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## ROLE OF SURFACE INTERACTIONS IN DETERMINING SURFACE STRUCTURE AND STATE FORMATION IN III-V SEMICONDUCTORS

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### Abstract

GaAs(100), (110), and (111) surfaces are chosen as a vehicle to explain the plethora of surface relaxation and reconstruction phenomena seen for III-V compound semiconductors. These relaxation and reconstruction processes directly affect the formation of surface states. The occupation of these states, in turn, can have a profound influence on device performance. The purpose of this work is to attempt to provide a unified description of the phenomena responsible for surface relaxation and reconstruction on these surfaces. Our work makes use of an *ab initio* effective core potential scheme based on the Hartree Fock approximation. We discuss the critical steps involved in both the surface reconstruction process and surface energy band structure evolution for (100) surfaces. It is shown that the reconstruction mechanism is driven by the need to satisfy the surface dangling bonds and by a steepening relaxation. (111) A and B surface reconstruction is discussed by reference to Ga<sub>6</sub>As<sub>6</sub>H<sub>18</sub> model cluster calculation results. The importance of site specific chemical character on bonding and reconstruction is underlined. The main factors responsible for relaxation and reconstruction of III-V compound semiconductor surfaces are thus shown to include satisfying dangling bonds, steepening relaxation and site specific chemical character.

**Key Words:** Surface structure, surface states, GaAs, surface reconstruction, cluster calculations, *ab initio*, computer modelling.

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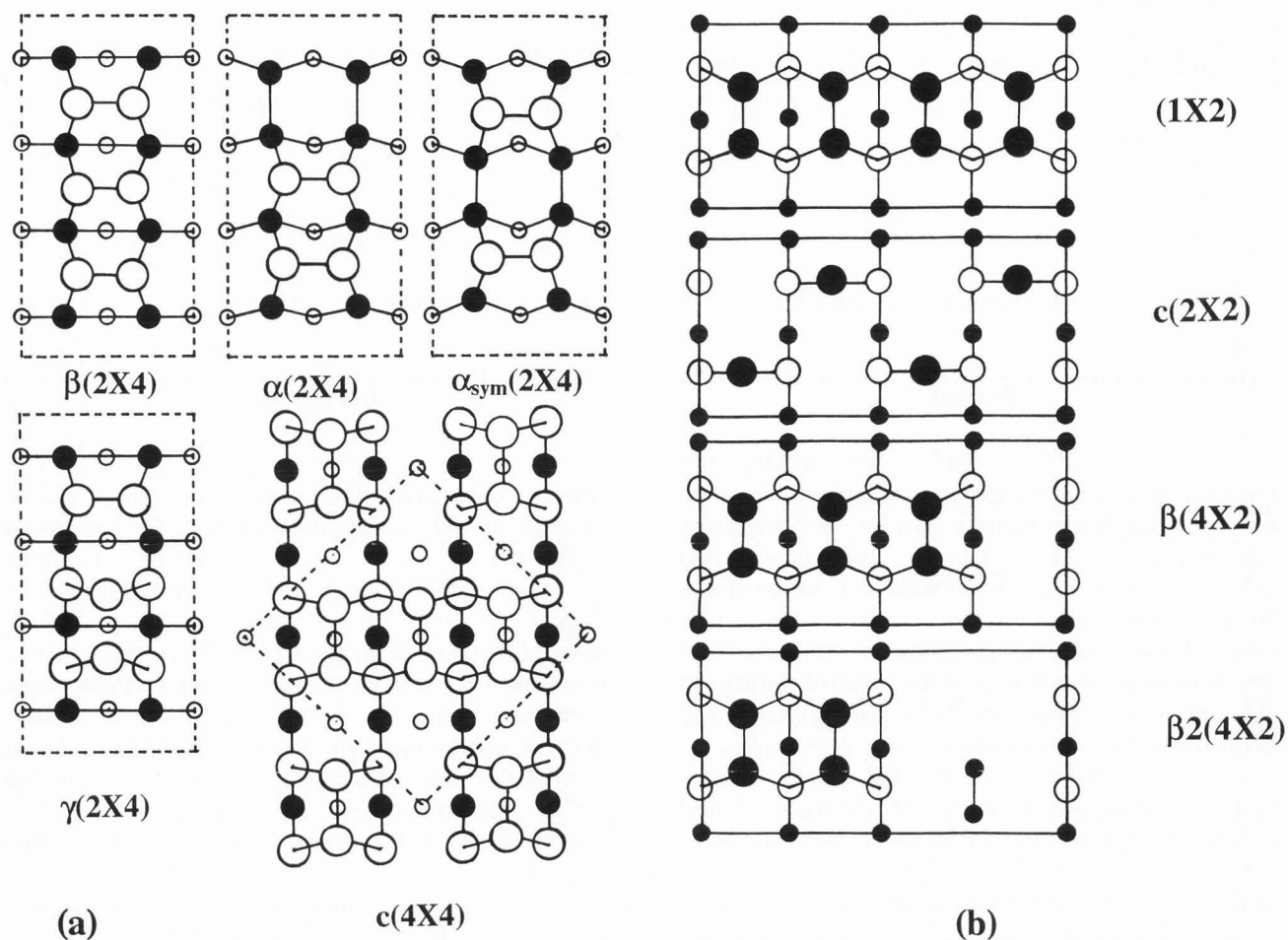
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### Introduction

