

FEATURE ARTICLE

The GaAs(001)-(2 × 4) Surface: Structure, Chemistry, and Adsorbates

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A series of *ab initio* simulations, based on density functional theory, of the structure of the clean GaAs(001)-(2 × 4) surface and of C₂H₂, C₂H₄, and trimethylgallium (TMGa) adsorbates are described. This surface was selected because of its importance in the growth of GaAs by molecular beam epitaxy. After summarizing briefly the theoretical basis of the computational methods used in the paper, we review critically what is known from experiment and theory about the structure of the clean surface. We argue that there is now strong evidence in favor of the “trench dimer” model for the β -phase of the clean surface, while the structures of the α and γ phases are less settled. We then present *ab initio* simulations of the trench dimer, the three dimer, and the gallium rebonded models of the clean GaAs(001)-(2 × 4) surface and discuss their common structural and bonding features. *Ab initio* simulations of C₂H₂ and C₂H₄ adsorbates at arsenic dimers of the GaAs(001)-(2 × 4) surface are then presented. The changes in the bonding configurations of both the adsorbates and the surface arsenic dimers are explained in terms of changes in the bond orders and local hybridization states. The As dimer bond is broken in the stable chemisorbed states of the molecules. However, an intermediate state, in which the As dimer is still intact, provides a significant barrier to chemisorption in both cases. This barrier, and its absence at the Si(001) surface, stems from the two extra electrons in the As dimer compared with the Si dimer. We then go on to describe the results of 14 *ab initio* simulations of structures connected with the chemisorption and decomposition of TMGa on the GaAs(001)-(2 × 4) surface. TMGa is commonly used in the growth of GaAs crystals from the vapor phase. The results of these simulations are used to explain a number of experimental observations concerning the surface coverage and the decomposition of TMGa to dimethylgallium and monomethylgallium. Significant technical aspects of the calculations, notably the number of relaxed layers in the slab calculations and the necessity to use gradient-corrected adsorption energies, are stressed. The paper also contains critical comments about *ab initio* simulations of the GaAs(001)-(2 × 4) clean surface and about the model based on a “linear combination of structural motifs”. Discussion of related experimental results appears throughout the paper.

1. Introduction

The arsenic-terminated GaAs(001)-(2 × 4) surface has been studied extensively, as it is the principal structure obtained during the growth of GaAs by molecular beam epitaxy (MBE). Three surface phases, α , β , and γ , exist, in order of increasing arsenic coverage. Despite considerable experimental^{1–12} and theoretical^{13–20} analysis, it is only recently that the structure of even the most stable phase, β , has been settled, and there remains some dispute over the α and γ phases. In this paper we review the evidence and our reasons for supporting the identification of the β phase with the “trench dimer” (or β_2) structure.

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Our main interest in the surface, however, is not the clean surface, but the reactions of a number of important organic gases on the surface. In order to model these reactions, it is essential first to obtain a good understanding of the clean surface. For that reason, the first third of this paper comprises an overview of what is known about the (widely studied) clean surface, concluding with a discussion of our density functional theory (DFT) calculations, which were used as a benchmark for adsorption results. The second section considers the adsorption of C₂H₂ and C₂H₄ on the surface, compared with the reaction on the better understood Si(001)-(2 × 1) surface. Finally, the third section considers part of the adsorption and decomposition of the potentially important gas-phase growth reagent trimethylgallium (Ga(CH₃)₃ or TMGa) with the GaAs(001)-(2 × 4) surface.

2. Computational Methods

The calculations described in this work, by both ourselves and others, fall into two groups: those based on density functional theory (DFT), referred to here as *ab initio* calculations, and those based on the tight-binding approximation. The

two methods are briefly described below, including the technical details of our calculations.

2.1. Density Functional Theory. Modern first principles calculations for extended systems of metals, semiconductors, and insulators are often based on density functional theory. The theory was placed on a rigorous foundation by Hohenberg and Kohn²¹ who showed that the properties of a system of electrons and nuclei, in the ground state, are determined uniquely by the electronic charge density. The total energy of the system is therefore a unique functional of this charge density. Furthermore, they showed that the functional, whatever it is, is minimized by the true electronic charge density. The next important step was taken by Kohn and Sham,²² who showed that the problem of N interacting electrons could be mapped exactly onto N independent electrons, each moving in an effective single particle potential which emulates the interactions with all other electrons. In this way density functional theory has reformulated the many interacting electron problem, in which the central quantity is the many electron wave function, in terms of noninteracting electrons moving in an effective potential that describes all the electron interactions and in which the central quantity is the electronic density. The single particle equations are

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right)\Psi_i(\mathbf{r}) = \epsilon_i\Psi_i(\mathbf{r}) \quad (1)$$

where the effective single particle potential, $V_{\text{eff}}(\mathbf{r})$, is itself a functional of the electronic charge density:

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \frac{e}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \quad (2)$$

The self-consistent loop is closed by the relation between the electronic charge density $\rho(\mathbf{r})$ and the single particle wave functions of the occupied states:

$$\rho(\mathbf{r}) = e \sum_{i=1}^n |\Psi_i(\mathbf{r})|^2 \quad (3)$$

These three equations are known as the Kohn–Sham equations. In eq 2 $V_{\text{ext}}(\mathbf{r})$ is the potential arising from the nuclei, if all the electrons in the system are treated explicitly, or from the ion cores if pseudopotentials are used. The second term describes the Coulomb interactions between all the electrons. The third term is called the exchange–correlation potential and accounts for the interaction between each electron and the “exchange–correlation hole” in the electronic charge density surrounding each electron in the system.

Although density functional theory proves that an exchange–correlation energy functional, $E_{\text{xc}}[\rho(\mathbf{r})]$, exists, it does not tell us what this functional is. However, exact calculations of $E_{\text{xc}}[\rho(\mathbf{r})]$ exist for a homogeneous electron gas where $\rho(\mathbf{r})$ is a constant, ρ_0 . Thus, we can evaluate the exchange–correlation energy functional $E_{\text{xc}}[\rho_0]$ for different constant electron densities ρ_0 .^{23–27} In the local density approximation (LDA) one approximates the exchange–correlation energy functional $E_{\text{xc}}[\rho(\mathbf{r})]$ for an inhomogeneous electron gas by a sum of contributions for homogeneous electron gases of density ρ_0 equal to the local density $\rho(\mathbf{r})$ at each point $\mathbf{r}$ in space:

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho) d\mathbf{r} \quad (4)$$

The LDA works reasonably well in regions of high electronic density, although it almost always leads to overbinding of molecules and solids and bond lengths that are smaller than

observed experimentally. Weaker interactions, such as those involved in hydrogen bonding, and between “nonbonded” parts of adsorbates and surfaces are too strong in LDA. This can be corrected by introducing the generalized gradient approximation (GGA)^{28,29} in which the exchange–correlation energy functional depends not only on the local electronic density but also on its local gradient. The GGA exchange–correlation energy can be used in a self-consistent manner. However, we have followed White *et al.*³⁰ and Hammer *et al.*³¹ by applying the GGA to the self-consistent charge density determined by LDA. This *post-hoc* correction turns out to be very important in our studies of TMGa on GaAs.

We have used pseudopotentials in order to focus the computational effort on the valence electrons where all the chemistry occurs. The one-electron states of the system were expanded in a plane wave basis set. Rather than solving the Kohn–Sham equations directly, we implemented the approach pioneered by Car and Parrinello³² of minimizing the total energy of the system with respect to the plane wave expansion coefficients and the ionic positions, while maintaining orthogonality between the electronic states. This approach is computationally much faster than the direct solution of the Kohn–Sham equations, and it allows a much larger basis set to be used because only the occupied states of the system are solved for.

The technical details of our density functional calculations are as follows: calculations for the clean surface were carried out using the parallelized implementation (CETEP)³³ of the pseudopotential total energy method,³⁴ Perdew and Zunger’s parameterization³⁵ of the exchange–correlation energy, and norm-conserving pseudopotentials of the Kerker type³⁶ in the Kleinman–Bylander form,³⁷ with a real space representation of the nonlocal parts of the pseudopotentials.³⁸ For our later calculations it was necessary to treat a (4×4) unit cell, containing two (2×4) unit cells on each of the top and bottom surfaces, with periodic boundary conditions in all directions. A vacuum gap of more than 12 Å separated periodic images of the slab in the [001] direction. Minimization of the total energy was performed using a band-by-band conjugate gradient algorithm.³⁹ Structures were deemed relaxed when all forces were less than 0.1 eV/Å. A single k -point, $1/4[010]$, was used. As the top and bottom surfaces of the slab are rotated by 90° with respect to one another, and their equivalence was maintained throughout the calculation, this is equivalent to sampling two unique k -points in the surface Brillouin zone and four with the time-reversal symmetry points. A four k -point (equivalent to 16 in the surface zone) was performed on relaxed structures to confirm k -point convergence for the relaxed structures. A plane wave cutoff of 200 eV was used; forces evaluated for the relaxed structures with a 350 eV plane wave cutoff remained less than 0.1 eV/Å, confirming convergence with respect to the plane wave basis set.

