	2	0	1	1	2	0	0	1	1	2.54
	2	1	1	2	0	1	1	0	2	0	2.12
	2	2	0	0	0	2	0	2	2	2	1.76
	2	2	2	2	0	0	0	0	2	0	1.41
	2	2	0	2	0	1	1	0	1	1	1.28
	2	1	0	1	0	2	1	0	2	1	1.22
	2	2	1	2	1	1	0	0	1	0	1.19
	2	1	1	1	1	2	0	0	2	0	1.13
	2	2	0	1	1	1	1	0	2	0	0.94
	0	2	0	2	0	2	0	2	2	0	0.86
											Sum 87.55
Intermediate 3 (5.00,4.30)	2	2	0	2	0	2	0	0	2	0	45.18
	2	2	1	1	0	1	0	0	2	1	13.00
	2	2	0	0	0	2	0	0	2	2	6.24
	2	2	2	2	0	0	0	0	2	0	4.64
	2	2	2	0	0	0	0	0	2	2	3.74
	2	2	0	1	1	2	0	0	1	1	2.79
	2	1	1	2	0	1	1	0	2	0	2.27
	2	2	2	0	0	2	0	0	2	0	1.71
	2	1	0	1	0	2	1	0	2	1	1.64
	2	2	1	2	1	1	0	0	1	0	1.53
	2	2	0	2	0	0	0	0	2	2	1.44
	2	2	0	2	0	1	1	0	1	1	1.02
	2	1	1	1	1	2	0	0	2	0	0.93
											Sum 86.13
TS (5.71,4.22)	2	2	1	1	0	1	0	0	2	1	20.00
	2	2	2	0	0	0	0	0	2	2	18.20
	2	2	0	2	0	2	0	0	2	0	17.70
	2	2	0	0	0	2	0	0	2	2	12.90
	2	2	2	2	0	0	0	0	2	0	10.35
	2	1	1	0	0	1	1	0	2	2	1.04
	2	1	1	2	0	1	1	0	2	0	0.91
	2	2	2	0	0	2	0	0	2	0	0.83
											Sum 81.93

[a]The two values in parentheses are the distance between the As_2 and Ga surface and the As-As distance, respectively. Units are in a.u.

TABLE IV. Occupation numbers of the CASSCF active orbitals of the As_2-$(GaH_2)_4$ cluster.

Sample	$4a_1$	$5a_1$	$6a_1$	$3a_2$	$4a_2$	$4b_1$	$5b_1$	$6b_1$	$3b_2$	$4b_2$
Stable dimer	1.95	1.93	0.06	1.94	0.05	1.95	0.08	0.05	1.94	0.05
Intermediate 1	1.94	1.92	0.11	1.88	0.09	1.89	0.10	0.06	1.91	0.11
Intermediate 2	1.95	1.88	0.20	1.78	0.13	1.80	0.13	0.04	1.87	0.21
Intermediate 3	1.96	1.86	0.49	1.46	0.15	1.51	0.15	0.04	1.85	0.53
TS	1.96	1.86	0.98	0.96	0.14	1.03	0.14	0.04	1.85	1.03

quintet contribution has an energetic advantage. The "cost" to prepare this valence excited state is paid by the formation of Ga-As covalent bonds. A similar favor was found in Ref. 1, where the triplet excited state $^3\Pi$ [$T_e = 3.68$ eV (Ref. 40)] is more favorable than the quasibound singlet one $^1\Pi$[~ 4.99 eV (Ref. 40)] for the covalently adsorbed GaCl. The $^5\Sigma_g^+$ R_e of 5.16 a.u. is definitely comparable to 5.14 a.u. for the stable As dimer on the Ga surface (see Table II). The effective configuration of $^5\Sigma_g^+$ is calculated to be

$$\sigma_g^{1.87}\pi_u^{2.02}\pi_g^{1.98}\sigma_u^{0.13} \tag{5}$$

and corresponds well to that of the stable dimer (4) except for the π_u occupation increase. Recall that Alstrin *et al.* pointed out the weakness of the dimer bond for the As_2/Si system.[53] The spectroscopic constants of $^5\Sigma_g^+$ are in line with Ref. 53. As a whole, the main origin of the $^1A_1$ stable dimer structure for As_2-$(GaH_2)_4$ could be the quintet-quintet combinations of $^5\Sigma_g^+$ ($= {}^5A_1$) of As_2 and $^5A_1$ of $(GaH_2)_4$. Through nondynamical correlations, this combination should be dissolved toward the desorption limit.

Table V also contains the Mulliken overlap charges. The overlap charge could reflect the strength of the bond. Apparently, the overlap charges of Ga-As decrease when the desorption proceeds. In contrast, those of As-As increase. The changes of occupations in π_u and π_g consistently synchronize, describing the reproduction of the two π bonds during the desorption. Note again that the As-As overlap charge of 0.11 at the stable dimer compares with that of 0.07 for $^5\Sigma_g^+$ As_2. The effective configuration and the As-As overlap charge at the TS are similar to those of the free $X\,^1\Sigma_g^+$ As_2 molecule. This also agrees with the "late-barrier"[52] character of the TS.