III-V compound semiconductors are now the cornerstone of the rapidly developing optoelectronic device industry, as well as important materials for high speed digital and microwave device applications. It is now well established that electrical and/or optical properties of devices not only depend on the properties of the bulk material, but also on the surface structural and electronic properties (Bessolov *et al.*, 1993). For example, there have been a number of experimental and theoretical studies that show that GaAs-based semiconductors do not fulfill the promise of their excellent bulk electrical and optical properties owing to high densities of surface states which degrade properties (Fan *et al.*, 1988). Surface states can arise from surface relaxation and surface reconstruction, and may be introduced by surface defects and foreign atom adsorption. Moreover, since as growth proceeds, surfaces become buried, surface structure will inevitably dictate interface structure. In particular, band offsets at heterojunction interfaces have been shown to be sensitive to the interface structure (Tsutui *et al.*, 1990). Thus, gaining insight and understanding into the surface structure and the mechanisms for surface phase transitions has clear scientific and technological importance.

In this paper, we focus on GaAs as a prototypical III-V semiconductor. We begin by briefly reviewing the various surface relaxations and reconstructions commonly found for GaAs (100), (110) and (111) surfaces. We then focus on the polar (100) and (111) GaAs surface. Thus, for the (100) surface, we explain how the surface energy band structure changes when an ideal surface undergoes reconstruction to the 2X1 structure. Detailed discussions of (111) surface reconstruction are made by reference to a series of cluster models of increasing cluster size. We underline throughout the role of surface interactions in dictating surface structure and in turn, the formation of surface states.

Our calculations made use of an *ab initio* effective core potential (ECP) scheme based on the Hartree Fock (HF) approximation (Kahn *et al.*, 1976; Hay and Wadt,



**Figure 1.** Schematic representations of possible reconstructions for (100)GaAs surfaces taken from Northrup and Froyen (1993). Filled (open) circles denote Ga (As) atoms and dashed lines indicate unit cell boundaries for (a) As-terminated and (b) Ga-terminated surfaces.

1985). A key aspect of this approach was to generate an ECP in the valence region and to allow the eigenvalue of the corresponding pseudo-orbital equation to have the same orbital energy as the self-consistent HF method. Since our selected model clusters corresponded to open-shell electronic systems, unrestricted HF functions (UHF; Pople and Nesbet, 1959) and restricted open-shell HF functions (ROHF; McWeeny and Dierksen, 1968) were used. Calculations made use of the Gaussian 92 computer program (Frisch *et al.*, 1992) with three primitive Gaussian functions being used to fit each Slater-type valence orbital.