The DFT calculations for C_2H_2 , C_2H_4 , and TMGa adsorption were performed in the same manner as for the clean surface, but with the following modifications; in order to deal with the somewhat deeper carbon pseudopotential, a plane wave cutoff of 350 eV was used, and adsorption energies were evaluated using the self-consistent charge density in both LDA and GGA⁴⁰ approximations. For reasons of computational efficiency Γ -point only k -point sampling was used, with an all bands conjugate gradient algorithm.⁴¹ In order to ensure the validity of energy comparisons, all calculations were carried out in an identical supercell and with identical k -point sampling and plane wave cutoff.

2.2. The Tight-Binding Approximation. The tight-binding approximation is a semiempirical approach in which the binding

energy of a molecule or solid is expressed as a covalent bonding term, E_{cov} , a promotion energy, E_{pro} , and a sum, E_{pair} , of pair potentials describing the short-range repulsion. This form of the binding energy can be justified starting from density functional theory,⁴² where E_{cov} is identified as the sum of covalent bond energies and E_{pair} is the change in the total electrostatic and exchange-correlation energies on condensing “prepared” atoms to form the molecule or solid. The promotion energy is the energy associated with promoting electrons from lower to higher atomic valence states in order to form favorable hybrids; e.g., the promotion energy associated with promoting an s electron to a p state when s^2p^2 carbon atoms are condensed to form sp^3 hybrids in diamond is $\epsilon_p - \epsilon_s$. As shown by Sutton *et al.*,⁴² it is important that the values of ϵ_s and ϵ_p are those of the molecule or solid and not those of the free atoms. This is what is meant by “preparing” atoms before the imaginary condensation process.

An atomic-like basis set is assumed in tight-binding theory, although in semiempirical implementations, such as in this paper, no explicit functional forms for the basis states are used. Instead, one fits the radial dependencies of the Hamiltonian matrix elements in the localized basis set and the pair potentials to experimental data such as the binding energy and elastic properties and also to energies, obtained from *ab initio* calculations, of the material in different crystal structures and densities. The angular dependences of the hopping integrals are determined by fundamental transformation properties for atomic-like orbitals first written down by Slater and Koster.⁴³

Tight binding theory is probably the simplest quantum mechanical treatment of bonding which captures the angular character of bonding. It grew out of extended Hückel theory, which was developed by chemists for π -bonded systems. A tight binding calculation is typically between 2 and 3 orders of magnitude faster than *ab initio* calculation on the same number of atoms. We have compared structures obtained with our tight binding models and those obtained by *ab initio* calculations, and the agreement is always very close. In this work we have applied tight binding models to problems where the numbers of atoms involved were too large for *ab initio* calculations to be done.

Just as the charge density is the central quantity in density functional theory, so the density matrix is the central quantity in tight binding theory. Once one has the density matrix then the structure and total energy of the system are easily calculated. Diagonal elements of the density matrix describe the occupation of atomic states. Off-diagonal elements describe partial bond orders between atomic states on different atoms. When there is an energy gap between occupied and unoccupied states, as in a semiconductor or insulator, the magnitudes of off-diagonal density matrix elements decrease exponentially with the separation between atoms. This observation underpins recent work on the development of methods for solving tight-binding Hamiltonians that scale linearly with the number of atoms in the system, the so-called $O(N)$ (“order N ”) methods. Bond orders between atoms that are separated by more than some critical distance are set to zero. Thus, there is a finite number of bond orders centered on each atom that has to be considered, and that is why these methods scale linearly with the number of atoms in the system.

The tight-binding calculations were carried out using our own implementation⁴⁴ of the $O(N)$ density matrix method of Li, Nunes, and Vanderbilt.⁴⁵ We have also developed our own tight binding parameterization for GaAs by fitting to the structures of GaAs(001) obtained by DFT–LDA. (This is described in section 3.3.) Harrison’s prescription⁴⁶ was used to obtain parameters for Ga–C, As–C, and C–H bonds.

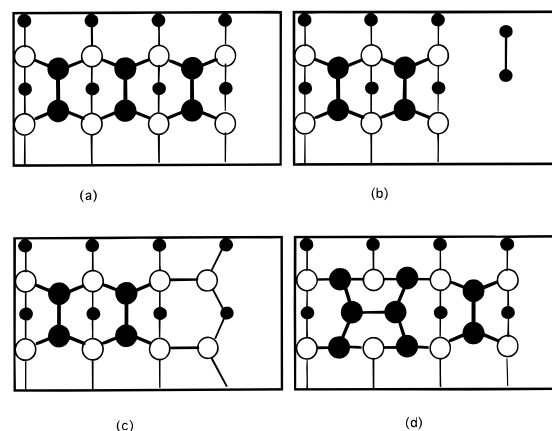


Figure 1. Schematic structures of proposed GaAs(001)-(2 × 4) structures: (a) “three dimer”, (b) “trench dimer”, (c) “gallium rebonded”, (d) “extra dimer”. Arsenic atoms are represented by filled circles and gallium atoms by open circles. Smaller filled circles represent the third layer arsenic atoms.

All structures were initially relaxed using the tight-binding approximation; we also refer in section 3.3 to tight-binding results performed on larger unit cells.

3. Clean GaAs(001)-(2 × 4)

3.1. Experimental Review. Gallium arsenide bulk has the zincblende structure, comprising a face-centered-cubic lattice, with a basis at each lattice point of two atoms, one of each species, at (0,0,0) and (0.25,0.25,0.25). Atomic (004) planes therefore alternate between being 100% arsenic and 100% gallium. An ideal bulk terminated (001)-As surface would be a (1 × 1) array of arsenic atoms, each with two dangling bonds, containing 5/4 electrons each. A (2 ×) periodicity is obtained by forming arsenic dimers. This was proposed by analogy with the silicon(001)-(2 × 1) surface by Cho⁴⁷ and supported by tight-binding¹³ and DFT-LDA¹⁴ calculations. Experimental evidence for a (2 ×) periodicity came first from diffraction; Larsen *et al.*⁶ demonstrated the existence of a (2 × 4) phase, but their proposed structure has since been discounted as being inconsistent with the surface arsenic coverage⁷ and with scanning tunneling microscopy (STM) images.^{10–12} Joyce *et al.*⁸ identified a range of (001) reconstructions from the gallium-rich (4 × 2) through (4 × 1), (3 × 1), (4 × 6) to the arsenic-rich (2 × 4) and arsenic-superrich (c4 × 4). For a given arsenic background, the arsenic coverage increases with decreasing substrate temperature. Farrell and Palmstrom⁹ showed that there are three distinct phases within the (2 × 4) region, which they labeled, in order of decreasing substrate temperature, and therefore increasing arsenic coverage, as α , β , and γ .

The next significant source of experimental data for this surface came from STM. Early STM¹⁰ of the (2 × 4)- β surface (which is the easiest of the three phases to prepare and has the greatest long-range order) showed that the (×4) periodicity is due to missing dimers, rather than the periodic tilting of dimers proposed by Larsen *et al.*⁶ Two such structures had previously been proposed by Chadi¹³ (Figure 1a,b), and two more were later proposed by Farrell and Palmstrom⁹ (Figure 1c,d). Inspection of high-quality STM images obtained more recently^{10–12} allow the “extra dimer” model to be ruled out (the ad-dimer is not observed), leaving three candidate structures: the “three dimer”, “trench dimer”, and “gallium rebonded” models.

A brief note on notation is required here. As mentioned above, Farrell and Palmstrom⁹ labeled the three phases of the (2 × 4) reconstruction α , β , and γ , a notation we adopt in this

paper. Unfortunately, it has also become common to refer to the three proposed reconstructions of the β phase as the α , $\beta 2$, and β structures, respectively. In order to avoid the possible confusion (and the implicit identification made between phases and structures), we will refer to the structures by name and the surface phases by Greek character. In this way we hope to avoid some of the confusion we believe exists in the literature.

Although early STM images suggested that the “three dimer” structure corresponded to the β -phase, the most recent, and higher resolution, STM work of Avery *et al.*¹¹ and Hashizume *et al.*¹² suggests that in fact there are only two dimers on the surface in the unit cell. Opinion appears to be converging on the “trench dimer” structure corresponding to the β -phase; the α - and γ -phases remain more disputed. This issue will be returned to in section 3.3.