At the TS, the active orbitals of $6a_1$, $4b_1$, $4b_2$ and $3a_2$ correspond, respectively, to DBa_1, DBb_1, DBb_2, and DBa_2 on the Ga-DB site. The reason why each occupation number is close to unity can probably be attributed to the neglect of the reconstruction for the Ga-DB site in the present model cluster. However, this may not be serious, since the Ga-Ga σ dimer bond on the surface is expected to be not so stable. The ground state of the Ga_2 molecule (or the free Ga dimer) is $^3\Pi_u$ with the "formally single" bond given by $\sigma_g^1\pi_u^1$ and its D_e is known to roughly be 1 eV.[40,42,56,57] But this state cannot be directly referred. The usual σ bonded state for Ga_2 is $^1\Sigma_g^+$. Shim, Mandix, and Gingerich have theoretically estimated that the T_e for $^3\Pi_u \rightarrow {}^1\Sigma_g^+$ is 0.36 eV and the D_e is only 0.78 eV.[57] Because of some distortions, the σ bond of the dimer on surface could be weaker than that of the free $^1\Sigma_g^+$ Ga_2. This leads to the dimer bond of Ga-DB being easy to break when some perturbations such as the interaction with As_2 take place. Therefore, even around the TS, the imposed fixation of $(GaH_2)_4$ geometries seems to be acceptable. Note that the all in-phase DBa_1 orbital has the smallest occupation at the TS. The largest repulsion with the π_{uz} electrons of the As_2 side should be responsible for it. Panas, Siegbahn, and Wahlgren also pointed out the similar effect due to the repulsion between O_2 π_{uz} and the Ni surface.[38]

Finally, we will discuss the context of the As_2 adsorption onto the Ga-DB site. In the ALE and MBE methods, the active As carrier is considered to be mainly the As_4 molecule.[58] However, the As_2 molecule should coexist because of the thermochemical equilibrium:[59]

$$2As_2 \leftrightarrow As_4 + 2.35\ \text{eV}\ . \tag{6}$$

Foxon and Joyce measured the sticking coefficients onto the Ga surface for both As_4 and As_2 and speculated that

TABLE V. Summary of Mulliken analyses: effective occupation numbers of the As_2 fragmental orbitals, overlap charges, and net charges. Occupations of As_2 orbitals are estimated by the Mulliken analyses on the active orbitals. The π_z components in a_1 and b_1 symmetries are obtained by summing up the triply divided $4p_z$ AO's and the polarization $4d_{zx}$ AO.

Sample	σ_g	π_u	π_g	σ_u	Ga-As[a]	As-As	$q(As_2)$
Stable dimer	1.83	2.41	2.07	0.08	0.44	0.11	−0.49
Intermediate 1	1.82	2.53	2.02	0.02	0.36	0.12	−0.44
Intermediate 2	1.87	2.70	1.78	0.02	0.30	0.16	−0.37
Intermediate 3	1.92	3.12	1.16	0.03	0.15	0.42	−0.23
TS	1.96	3.58	0.41	0.11	−0.01	0.81	−0.06
Free As_2	1.96	3.76	0.24	0.04		0.97	

[a] Value for the single Ga-As bond.

the sticking mechanisms through adsorption are different from each other.[60,61] The sticking coefficients are close to unity for As_2 but less than half for As_4. According to the detailed balance, the present study on As_2 desorption could be suggestive for As_2 adsorption as the reverse process. When the As_2 approaches the reactive Ga-DB site, the π bond should immediately start to break. Then, the As_2/Ga adsorption system reaches the TS of the "early-barrier" type.[52] If the system passes through the "early" TS, the As_2 molecule is stuck onto the Ga surface by the attractive well which results from the Ga-As covalent-bond formation through significant configuration mixing. The experimental fact that the sticking coefficient of As_2 is nearly unity[60] could be consistent with the feature of presently calculated PES. Some trajectory calculations using this PES would be informative in understanding the behavior of incoming As_2 molecules.[62] During the preparation for the present paper, Fukunishi and Nakatsuji have reported the SCF and the second-order Møller-Plesset perturbation (MP2) MO calculations on the As_2 adsorption process.[63] Unfortunately, their calculations were based on the single-configurational wave function. Note again that the multiconfigurational nature is essential to describe the interaction between the As_2 molecule and the Ga-DB site.

IV. SUMMARY

The As_2 desorption from the fourfold-hollow Ga-DB site was investigated by the *ab initio* CASSCF calculations on the As_2-$(GaH_2)_4$ cluster model. At the stable As dimer structure, the electronic configuration of the As_2 unit is revealed to be $\sigma_g^2\pi_u^2\pi_g^2$. In contrast, the desorbed As_2 molecule is triply bonded with the $\sigma_g^2\pi_u^4$ configuration. Namely, the four π orbitals of As_2 are used to form the four Ga-As bonds by the double excitation. A remaining As-As σ bond is very weak. The calculations showed that the As_2 desorption process can be considered as just the chemical reaction of multiple bond conversions. Nondynamical correlations are essential to describe properly the desorption. The TS of As_2 desorption is found to be of the "late-barrier" type.

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[62] Since the As atoms are very heavy, the classical trajectory calculations on PES should be enough to estimate the sticking probability. Such a study will be our next project. However, if requested, the numerical values of calculated grids are available: Please send the request to electronic address mochi@exp.cl.nec.co.jp

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