#### Relaxation and Reconstruction of GaAs Surfaces

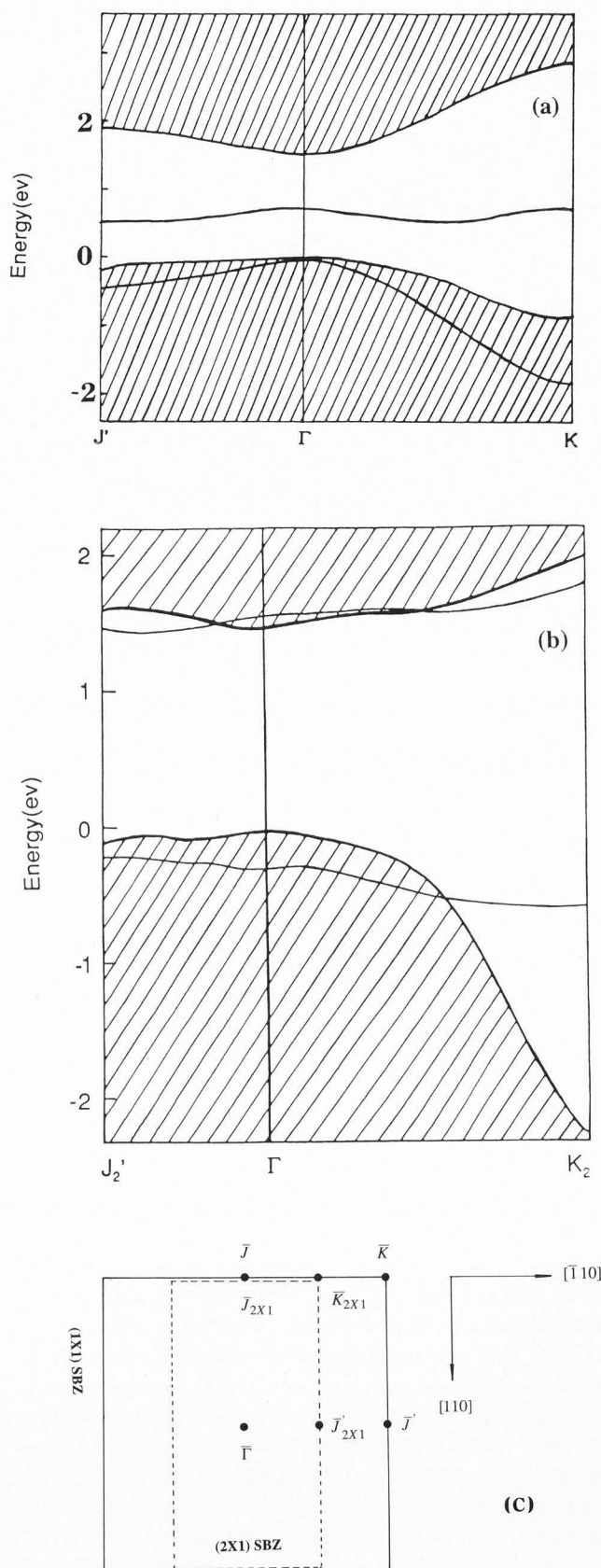
Previous experimental studies have shown that  $1 \times 1$  (110) surfaces can be obtained by cleaving GaAs crystals under ultra high vacuum (UHV) conditions, without re-