3.2. Computational Review: DFT-LDA. The success of the local density approximation in predicting the formation of arsenic dimers¹⁴ suggested that identifying the correct reconstruction for the stable phases by total energy calculation should be relatively straightforward. However, this early work was prevented by the limitations of computer power from considering a (2×4) unit cell, and it was only in 1993 that the first DFT-LDA calculations^{15,16} were performed for the (2×4) unit cell. Ohno¹⁵ argued that the “gallium rebonded” structure was, in fact, not rebonded, but that instead the gallium atoms remain two-coordinate. However, both Northrup and Froyen^{16,17} and we have found the rebonding to lower the energy of the system by around 2 eV per (2×4) unit cell. Rebonding is also predicted by the electron counting¹⁰ or octet rule.¹⁸ A disagreement of this magnitude is rather hard to explain; it may be due to the use of a rather small number of layers in the computational slab. Unfortunately, Northrup and Froyen omitted the trench dimer structure from their initial calculations but included it in a later, more complete discussion.¹⁷

Sole reliance on DFT-LDA calculations for the structure of GaAs(001) is subject to a number of criticisms. First, as alluded to above, the limitations of computing power place a restriction on the number of layers that can be relaxed in the computational unit cell. We will examine the errors that may be adduced to this problem in the next section; suffice for the present to say that in our calculations, where a (4×4) unit cell was used (in order to isolate adsorption events in the later calculations), we were able to relax only the top three layers of the surface and consider the total energies we obtained to be of insufficient accuracy to make a judgment between rival reconstructions based upon them.

Second, in order to compare structures with differing stoichiometries, the heat of formation of bulk GaAs must either be evaluated in identical conditions of k -point sampling and plane wave cutoff, or *both* surface and bulk calculations must be performed to convergence of the total energy with respect to k -point sampling and plane wave energy cutoff. Most plane wave DFT-LDA calculations are carried to convergence in energy differences. This may be achieved without convergence in the absolute total energies through a cancellation of errors obtained by two calculations, provided identical k -point samplings and plane wave cutoffs are used. It is not sufficient to obtain convergence of the total energy for only the perfect crystal (which is relatively simple), without also completely converging the calculation for the slab, as the required error cancellation will not occur. The variation of the heat of formation of GaAs between different DFT-LDA calculations is quite alarming; Northrup and Froyen¹⁷ obtained 0.92 eV per GaAs pair, Moll *et al.*¹⁹ obtained 0.64 eV, and the experimental

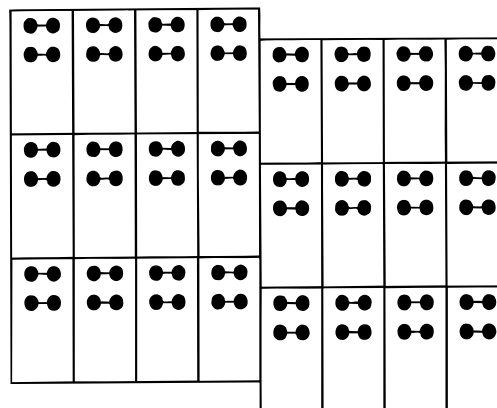


Figure 2. Schematic representation of “kinks” in the GaAs(001)- (2×4) surface. The rectangles represent (2×4) unit cells, with two arsenic dimers marked, and the kink runs down the middle of the figure. The kink energy is defined as the increase in surface energy per unit length of kink.

value is 0.74 eV.⁴⁸ We do not believe that adequate attention has, in general, been paid to this point.

Third, the thermodynamics needs to be examined carefully. Since the structures proposed differ in stoichiometry, comparisons at 0 K must be made between grand potentials instead of internal energy, involving the chemical potentials for the two species, μ_{As} and μ_{Ga} . This has been reduced^{16–19} to a single parameter, μ_{Ga} or μ_{As} , by equating $\mu_{\text{As}} + \mu_{\text{Ga}}$ with the cohesive energy of bulk GaAs. This single parameter is taken to be related the growth conditions (and in particular, the arsenic flux). Besides the problems with the cohesive energy outlined above, this makes the assumption that the growth surface is in thermodynamic equilibrium with the same perfect bulk, regardless of the growth conditions. But this is not the case, as GaAs grown under differing conditions will have differing bulk stoichiometries (due to vacancies, antisite defects, etc.), which will in turn result in differing cohesive energies.

For these reasons we do not believe that DFT calculations of the total energy alone provide an appropriate tool for the determination of the surface reconstructions in MBE growth.

3.3. Computational Review: Tight Binding. Let us now consider the contribution made by tight-binding calculations to the study of the clean surface. Tight binding has always benefited from the ability to describe considerably larger systems at a not incomparable accuracy. For this reason the first predictions of the structures which are now considered serious contenders were made on the basis of tight-binding results.¹³

More recently, using a linear scaling tight-binding code⁴⁴ based on the density matrix method,⁴⁵ tight-binding calculations of kink energies¹¹ (involving more than 600 atoms) have given further insight into the β and γ phases. Noting that the β phase has a very high degree of long-range order, with areas of several hundred angstroms of entirely straight missing dimer rows, whereas the γ surface phase, formed with only a slightly higher arsenic coverage (up to 0.25 ML), has a very high density of “kinks” in the dimer rows, Avery *et al.*¹¹ calculated the energy of “kink” defects (Figure 2) for the proposed structures and found that only the “trench dimer” structure had a sufficiently high kink energy to explain the observed long-range order. Furthermore, they found that on adding a small amount of excess arsenic (0.03–0.25 ML) the minimum-energy structure involved kinking of the missing dimer rows (Figure 3). They concluded that the β phase corresponds to the “trench dimer” structure and that the γ phase corresponds to the structure in Figure 3.

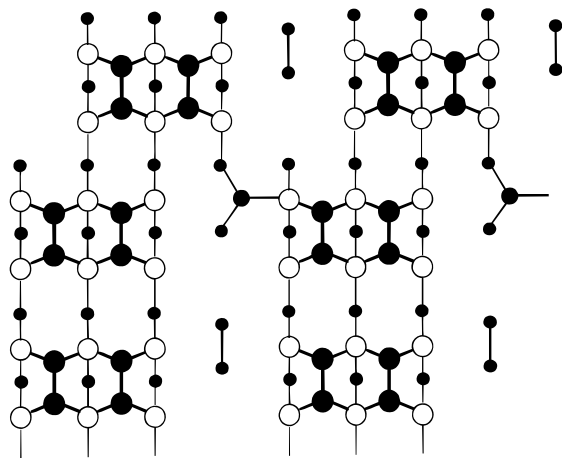


Figure 3. Minimum-energy structure for the addition of a small amount of arsenic to the "trench dimer" structure. It is proposed that the disorder introduced by the kinking is responsible for the β to γ transition. Arsenic atoms are represented by filled circles and gallium atoms by open circles. Smaller filled circles represent the third layer arsenic atoms.

TABLE 1: The sp^2s^* Tight Binding Parametrization Used for GaAs(001) Surface Calculations (Energies in eV, Lengths in Å)

(a) On-Site Energies									
	E_s	E_p					E_{s^*}		
Ga	-2.657	3.669					6.739		
As	-8.343	1.041					8.591		
(b) Equilibrium Intersite Hopping Parameters (h_0), Pair Energy (U_0) and Bond Length (r_0), and Scaling Powers (n), Defining the Nonequilibrium Values, $h(r) = h_0(r/r_0)^{n_h}$ and $U(r) = U_0(r/r_0)^{n_U}$									
	r_0	h_{0ss}	h_{0sp}	$h_{0pp\sigma}$	$h_{0pp\pi}$	h_{0s^*p}	n_h	U_0	n_U
Ga-As	2.4465	-1.613	2.504	3.028	-0.781	2.082	-2.6	4.0801	-5.65
As-Ga	2.4465	-1.613	1.940	3.028	-0.781	2.097	-2.6	4.0801	-5.65
As-As	2.2753	-1.613	2.204	3.028	-0.781	2.089	-2.1	4.0801	-4.56
Ga-Ga	2.4147	-1.613	2.204	3.028	-0.781	2.089	-2.1	4.0801	-4.56

As the tight binding parametrization used for this calculation has only previously appeared in a thesis,⁴⁹ it is reproduced in Table 1.

We have also used tight binding calculations to investigate the errors introduced by using insufficiently thick slabs in the computational unit cell.⁵⁰ Figure 4 shows the error in excess surface energy, σ , introduced by constraining atoms in a thick slab to remain in bulklike positions, as a function of the number of layers allowed to relax. The absolute value of σ does not converge until at least nine layers are allowed to relax, but more significantly, the energy difference between the "three dimer" and "trench dimer" structures does not converge to less than 0.01 eV/(1 $\times$ 1) unit cell until six layers are relaxed, as a direct consequence of the deeper relaxations induced in the trench dimer structure owing to the existence of the dimer in the trench. We believe that errors of this form may explain why early tight-binding¹³ and DFT-LDA¹⁴ calculations favored the "three dimer" structure, whereas later DFT-LDA calculations, performed with a thicker slab,¹⁷ favored the "trench dimer" structure, although there may also be electrostatic differences, as discussed in the next section.