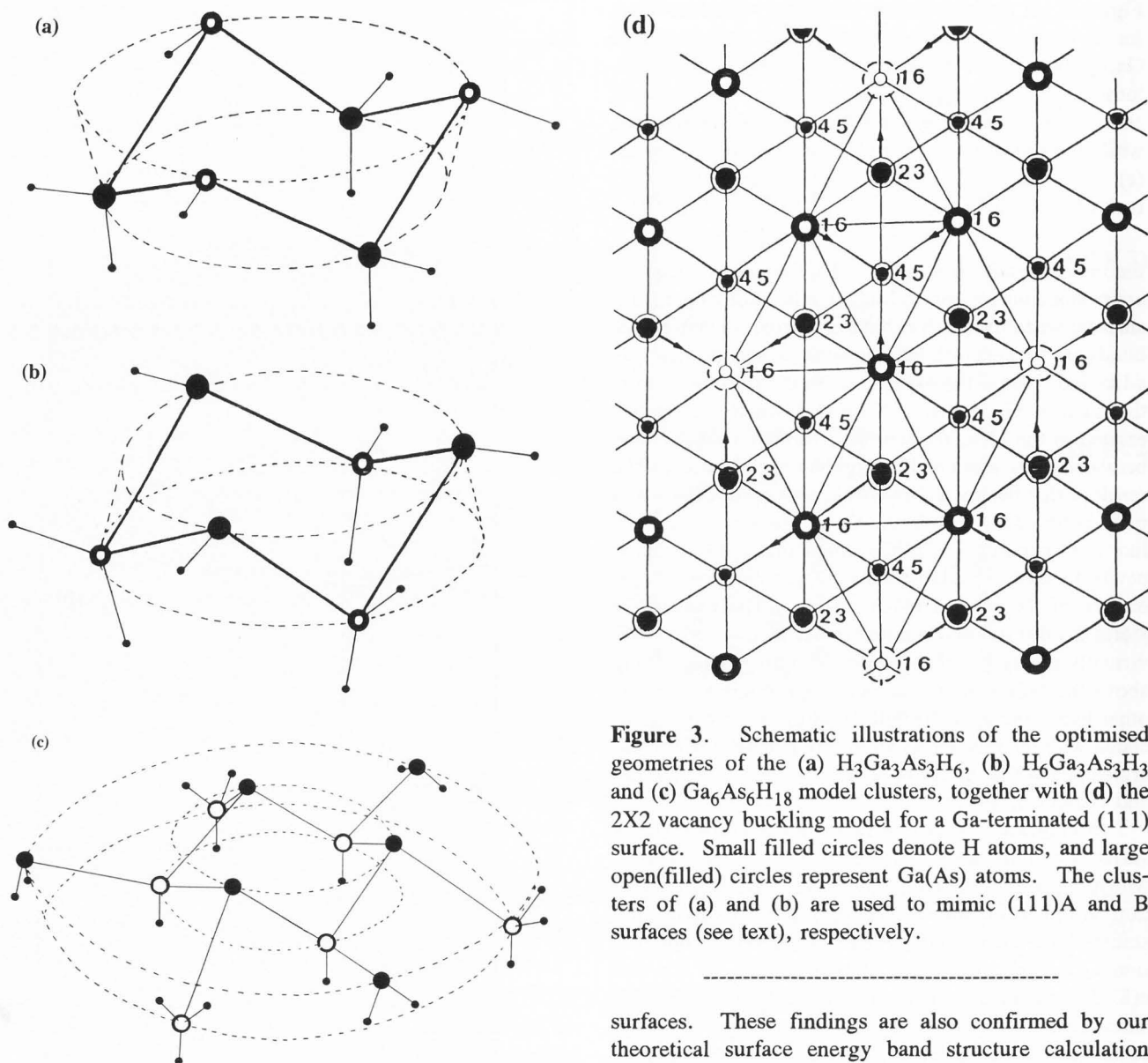
course to any heat treatment (Lubinsky *et al.*, 1976; Miller and Haneman, 1977; Chadi, 1978). On cleaving, low energy electron diffraction (LEED) measurements reveal the  $1 \times 1$  reconstruction pattern; this originates from the fact that each surface unit cell contains one anion and one cation. The surface anions and cations are linked in zigzag chains parallel to the  $[110]$  direction. Electron paramagnetic resonance (EPR) measurements indicate that the (110) surfaces are distorted (Lubinsky *et al.*, 1976). Surface relaxation has caused the surface Ga atoms to be pulled towards their three neighbours (two in the surface plane and one in the second layer), while the surface As atoms are tilted up, away from the ideal surface plane. This surface relaxation has been shown to have a profound influence on the electronic structure at the surface, causing shifts of up to about 1 eV in the surface state energies distorted (Lubinsky *et al.*, 1976; Chadi, 1978). Experimental and

**Figure 2 (at right).** The surface energy band structure for (a) ideal and (b) an As-terminated 2X1 reconstructed GaAs(100) surface, together with (c) the surface Brillouin zone. The heavy lines correspond to the bulk energy bands projected onto the first Brillouin zone, while the light curves are for the surface energy bands. (c) The surface Brillouin zone for ideal and 2X1 reconstructed surfaces.

theoretical results then indicate that the following factors are responsible for controlling the relaxation of the (110) surface; when the (110) surface is created, the interfacial bonds are broken such that the surface As atoms gain an s-like lone pair at the expense of an electron taken from the surface Ga atoms. Note that when this couple existed in the bulk, the lone pair formed a dative bond between an As atom and a neighbouring Ga atom. The result is that the As atoms on the new surface assume a more p-like form, while the Ga atoms assume an  $sp^2$ -like configuration. It is the interaction between these newly formed orbitals which is responsible for the geometry of the relaxed (110) surface. The relaxed Ga atoms exhibit  $sp^2$ -like bonding rather than  $sp^3$ -like, with virtually empty  $p_z$ -orbital states (dangling bonds) lying above the bulk conduction band edge minima. On the other hand, the virtually full dangling bond states associated with the relaxed As atoms are pushed down to energies below that of the bulk valence band edge (Miller and Haneman, 1977).

In contrast to (110) surfaces, polar (100)A and B surfaces exhibit many different surface reconstructions which depend on the temperature, the surface composition and how the surface was prepared. Experimental studies have uncovered a range of surface reconstructions spanning from the As-rich c(4X4) to Ga-rich c(8X2) structures. Theoretical investigations of (100) surface structures also confirm that a range of reconstructions can be stable. Figure 1 illustrates some of the proposed reconstruction models for these (100) surfaces. For example, recent high resolution medium energy ion scattering experiments (Falta *et al.*, 1993) reported that starting from a well-ordered c(4X4) As-rich surface, after annealing at 480-500°C for 5 minutes, the structure changes to a well-ordered c(2X8) structure; annealing at lower temperatures resulted in a change to a disordered c(2X8) structure. Continuing under progressively more Ga-rich conditions, for example by either annealing in a Ga-flux at about 550-600°C or by a brief flash anneal at high temperatures (approximately 640°C), results in a progression from (4X6) to (2X6) and finally to c(8X2) reconstruction (Fig. 1a). First principles pseudopotential density functional calculations (Northrup and Froyen, 1993; Ohno, 1993) have also confirmed that a variety of reconstructions occur on these (100) surfaces (Fig. 1b).