Also shown in Figure 4 are the errors in dimer bond length due to the same constraint. When only four layers are allowed to relax, the trench dimer bond length is overestimated by 3%. We believe this is responsible for the difference in bond length between the surface and trench dimers reported by Srivastava and Jenkins,²⁰ rather than their proposal of the difference in chemical environments. In general, we would argue that a

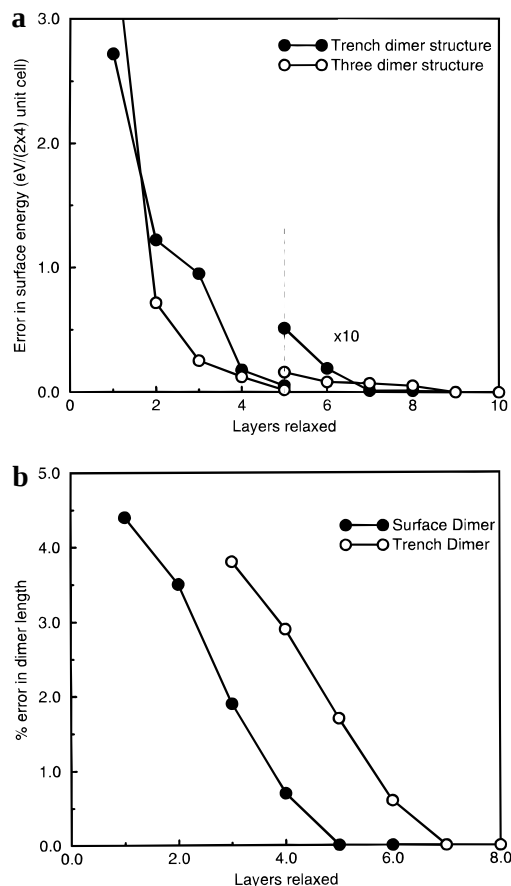


Figure 4. Error in (a) surface energy (in electronvolts per (2 $\times$ 4) unit cell) and (b) dimer bond length as a function of the number of atomic layers allowed to relax from bulklike positions. The zero is defined by a slab 31 layers thick in which all atoms are relaxed.

detailed structural analysis of atomic positions in the third layer when only some fourth layer atoms are allowed to relax is not justified.

3.4. Computational Review: Linear Combination of Structural Motifs. Recently, a new method for studying more complex reconstructions on the GaAs(001) surface, called "linear combination of structural motifs" (LCSM), has been proposed.¹⁸ Although the larger reconstructions which are the main target of this method are beyond the scope of this paper, a number of relevant points may be drawn from it.

In LCSM, the various reconstructions of GaAs(001) are described as linear combinations of five one-site and two two-site atomic motifs, each with a characteristic energy. The total surface energy, as a function of the chemical potential for one species, μ_{Ga} (repeating the assumption of thermodynamic equilibrium discussed in section 3.2), is written as the sum of these characteristic energies, plus both a Madelung term and a surface arsenic dimer term. The characteristic energies were fitted to DFT-LDA results for four bulk defects and three surfaces; the surface arsenic dimer term is an additional energy applied to arsenic-arsenic bonds at the surface but not in the bulk. The method was then applied to 13 other surfaces which have been studied by DFT-LDA calculations and predicted the surface energies to within ± 0.05 eV/(1 $\times$ 1) unit cell.

In the context of GaAs(001)-(2 $\times$ 4) it is the Madelung term in the LCSM method which is of particular interest. Charges are assigned to the surface atoms by invoking the "octet rule" and the "partition rule". The "octet rule" specifies that the dangling bonds of three coordinate arsenic atoms contain a lone pair, and those of gallium atoms are empty. The "partition rule" specifies that all Ga-As bonds contain 3/4 of an electron from

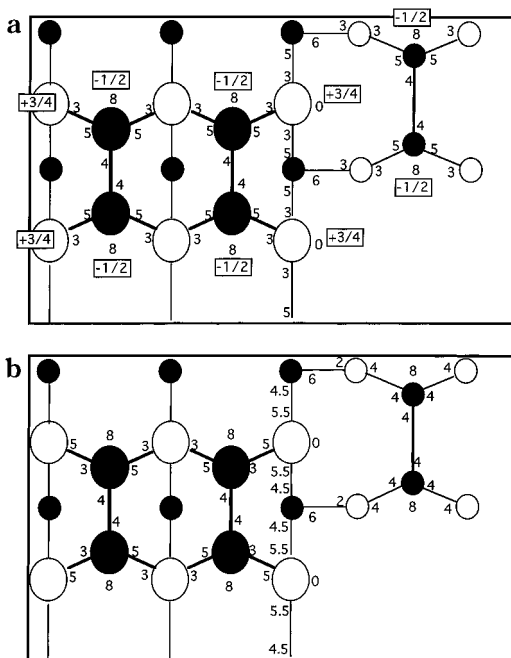


Figure 5. Partition rule and local charge neutrality as two limits of charge transfer. The small figures on each end of the bonds indicate the contribution to that bond from each atom, in units of 1/4 electron. In (a), the partition rule is obeyed; as a result, there are charges (indicated by boxed numbers) on some atoms. In (b), local charge neutrality is obeyed; there are therefore no charges on any atoms. Smaller filled circles represent the third layer arsenic atoms.

the Ga and 5/4 of an electron from the As, regardless of where the Ga–As bond is located. To maintain two electrons per bond, it is further assumed that in an As–As dimer each As contributes one electron. When these rules are applied, one obtains a set of charges for each atom, from which a Coulomb energy is calculated using a fitted relative permittivity, ϵ_r . Two results are important in the present context: first, that the trench dimer structure has a lower Coulomb energy than the three dimer structure by 0.05 eV/(1 × 1), and second, that for both of these structures (and a wide range of others) a disordered or c(4 × 4) structure would have lower Coulomb energy than the ordered (2 × 4). Of the proposed structures, only the trench dimer structure is unlikely to display this disorder owing to the high kink energy stemming from the dimer in the trench.¹¹ As the Coulomb energy is not included in tight-binding calculations, this may be another explanation why Chadi¹³ found the three dimer structure to be lower in energy than the trench dimer structure, whereas DFT-LDA calculations find the opposite ordering.¹⁷

The assumption made in assigning charges by the octet and partition rules needs some further consideration. In a system which is not locally charge neutral (that is, where the characteristic screening length is greater than the atomic separation), there may be some charge transfer of the type described. Our calculations support the octet rule because the three-coordinate gallium and arsenic atoms display sp^2 and sp^3 hybridization coordinations, respectively, and the As lone pair state is filled and the Ga p state is empty. However, it is possible to obtain such an electronic structure and maintain each atom charge neutral if the partition rule is relaxed, as the arsenic–gallium bonds in the surface may be differently constituted from those in the bulk. Enforcing the partition rule (Figure 5a) and enforcing local charge neutrality (Figure 5b) represent two limits; in the first case there is an electrostatic contribution to the surface energy, while in the second there is no electrostatic

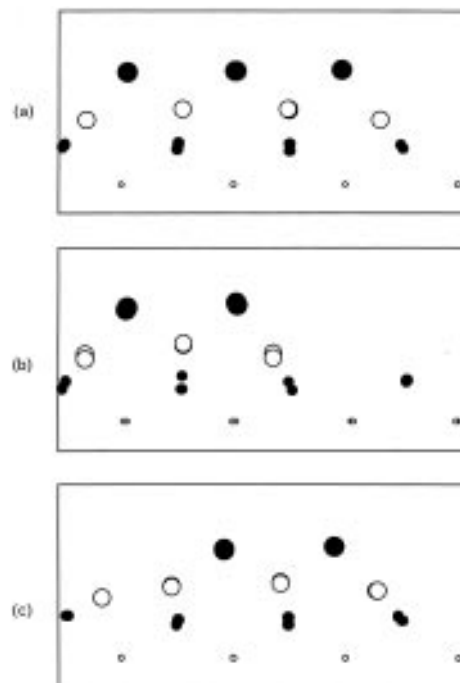


Figure 6. Elevation views of relaxed configurations of three proposed GaAs(001) reconstructions: (a) “three dimer”, (b) “trench dimer”, (c) “gallium rebonded”. Arsenic atoms are represented by filled circles and gallium atoms by open circles. Smaller circles represent the third and fourth layer atoms.

contribution. The minimum total energy will presumably lie between these two limits, suggesting that the charges used in the Madelung energy should be smaller than those assigned by LCSM. However, within the LCSM framework, any reduction in the actual charges in the system can be reflected, at least approximately, by a corresponding increase in the relative permittivity. It is important, however, to recognize that the LCSM model does not require that there are formal charges of the magnitude indicated in Figure 5b.

There are two other important criticisms of the LCSM method. First, the additional energy allocated to surface arsenic dimers is rather unsatisfactory; it is not clear whether additional arsenic adatoms should have this energy allocated to their bonds. Second, structures that do not obey the octet rule cannot be described in terms of the motifs; in particular, the arsenic induced kink structure proposed by Avery *et al.*¹¹ (Figure 3) cannot be compared with other possible γ structures.

3.5. Conclusions about Clean GaAs(001)-(2 × 4). We are now in a position to draw some conclusions about the structure of at least the β phase of GaAs(001)-(2 × 4). Following an initial acceptance of the “three dimer” structure, it is now clear experimentally^{11,12} and theoretically from DFT-LDA calculations,¹⁷ tight-binding calculations of kink energies,¹¹ and electrostatic considerations^{17,18} that the “trench dimer” structure must be preferred.

The α phase remains experimentally the most elusive. DFT-LDA calculations¹⁶ support identification with the gallium rebonded phases; electrostatic arguments suggest this structure should be disordered, which is consistent with STM observations.¹²

For the γ phase, there are two candidate structures. Hashizume *et al.*¹² and Zhang and Zunger¹⁸ argue that it is a mixture of the trench dimer structure and the c(4 × 4) structure; however, there is no clear evidence of the ad-dimers seen in c(4 × 4) in the STM images of Avery *et al.*¹¹ The arsenic-induced disorder model of Avery *et al.*¹¹ is more likely in our view. This model

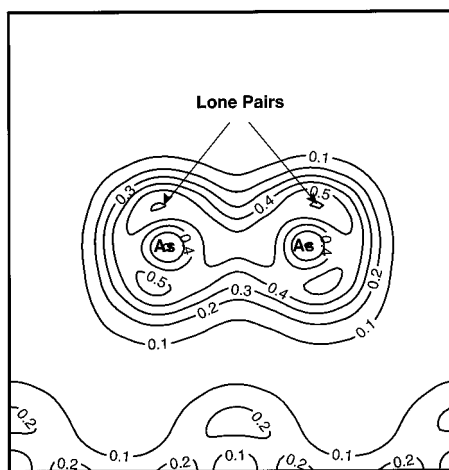


Figure 7. Charge density contours for the "trench dimer" structure in the plane of an arsenic dimer on the surface. Units are $\text{e}/\text{\AA}^3$. Because the pseudocharge density is plotted, the arsenic cores appear as minima. The maxima just above the arsenic atoms indicate the presence of lone pairs.

has not been the subject of DFT-LDA calculations and is beyond the realm of LCSM, but it has some supporting tight-binding calculations and is consistent with STM images.

4. Adsorption on GaAs(001)-(2 × 4) β : Clean Surface Base Line Calculations

We performed DFT-LDA calculations for the clean surface for three reasons: first, to gain insight into the possible structures of the surface phases, second, to test assumptions made about the electronic structures of these surfaces, and third, to provide a base line from which to perform adsorption simulations.

The relaxed structures of the proposed GaAs(001)-(2 × 4) reconstructions are shown in Figure 6. The key features of all three reconstructions are, first, the symmetric dimerization of the surface arsenic atoms (contrasted with the silicon surface in which the minimum-energy structure is a tilted dimer⁵¹) with a dimer bond length of 2.45 Å. The arsenic dimer atoms have approximately tetrahedral coordination, with a lone pair in place of one bond, which can be seen in Figure 7 showing a slice through the pseudo-charge density perpendicular to the surface and in the plane of the dimer. These lone pairs can be thought of as filling both π and π^* arsenic–arsenic bond orbitals.

A second effect that is noted in all three structures is that the four 3-coordinate gallium atoms in the second layer adjacent to the missing dimer row relax inward, making their bonding more planar. As can be seen from a slice through the pseudo-charge density perpendicular to the dimers (Figure 8), the charge density in the "dangling bond" of these gallium atoms is small. This "flattening" is consistent with a change in hybridization of the gallium atoms from sp^3 to sp^2 , resulting in a reduction in the promotion energy. In the trench dimer and gallium rebonded phases the steepening is more complex, but still involves four 3-coordinate gallium atoms becoming more planar. This result is consistent with the octet rule discussed in section 3.4, as, in each case, the reconstruction consists of 3-coordinate arsenic atoms adopting tetrahedral bonding with a lone pair and 3-coordinate gallium atoms adopting planar bonding with an empty p state. These configurations are common for elements of groups V and III, respectively. (Compare, for instance, with the pyramidal structure of AsH_3 and the planar structure of $\text{Ga}(\text{CH}_3)_3$.)

Third, we find significant relaxation in all three structures in the third layer, in which the arsenic atoms situated below the

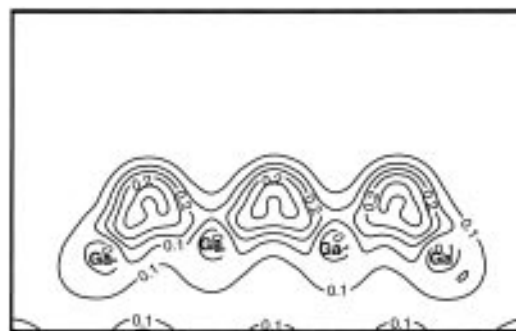


Figure 8. Charge density for the "three dimer" structure in the plane of the second layer gallium atoms, perpendicular to the dimers. The gallium atoms are positioned at the four roughly circular $0.1 \text{ e}/\text{\AA}^3$ minima. Note the absence of any lone pair charge density on the edge gallium atoms.

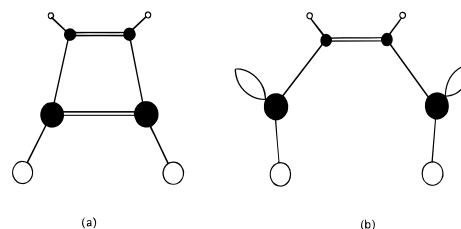


Figure 9. Schematic of proposed adsorption geometries for C_2H_x on an arsenic dimer with dimer σ -bond (a) intact and (b) broken. Large filled circles indicate the arsenic dimer, and large open circles indicate the second layer gallium. Smaller filled circles indicate carbon, and smaller open circles indicate hydrogen. The configurations shown are for C_2H_2 ; in C_2H_4 the hydrogen atoms are out of plane. Filled lone pair orbitals on the arsenic atoms are indicated in (b).

dimer move downward from their unrelaxed positions by around $0.12 \text{ \AA}$, and those not situated below the dimer move upward by $0.1 \text{ \AA}$. The exact magnitude of this relaxation should be treated with caution, for the reasons associated with a thin slab calculation discussed in section 3.3, but we believe it is a real effect, both because it has been previously noted in our tight-binding calculations of both gallium arsenide and silicon (001)⁵² and because it can be understood as arising from the rotation of the gallium atoms in the second layer about a $[110]$ axis due to the relaxation of the arsenic atoms forming dimers. The rotation ensures that the bond angles at the second layer gallium atoms are closer to the ideal tetrahedral angle of 109.47° . This effect was also noted, but not discussed, by Srivastava and Jenkins.²⁰

5. C_2H_x Adsorption

We have modeled the adsorption of C_2H_4 and C_2H_2 using DFT with gradient corrections, as described in section 3.2. The carbon pseudopotential was tested for convergence in diamond and as a C_2 dimer;⁵³ for the present work it was tested in the molecules C_2H_6 , C_2H_4 , and C_2H_2 to identify the minimum plane wave cutoff required to ensure accurate representation of single, double, and triple carbon–carbon bonds, the convergence criterion being the relative lengths of the three carbon bonds. At a plane wave cutoff of 350 eV the isolated molecules all had converged bond lengths which were 5% shorter than the experimental values, as is usual with DFT-LDA, and the bond length ratios ($1.0000:0.886:0.798$) were close to experimental values ($1.0000:0.864 \pm 0.005:0.782 \pm 0.005$).

The configurations of the adsorbed C_2H_2 and C_2H_4 species are shown in Figure 9, and details of the geometry are given in Table 2. We note first that the C–C bond length for the adsorbed C_2H_2 molecule is very close to that of the isolated

TABLE 2: Geometry and Adsorption Energies for C_2H_x Isolated and Adsorbed on an Arsenic Dimer with σ -Bond (a) Intact and (b) Broken; Arsenic–Arsenic Separations Are Also Given, for (c) the Ideal Bulk Terminated Surface and (d) the Clean Dimerized Surface

	bond lengths (Å)			bond angles (deg)		E_{ad} (eV)	
	C–C	C–H	As–As	C–As	C–C–H H–C–H	LDA	GGA
C_2H_2	1.172	1.088			180.0		
C_2H_4	1.301	1.111			116.0	122.0	
C_2H_6	1.469	1.191			110.6	104.9	
GaAs(c)			3.856				
GaAs(d)			2.453				
$C_2H_2(a)$	1.309	1.106	2.326	1.971	126.2	–0.84	+0.27
$C_2H_2(b)$	1.309	1.120	3.880	1.876	110.9	–1.74	–0.99
$C_2H_4(a)$	1.469	1.116	2.326	1.951	115.5	107.3	–0.25 +0.49
$C_2H_4(b)$	1.477	1.124	3.890	1.928	103.8	108.0	–0.76 –0.05

C_2H_4 molecule and that of the adsorbed C_2H_4 molecule is very close to that of the isolated C_2H_6 molecule (irrespective of the breaking of the arsenic dimer σ bond), which we interpret as a reduction in the order of the C–C bond from 3 to 2 and from 2 to 1, respectively. We also note that the intact As–As dimer is 5% shorter than on the clean surface. This is because the clean As–As dimer has filled σ , π , and π^* orbitals. When the molecule is adsorbed, the π^* electrons are used to form the As–C bonds, increasing the As–As bond order. However, the gradient-corrected adsorption energies show the broken arsenic dimer structure to be lower than the intact dimer structure by 0.54 eV/molecule (1.26 eV/molecule) for C_2H_4 (C_2H_2), as a result of the strengthening of the C–As bond, which is shorter by 1.7% (4.8%) in the broken dimer structure. The C_2H_4 (C_2H_2) molecule has a final adsorption energy of –0.05 eV/molecule (–0.99 eV/molecule).