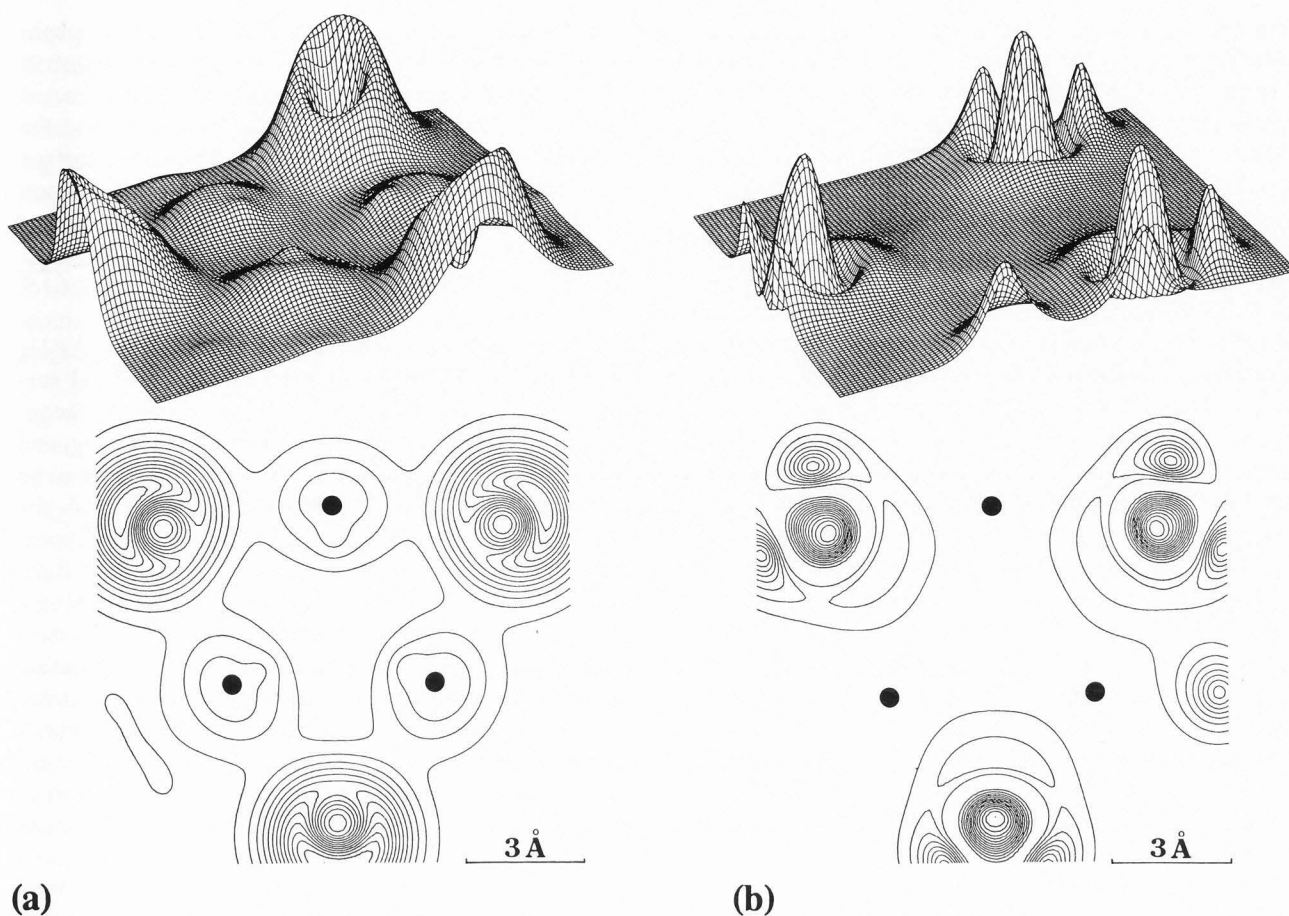




**Figure 3.** Schematic illustrations of the optimised geometries of the (a)  $\text{H}_3\text{Ga}_3\text{As}_3\text{H}_6$ , (b)  $\text{H}_6\text{Ga}_3\text{As}_3\text{H}_3$  and (c)  $\text{Ga}_6\text{As}_6\text{H}_{18}$  model clusters, together with (d) the 2X2 vacancy buckling model for a Ga-terminated (111) surface. Small filled circles denote H atoms, and large open (filled) circles represent Ga (As) atoms. The clusters of (a) and (b) are used to mimic (111)A and B surfaces (see text), respectively.