Pseudo-charge densities in the plane of the arsenic dimer and carbon–carbon bonds are shown for the two adsorption structures for C_2H_4 in Figure 10. These should be compared with the equivalent plot for the clean dimer (Figure 7). The carbon–carbon bond in the broken dimer case (Figure 10b) appears slightly weaker than in the intact dimer case (Figure 10a), but this is compensated by the carbon–arsenic bonds, which are considerably stronger. The charge in the arsenic σ bond is reduced compared to the clean dimer, even when it remains intact.

The importance of gradient-corrected energies can be seen in Table 2. Energies calculated with DFT-LDA suggest an adsorption energy for C_2H_4 (C_2H_2) of –0.25 eV/molecule (–0.84 eV/molecule) in the intermediate (intact arsenic dimer) configuration and of –0.76 eV/molecule (–1.74 eV/molecule) in the final (broken arsenic dimer) configuration. These figures would appear to suggest that chemisorption of both molecules, resulting in a breaking of the arsenic dimer, should be observed experimentally without difficulty. However, electron energy loss spectroscopy (EELS) studies⁵⁴ for C_2H_2 have shown no sign of the expected change in the carbon–carbon stretching mode, indicating that this reaction does not, in fact, take place. The gradient-corrected energies show why this is the case—the intermediate, physisorbed state has an adsorption energy of +0.49 eV/ C_2H_4 molecule and +0.27 eV/ C_2H_2 molecule, indicating a significant barrier between each physisorbed molecule and the stable chemisorbed state, as a result of which chemisorption does not occur.

Comparison of these results with the adsorption of the same molecules on Si(001), which has been studied both theoretically⁵⁵ and experimentally,⁵⁶ shows that the adsorbed molecules would be expected to adopt a very similar geometry on both surfaces. The H–C–C angle and the C–C bond length in C_2H_4 adsorbed on either surface are consistent with a reduction of

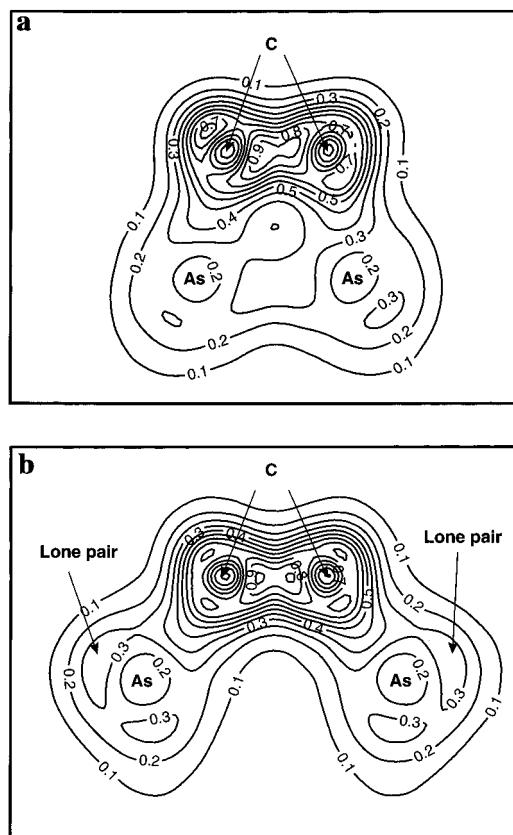


Figure 10. Charge density for C_2H_4 adsorbed on an arsenic dimer with the dimer σ -bond (a) intact and (b) broken. The main feature is the strong C–C bond. The hydrogen atoms lie out of the plane of the figure, the presence of the bonds can be seen in the charge density slightly above and to the left and right of the carbon atoms. In (b) the arsenic lone pairs are identified by the bulge in charge density, almost entirely absent in (a).

the C–C bond to a single bond and sp^3 hybridization, and similarly the H–C–C angle and C–C bond length in C_2H_2 adsorbed on either surface are consistent with a reduction to double C–C bond and sp^2 hybridization.

For the adsorption of either molecule on both GaAs(001) and Si(001) a structure has been found in which the σ dimer bond (arsenic or silicon) remains intact. However, on gallium arsenide the dimer bond length is reduced, whereas on silicon it is increased. The difference is explained by the presence of π^* electrons in the clean As–As bond which are removed to form the As–C bonds, resulting in an increase in the As–As bond order. The clean Si–Si bond has no π^* electrons, and when the π electrons are removed, the Si–Si bond order is reduced. (The lengthening of the silicon dimer bond in the presence of adsorbates has also been predicted, for the same reason, for SiH_2 adsorption.⁵⁷) However, on the As–As dimer this geometry is not the lowest energy; the angles between the new As–C bond, the (σ and π) As–As dimer bonds, and the As–Ga back bonds make this structure less favorable than breaking the σ and π As–As bonds and relaxing the arsenic atoms back to bulklike bond angles, where they are 3-coordinate with a lone pair—a stable configuration for arsenic atoms.

When the (001) silicon surface is hydrogenated, the electronic structure of the dimers is very similar to the arsenic dimers; the hydrogenated dimers are unbuckled⁵⁸ and do not react with C_2H_x . If, on the other hand, hydrogen is added to a dimer upon which a C_2H_x molecule is already adsorbed, the dimer σ bond breaks, creating a structure analogous to Figure 9b, with a silicon–hydrogen covalent bond in place of the arsenic lone pair.⁵⁹

In conclusion, the most significant difference between the reactions of C_2H_4 with Si(001) and GaAs(001)-(2 $\times$ 4) β is that in the former case chemisorption occurs, whereas in the latter it does not. We believe this can be explained fully by the presence of two extra electrons in the As-As dimer compared to the Si-Si dimer. Although these electrons occupy the π^* antibonding orbital, and thus weaken the bond, they also make the intermediate stage for adsorption unstable for the GaAs surface. In further support of this, we note that a hydrogen-saturated silicon dimer (which has the same number of electrons as the arsenic dimer) does not react with C_2H_4 .

6. Ga(CH₃)₃ Adsorption

6.1. Experimental Review. High-resolution electron energy loss spectroscopy (HREELS) samples the various vibrational modes of molecules on the surface and can in principle detect the characteristic frequency of a particular type of bond. However, as the masses of gallium and arsenic are very similar, HREELS does not, in general, give sufficient resolution to distinguish between them. Narmann and Yu² adsorbed TMGa on a cooled GaAs(001)-(2 $\times$ 4) surface and found that at -80 °C the molecule adsorbs intact, indicated by the shift in the "umbrella mode" (in which the three methyl groups move together perpendicular to the plane of the molecule) to a value consistent with three methyl groups attached to a 4-coordinate (sp^3) gallium atom.

A higher resolution spectroscopy technique, using infrared radiation, gives resolution sufficient to distinguish between gallium and arsenic. However, the energy window in which IR spectroscopy is possible does not allow the carbon-gallium or carbon-arsenic stretching modes to be detected. Gee *et al.*⁶⁰ measured the carbon-hydrogen vibrational modes and attempted to identify the species to which the methyl groups are bonded by comparing the shift in these modes with those observed in gaseous or solid TMGa and TMAs. Unfortunately, the experimental data with which the comparison is made is unreliable for the TMAs, as only a single result, for solid TMAs at 14 K, is available. Nonetheless, they were able to conclude that at room temperature, for low coverage, one methyl group becomes attached to an arsenic atom.

Yu *et al.*⁶¹ used a combination of X-ray and ultraviolet spectroscopy to identify first the fractional gallium coverage after dosing and second the fractional carbon coverage. At temperatures up to 300 °C they found a saturation gallium coverage of 0.1 ML, consistent with adsorption of a single TMGa molecule on 80% of (2 $\times$ 4) unit cells. The coverage of carbon is measured to be 0.2 ML, implying some methyl groups escape at room temperature; however, they admit an error of up to 50% in this value, so it is not possible to reach firm conclusions. The difference between the observed gallium coverage (0.1 ML) and the coverage implied by a single adsorption per (2 $\times$ 4) unit cell (0.125 ML) is better explained by incomplete saturation, as observed in STM.⁴ At 500 °C, Yu *et al.*⁶⁰ find all carbon to desorb, and saturation coverage of gallium appears to be around 0.2 ML (consistent with double occupation of 80% of unit cells).