Careful analysis of the variety of reconstructions on (100)A and B surfaces reveal that two basic factors are driving the surface reconstruction process: namely, (1) lowering of the electronic energy by the formation of surface dimers, and (2) the influence of site-dependent chemical character determining the bonding interactions. We note that dimerized structures exist on almost all (100) reconstructed surfaces. Thus, for example, for As-terminated surfaces, the ideal surface presents two dangling bonds for each As atom resulting in a high energy state and unstable surface. To lower the electronic energy and satisfy the surface As atom bonding requirements, pairs of surface As atoms approach each other to form surface As dimers. This helps to explain the preponderance of dimerized local structures on (100) GaAs

surfaces. These findings are also confirmed by our theoretical surface energy band structure calculation results for both unreconstructed (ideal) As-terminated surfaces and 2X1 reconstructed surfaces. In these calculations, the  $\text{sp}^3\text{d}_1\text{d}_2$  method was developed using a fourteen atomic slab model (Jiang and Ruda, 1993). For the ideal surface (Fig. 2a), the lowest surface conduction band lies within the lower half of bulk energy bandgap, while the highest surface valence band is located just below the highest bulk valence band. The surface energy band structure is in fact indirect: the highest occupied surface valence band maxima is located at the  $\Gamma$  point (at  $-0.002$  eV), while the lowest conduction surface band has its minimum located at the  $J'$  point (at  $0.558$  eV), providing an indirect surface energy band gap of  $0.560$  eV. The lowest surface conduction band has  $p_x$ -like character, while the highest energy valence surface band states have  $p_z$ -like character. The calculated energy



**Figure 4.** Calculated total valence electron density for the  $\text{Ga}_6\text{As}_6\text{H}_{18}$  model cluster in the (a)  $\alpha$ -spin and (b)  $\beta$ -spin states. The electron density scales for both the surface and contour plots are un-normalized. Ga atomic sites are indicated using filled dots and figures may be read by reference to the scale markers given.

positions of surface states are in agreement with the photoemission measurements (Larsen *et al.*, 1982) to within 0.50 eV. Figure 2b presents results for the band structure of a 2X1 reconstructed (100) surface together with the bulk energy band structure. While the bulk energy bandgap is direct (occurring at the  $\Gamma$  point), the surface energy bandgap is again indirect. The lowest energy surface conduction band is located at 1.462 eV (corresponding to the  $J_2'$  point), while the highest energy surface valence band is at -0.200 eV. The lowest energy surface conduction band has a  $p_x$ -like character, similar to that discussed previously for the ideal (100) surface conduction band. This is mainly due to the fact that the dangling bonds for ideal (100) surfaces are essentially of a p-non-bonding orbital character. Surface reconstruction changes the p-non-bonding states into bonding and antibonding states. The bonding states correspond to the highest energy valence band, while the antibonding states correspond to the lowest energy sur-

face conduction band. A key distinction between the surface energy band structure of the ideal and 2X1 reconstructed surfaces is that the surface energy bandgap is extremely large for the reconstructed surfaces (1.662 eV) as compared with that for ideal surfaces (0.560 eV). Thus reconstruction, principally involving As-dimer formation, considerably lowers the surface electronic energy.

The second factor driving the reconstruction process is a factor that has been termed "site-dependent chemical character". Previous work has emphasised how this factor influences the variety of geometric and bonding configurations displayed by Ga and As atoms (Balasubramanian, 1988, 1990; Bock *et al.*, 1991; Graves *et al.*, 1991; Ruda and Jiang, 1992). For example, for the case of the  $\text{GaAsH}_2$  molecule, Ga atoms exhibited monovalent bonding while the As atoms did not hybridize to form  $sp^3$  bonds, but rather showed pure  $p\sigma$ -bonds. In fact, the lone pair did not form a dative bond, but