Temperature-programmed desorption (TPD) studies by Creighton *et al.*⁶² showed that methyl release from arsenic-terminated surfaces occurred an order of magnitude more quickly than from gallium-terminated surfaces, suggesting that methyl elimination from the gallium-terminated (2 $\times$ 4) surface may be the rate-limiting step in MOCVD growth. This effect may also be relevant to the differences in behavior between the two types of step⁶³ on the arsenic-rich surface. Memmert and Yu¹ identified two methyl desorption channels after adsorption of

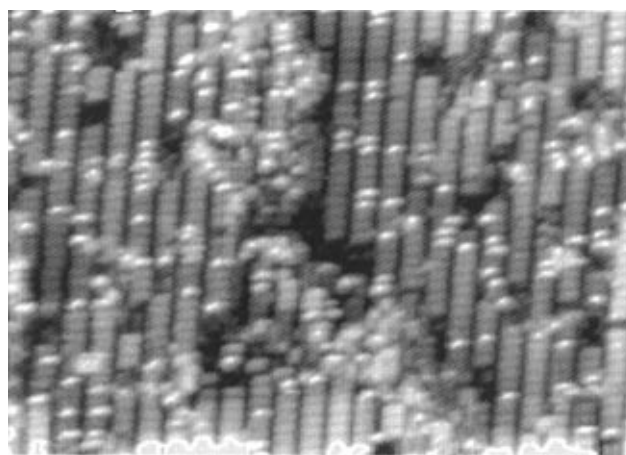


Figure 11. STM image of GaAs(001)-(2 $\times$ 4) β after exposure to TMGa. The gray features are the arsenic dimers, the dark lines running up and down the image are the missing dimer rows, and the bright features result from exposure to TMGa. There is a step running from center-top to bottom-right (approximately). Courtesy of Andrew Avery and Andrew Mayne.

TMGa on GaAs(001)-(2 $\times$ 4), operating at around 450 °C. They proposed that one channel represented desorption from MMGa on the surface and the other (with double the signal) from methyl groups attached directly to the surface. The main drawback of TPD is that it gives information, at best, about the final structure before desorption occurs, rather than the configuration in which adsorption occurs. If any changes occur in the surface between adsorption and desorption, TPD provides no information about the lower temperature state of the surface when adsorption occurs.

Yu⁶⁴ provides a summary of experiments performed which combine a pulsed beam source with mass spectrometry and concludes that the initial sticking coefficient for TMGa on GaAs(001)-(2 $\times$ 4) at room temperature is almost unity, and decreases with increase in substrate temperature, and that the adsorption is mediated by some precursor state.

GaAs(001)-(2 $\times$ 4) surfaces have been imaged by scanning tunneling microscopy (STM) before and after exposure to TMGa at room temperature by Avery *et al.*⁴ (Figure 11). The key results are that the adsorption results in bright features, of similar size and shape to the (2 $\times$ 4) unit cell, and that at saturation coverage around 75% of the (2 $\times$ 4) unit cells have been replaced by these bright features. Taking each such feature to represent a single adsorption event, and assuming a single TMGa molecule involved, this implies a saturation gallium coverage of 3/32 ML, consistent with the value of 0.1 ML obtained by Yu *et al.*⁶¹ A further observation⁶⁵ is that the adsorption events are not distributed at random around the surface but show a tendency to cluster in lines running parallel to the missing dimer trenches.

6.2. DFT Calculations. We have used the CETEP code to evaluate the total energy for 14 structures: the clean surface, the trimethylgallium (TMGa, Ga(CH₃)₃), dimethylgallium (DMGa, Ga(CH₃)₂), monomethylgallium (MMGa, Ga(CH₃)) molecules and methyl radicals in vacuum, four structures involving the adsorption of the entire TMGa molecule (intact or decomposed), and five involving the adsorption of part of the molecule. The structures considered are all those which can be obtained from the molecule (or parts thereof) adsorbing onto a single arsenic dimer and are illustrated schematically in Figure 12.

The adsorption energy of an isolated methyl group on the clean surface (-1.67 eV/molecule) was used to compare adsorption energies of structures with a different number of

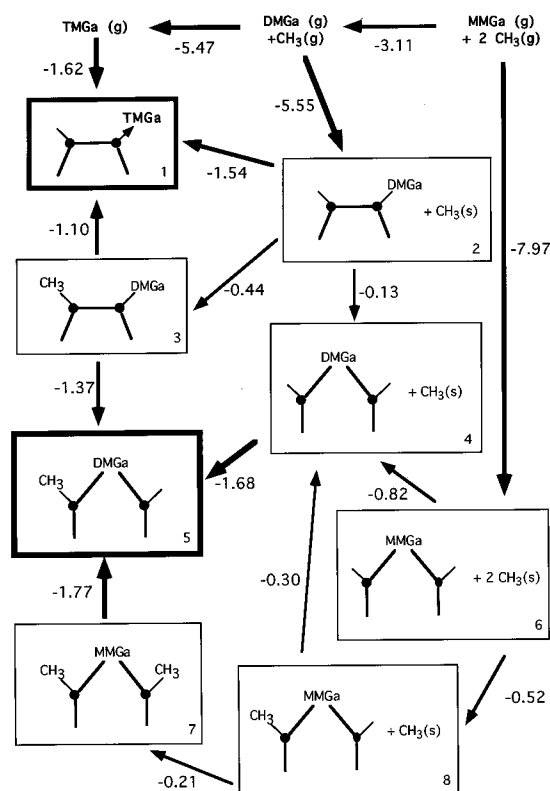


Figure 12. Schematic of the set of TMGa fragments considered in this work in the gas phase and adsorbed on an arsenic dimer. Arrows are labeled with energy differences (in electronvolts) and point from higher to lower energy states. CH₃(s) indicates methyl groups adsorbed elsewhere on the surface. (g) indicates gas phase. The arrow in box 1 indicates a dative bond. The numbers in the bottom right corner of each box label the calculation and are referred to in Tables 3 and 4.

TABLE 3: Difference in Adsorption Energy Calculated by LDA and GGA^a

adsorbed molecule	$E^{\text{LDA}} - E^{\text{GGA}}$ (eV)	adsorbed molecule	$E^{\text{LDA}} - E^{\text{GGA}}$ (eV)
TMGa (1)	-0.27	MMGa* (6)	-0.28
DMGa (2)	-0.41	MMGa* + 2CH ₃ (7)	-0.98
DMGa + CH ₃ (3)	-0.54	MMGa* + CH ₃ (8)	-0.63
DMGa* (4)	-0.11	CH ₃	-0.77
DMGa* + CH ₃ (5)	-0.55		

^a Asterisk indicates gallium insertion into the arsenic dimer, and numbers in parentheses refer to the configuration labeled in Figure 12.

methyl groups within the computational cell. In this way any methyl groups not included within the computational cell were assumed to be bound elsewhere on the surface.

The inadequacy of DFT-LDA calculations for molecular adsorption is shown in Table 3. In every case, LDA overestimates the binding energy compared to GGA, by between 0.11 and 0.98 eV/molecule. Structures in which methyl groups are directly attached to the surface are most strongly overbound. We suspect that this is due to an overestimate of the strength of hydrogen bonding between the arsenic dimer lone pairs and the methyl groups.

The relative (GGA) energies of the structures are shown in Figure 12. Structures that differ from one another only by a single step (such as removal of a methyl group or insertion into the arsenic dimer) are joined by an arrow from the higher energy to the lower, with the energy difference in electronvolts/TMGa molecule indicated. Two structures are lower in energy than any neighboring structure: these are indicated by heavier boxes and will be referred to as "locally stable". Selected bond

TABLE 4: Summary of Geometry and Binding Energy (Calculated by DFT-GGA) for the Structures Considered (Lengths in Å and Angles in deg)^a

adsorbed molecule	dimer length	mean length		smallest angle		E_{bind} (eV)
		Ga-As	Ga-C	at Ga	at As	
isolated	2.434		1.88	120.0	101.2	0.00
(1)	2.442	2.50	1.87	86.8	98.7	-1.62
(2)	2.413	2.35	1.79	114.1	94.8	-0.08
(3)	3.053	2.25	1.79	114.4	86.6	-0.52
(4)		2.44	1.82	110.8	114.9	-0.21
(5)		2.43	1.85	108.3	102.2	-1.89
(6)		2.49	1.82	119.2	94.8	+0.61
(7)		2.27	1.81	111.0	103.3	-0.12
(8)		2.44	1.82	114.0	100.3	+0.09

^a Binding energies for structures with fewer than three methyl groups assume other methyl groups individually are bound to remote arsenic dimers as described in the text. Configurations are numbered as in Figure 12.

lengths and angles are tabulated in Table 4. We make the following observations, in which figures in parentheses refer to Figure 12:

(i) The intact TMGa molecule (1) is locally stable. It is bonded datively, with the arsenic dimer lone pair donating into the empty p orbital on the TMGa molecule. The TMGa molecule rehybridizes considerably (seen in the change in C-Ga-C bond angles from 120° to 86.8°). This structure is consistent with the results of Narmann and Yu² on the change in frequency of the "umbrella" vibrational mode on adsorption at -80 °C.

(ii) The lowest energy structure consists of DMGa inserting into the arsenic dimer, with the remaining methyl group also attached to one of the arsenic atoms of the same dimer (5).

(iii) Structures involving the removal of methyl groups to other arsenic dimers (2, 4, 6, 8) are generally energetically unfavorable.

(iv) The energetically favorable structures (1, 5) obey the "octet" rule. The only structure which obeys this rule and is not energetically favorable is MMGa inserted into the arsenic dimer with two methyl groups removed elsewhere on the surface (6).

(v) If a single methyl group is removed (as in desorption), the lowest energy structure is DMGa inserted into the arsenic dimer (4). The second methyl group is considerably easier to remove, leaving MMGa inserted into the arsenic dimer (6).

(vi) The adsorbed DMGa molecule has a total extent of 4.9 Å perpendicular to the dimer. As the dimer-dimer separation in the unit cell is only 3.85 Å, steric hindrance will prevent a second molecule from adsorbing within the unit cell until the decomposition has proceeded to MMGa.

Charge densities for four key structures in the adsorption process are shown in Figure 13: (a) the clean surface, (b) the TMGa molecule adsorbed intact, (c) the proposed intermediate, energetically unfavorable stage, and (d) the lowest energy structure obtained. The reason for the high energy of the intermediate stage is the considerable weakening of the arsenic dimer bond, which can be seen to be "pinched" in (c).

We are now in a position to interpret tentatively several experimental papers. Below room temperature TMGa adsorbs intact.² At room temperature it is able to decompose into DMGa plus methyl.⁶⁰ One such pair of molecules can be accommodated within each (2 × 4) unit cell, giving 0.125 ML saturation coverage for a perfect surface, which compares favorably with the experimentally observed value of 0.1 ML.^{4,61} At 450 °C methyl groups start to be removed from the surface.⁶² Our calculations suggest that the desorption will lead directly

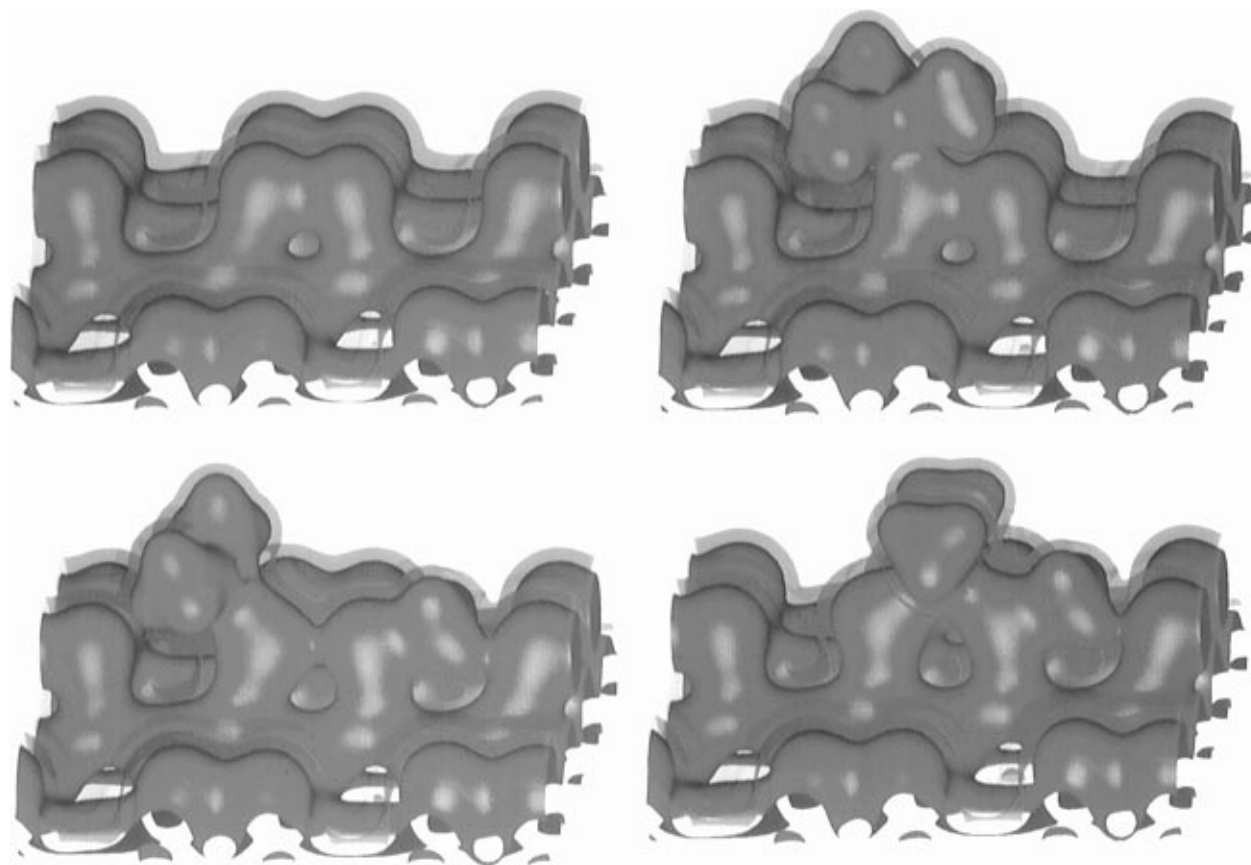


Figure 13. Surface of constant charge density at four stages in the adsorption process: (a, top left) clean GaAs, (b, top right) TMGa adsorbed intact (1 in Figure 12), (c, bottom left) DMGa and CH₃ adsorbed on intact dimer (3 in Figure 12), (d, bottom right) final adsorption site (5 in Figure 12). In each case, the red surface represents a density of 0.2 electrons/Å³, the green surface 0.02 electrons/Å³, and the blue surface 0.002 electrons/Å³.

to MMGa (6), in which structure a second molecule could be accommodated, which corresponds to a coverage that compares favorably with the experimental value of 0.2 ML.⁶¹

As methyl groups are less strongly bound to the clean surface than to the adsorbed gallium, we believe that the cause of high carbon incorporation is the difficulty in removing the final methyl group from the gallium atom as the reaction proceeds beyond the point we have described, rather than the removal of methyl groups bound to arsenic on the surface; this is consistent with the observation that methyl elimination from the arsenic-rich surface is much faster than from the gallium-rich surface.⁶²

7. Summary and Conclusions

On the basis of an extensive review of the available experimental and computational evidence, we concluded in section 3.5 that the β phase of the GaAs(001)-(2 $\times$ 4) surface adopts the trench dimer structure. The structures of the α and γ phases are less clear-cut, and the most likely candidate structures were summarized in that section.

Ab initio calculations in section 4 of the relaxed structures of the trench dimer, three dimer, and gallium rebonded models of the β phase of the GaAs(001)-(2 $\times$ 4) surface revealed three common features. The arsenic dimers adopt symmetric configurations, i.e., in contrast to the dimers on Si(001) they are not tilted, and each arsenic atom is associated with a filled lone pair state. Second, gallium atoms at the surface adopt planar sp² geometries wherever they are free to do so, with empty p states normal to the plane. Third, there are significant relaxations in the third layer beneath the surface.

The *ab initio* simulations of chemisorption of C₂H₂ and C₂H₄ at arsenic dimers of the GaAs(001)-(2 $\times$ 4) surface reported in

section 5 revealed changes in molecular bond lengths and angles consistent with rehybridization of the carbon atoms from sp to sp² and from sp² to sp³ states, respectively. The As dimer bond length decreased by 5% following adsorption owing to the increase in bond order resulting from the flow of antibonding π^* electrons out of the As dimer bond into bonds with the carbon atoms. The As dimer bond is broken in the stable chemisorbed states of the molecules, and the chemisorption energies are -0.05 eV/C₂H₄ molecule and -0.99 eV/C₂H₂ molecule. However the intermediate state, in which the As dimer is still intact provides a significant barrier to chemisorption in both cases (+0.27 eV/C₂H₄ molecule and +0.49 eV/C₂H₂ molecule). This barrier, and its absence at the Si(001) surface, is a result of the two extra electrons in the As dimer compared with the Si dimer, which favor the breaking of the arsenic dimer bond, resulting in each arsenic atom having only three neighbors and a filled lone pair state.

In section 6 the results of 14 *ab initio* simulations of structures connected with the chemisorption and decomposition of TMGa on the GaAs(001)-(2 $\times$ 4) β surface were described. The TMGa molecule may bond datively to one atom of an arsenic dimer forming a locally stable intact configuration at temperatures below room temperature. The lowest energy structure we found consists of DMGa inserted into the arsenic dimer, with the remaining methyl group also attached to one of the arsenic atoms of the same dimer. Structures involving the removal of methyl groups to other arsenic dimers are generally energetically unfavorable. Energetically favorable structures (1, 5) obey the "octet" rule. If a single methyl group is removed, the lowest energy structure is DMGa inserted into the arsenic dimer. The second methyl group is easier to remove, to leave MMGa inserted into the arsenic dimer. Several

experimental results were discussed in section 6 in light of our computations.

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