remained located entirely on the As atom as a pure s-like electron (Jiang and Ruda, 1993). In the case of  $(\text{GaAs})_2$  isomers, the  ${}^1A_g(D_{2h})$  ground state has a rhombohedral structure; the symmetry is linear  ${}^1S_g^+$ , corresponding to a Ga-As-As-Ga linear configuration and the  ${}^3B_{2u}$  state has a rhombohedral geometry. The rhombohedral structure for doubly bonded As=As has a bond length of 2.273 Å, close to the experimentally reported value and a As-Ga bond length of 2.701 Å. The As-Ga-As and Ga-As-Ga bond angles are 49.77° and 130.23°, respectively, and showed no  $sp^3$  hybrid character. The aforementioned example of an As lone pair not forming a dative bond and remaining entirely located on the As atom as a pure s-like electron also occurs for the GaAs(100) surface. This phenomena is accounted for by the so-called electron counting model which states that a surface structure is only stable when the number of electrons per unit cell is sufficient to exactly fill all of the As dangling bonds, keeping all of the Ga dangling bonds empty (Chadi, 1987; Farrell *et al.*, 1990). In this process, electrons will be transferred from Ga atoms to As atoms with a concomitant change in the hybridization. This results in a so-called "steepening" of the As-dimer. This steepening of the As dimer block produces cumulative displacements which result in  $(2X4)\beta$ ,  $(2X4)\alpha_{\text{sym}}$  reconstructed phases appearing, depending on the stage at which bond severing occurs.

For polar GaAs(111)A and B surfaces, the structural and electronic properties are less complex than for (100) surfaces. At moderate temperatures, Ga-terminated (111) surfaces only exhibit a 2X2 structure (Guichar *et al.*, 1979); however, As-terminated (111) surfaces present 2X2,  $\sqrt{3}X\sqrt{3}$ , 3X3 and  $\sqrt{19}X\sqrt{19}$  structures depending on the preparation conditions. Two models have been postulated for the 2X2 Ga-terminated (111) surface. One is the "Buckling Model" (Haneman, 1961) and the other is the more popular "Vacancy Buckling Model" (Tong *et al.*, 1984). More recently, systematic theoretical research have been made using a first principles self consistent evaluation of the total energy in the local density function formalism (Kaxiras *et al.*, 1988; Biegelsen *et al.*, 1990). These results show that for the As-terminated surface under As-rich conditions, the most stable condition for the surface is the 2X2 reconstruction. This is formed by As-adatom trimers being bound to the underlying surface with an As coverage of 0.78. Under Ga-rich conditions, the  $\sqrt{19}X\sqrt{19}$  reconstruction is the most stable. It is formed from a two layer hexagonal ring with an As coverage of 0.47. For Ga-terminated (111) surfaces under As-rich conditions, the 2X2 reconstruction with an As-triangular geometry consisting of three As adatoms is most stable. When the chemical environment changes to Ga-rich conditions, the 2X2 Ga-Vacancy geometry is the most stable. Detailed

experimental research has revealed the surface phase transition process for As-terminated surfaces (Alonso *et al.*, 1985). Starting with an As-rich 2X2 reconstructed geometry and using short annealing cycles to raise the temperature to 770K under UHV conditions, the surface structure changes to  $\sqrt{3}X\sqrt{3}$ . Alternatively, using ion bombardment and annealing, the structure changes to 3X3 and eventually with increasing the annealing temperature (to 790K), the surface exhibits a  $\sqrt{19}X\sqrt{19}$  reconstruction.

Work focusing on two model clusters,  $\text{H}_3\text{Ga}_3\text{As}_3\text{H}_6$  and  $\text{H}_6\text{Ga}_3\text{As}_3\text{H}_3$ , has been used to simulate local surface structure and to study the driving force for reconstruction on GaAs(111)A and B surfaces (Jiang and Ruda, 1994). The total energy of a given cluster will be comprised of the electronic energy together with the classical nuclear repulsion energy. In the Born Oppenheimer approximation, the total energy given as a function of the nuclear co-ordinates, defines a potential surface. The points on this potential surface of the most immediate interest are the stationary points. The minima on this surface define the equilibrium geometries. The process of searching for these minima corresponds to atomic geometric optimisation. According to the energy minimisation principle, the equilibrium geometries actually correspond to the real structures that exist in nature.

For GaAs(100) surfaces, the pseudopotential local density approximation (LDA) method yields a set of surface reconstructions which are dependent on the chemical potential: surface Ga (and As) dimers are commonly found structures on reconstructed surfaces using such schemes. The *ab initio* ECP method is based on the HF approximation, where each selected cluster is treated as a separate molecule. When this method is applied to surface structure research, energy minimisation must ensure that the selected cluster adhere to specific local geometries. For example, we selected the  $\text{Ga}_7\text{As}_7\text{H}_{20}$  cluster in this work to clearly reveal surface Ga dimerization during geometric optimisation. This was in direct agreement with pseudopotential LDA calculation results (Northrup and Froyen, 1993; Ohno, 1993; Northrup, 1994).

The optimised geometry (at minimum energy) for the  $\text{H}_3\text{Ga}_3\text{As}_3\text{H}_6$  cluster was an inverted cone: the radii of three Ga and three As atomic rings were found to be 2.746 Å and 2.406 Å, respectively. The uniform geometric structure of the GaAs crystal is thus disrupted near the surface, where the site-dependent different chemical characteristics of Ga and As atoms acquire a new importance. For As-terminated (111) surfaces, the optimised geometric structure of the  $\text{H}_6\text{Ga}_3\text{As}_3\text{H}_3$  cluster is a normal cone. The radii of the three As and three Ga atomic rings were found to be 2.374 Å and 2.874 Å,

respectively. The restricted open-shell Hartree Fock (ROHF) approximation was used for geometric optimisation of both model clusters (Figs. 3a and 3b). The extension of each of the Ga atomic rings and corresponding contraction of each of the As atomic rings, results in the propagation of lateral forces on Ga(As)-terminated surfaces. These lateral interactions explain the fundamental inability of Ga(As)-terminated surfaces to match to underlying As(Ga) layers and hence result in Ga(As) atoms being removed from Ga(As)-terminated (111) surfaces.

These two cluster model are thus useful for explaining the driving force for surface reconstruction. Another important surface phenomena occurring on almost all of the (100), (110) and (111) surfaces, is surfaces roughening on an atomic scale (e.g., the steepening relaxation for (100)GaAs surfaces). This factor cannot be well described using the  $H_3Ga_3As_3H_6$  and  $H_6Ga_3As_3H_3$  model clusters because there are only three Ga(As) atoms in each plane. We therefore developed a new model cluster,  $Ga_6As_6H_{18}$ , to mimic the GaAs(111) local surface geometric structure. This is a critical size cluster model for (111) Ga-terminated surfaces. We define critical here to mean that the accumulation effect in this size of cluster has already clearly indicated which atoms would sever their bonds with underlying As atoms; however, these bonds have not yet been broken due to insufficient cumulative strain. Nevertheless, some Ga atoms may have broken their bonds with underlying As atoms and would therefore be missing from Ga-terminated surfaces. After optimisation of the geometric structure of the  $Ga_6As_6H_{18}$  model cluster, we find that the six Ga atoms (original located in the same atomic plane) are no longer coplanar. The radius of the inner ring of three Ga atoms is 2.435 Å, somewhat smaller than the corresponding radius of the ring of three Ga atoms for the  $H_3Ga_3As_3H_6$  model cluster (2.746 Å). However, for the larger model cluster, the ring formed from the three outermost Ga atoms is extremely extended (having a radius of 5.555 Å), resulting in much longer bond lengths for these three Ga atoms with their underlying As atoms, compared with the inner ring Ga atoms. After geometric optimisation, the plane of the outer ring of Ga atoms lies 0.603 Å below the plane of the ring of the three inner Ga atoms. This would suggest a rather rough surface and indeed, that the Ga-terminated surface would be arched. These findings are in accordance with experimental reports. The radius of the ring of the three outermost As atoms is 5.070 Å. Thus, the whole cluster geometry assumes the geometry of an inverted cone. This geometry is presented schematically in Figure 3c. These results also suggest that an intermediate step is required to completely understand the reconstruction mechanism for the 2X2

vacancy buckling model for the Ga-terminated (111) surface (Fig. 3d). Using the unrestricted Hartree Fock (UHF) method, we calculated the total electron density for the  $\alpha$  and  $\beta$  spin states, separately. Figures 4a and 4b present these results for the  $\alpha$  and  $\beta$  spins, respectively, plotted on the Ga atomic plane.

## Conclusions

The different surface relaxation and reconstruction phenomena for GaAs(100), (110) and (111) surfaces have been discussed. Using our band structure calculation results for (100) surfaces, we showed that satisfying dangling bond and the realisation of the steepening relaxation are the root causes for surface reconstruction. For (111)A and B surfaces, our cluster model calculation results revealed that the extension(reduction) of the surface structural unit for A(B) surfaces, roughens the surfaces and is responsible for the surface reconstruction mechanism.

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**Editor's Note:** All of the reviewer's concerns were appropriately addressed by text changes, hence there is no **Discussion with Reviewers**.