Adsorption of fullerenes C_n (n=32,36,40,44,48,60) on the GaAs(001)- $c(4 \times 4)$ reconstructed surface

Chenggang Zhou,^{1,2} Jinping Wu,^{1,2,*} Bo Han,^{1,2} Shujuan Yao,^{1,2} and Hansong Cheng^{1,*}

¹Institute of Theoretical Chemistry and Computational Materials Science, China University of Geosciences, Wuhan, People's Republic of China 430074

²Faculty of Materials Science and Chemical Engineering, China University of Geosciences,

Wuhan, People's Republic of China

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We present first principles studies using density functional theory on adsorption of fullerene molecules C_n (n=32,36,40,44,48,60) on the $c(4 \times 4)$ reconstructed GaAs(001) surface. Adsorption at various surface sites coupled with numerous fullerene orientations were systematically sampled to obtain energetically most stable structures. With the orientation of a fullerene with one of the hexagons facing down the substrate, the surface trenches were identified as the sites that give the strongest adsorption. The orientational preference for C_{32} adsorption is an exception due to its unique stability in its electronic structure. It was found that the As atoms with a dangling bond in the second surface layer play a most critical role in determining the adsorption structure and strength, while the top layer As dimers are only capable of forming weak bonding with fullerenes, which differs significantly from adsorption of fullerenes and small unsaturated organic molecules on silicon of fullerenes near the adsorption sites is observed. The calculated adsorption energy decreases as the size of fullerenes increases. The calculation yields useful physical insight into the adsorption mechanism and the physicochemical properties of the materials.

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I. INTRODUCTION

The development of materials for applications in microelectronics is a subject of intensive research in the past few years. As the size of semiconductor devices continues shrinking, there is an increasing demand for semiconductor materials with predetermined chemical and physical properties.^{1,2} Central to the research activities is the development of fabrication methods that make use of well-controlled chemical processes for materials design and development.^{3,4} A prominent example is the recent studies of depositing a variety of small unsaturated organic molecules on reconstructed silicon surfaces via Diels-Alder-type of cycloaddition reactions.⁵⁻²⁵ These deposition processes yield strong chemical bonds at the molecule-surface interface with well-oriented organic thin films. The growth of the deposition layers as well as the film properties can be tailored to meet increasingly challenging requirements for various applications in optoelectronic devices, sensor technologies, nonlinear optical materials and molecular electronics.³ An interesting development recently in this arena is the deposition of fullerenes, instead of unsaturated organic molecules, on semiconductor surfaces.²⁶⁻⁵³ Like those organic species, fullerenes possess many unsaturated chemical bonds; all carbon atoms adopt a quasi- sp^2 hybridization electronic configuration with the π electrons delocalized in the molecule. Unlike the unsaturated organic molecules, however, the curvature and the topology of fullerenes can significantly influence the interaction strength of these molecules at surfaces. Many studies have shown that fullerenes are capable of interacting strongly with semiconductor surfaces, forming genuine covalent chemical bonds.^{35,36,39,40,46,53} Some of the surface reactions can undergo similar Diels-Alder type of cycloaddition processes via reactions between the unsaturated π bonds of fullerenes and the dimers of reconstructed surfaces.^{43,53} It is anticipated that the uniformity of the deposited film is, to a large extent, determined by the size and topology of the fullerenes. In a previous paper, we reported computational studies of using density functional theory to investigate the deposition of C_{28} at $c(4 \times 4)$ reconstructed GaAs(001) surface.⁵³ It was found that the adsorption at the trench site with one hexagon of C_{28} facing down is energetically most favorable. Strong, covalent C-As bonds were observed at the interface upon chemisorption of C_{28} via either the [2+2] cycloaddition reaction or simple electron lone-pair mediated charge transfer from the substrate to the fullerene molecule. In this paper, we present systematic studies on adsorption of fullerenes with a range of diameters on the $c(4 \times 4)$ reconstructed GaAs(001) surface from C_{32} up to C_{60} . Our primary objectives are to gain insight into the deposition mechanisms of fullerenes with various sizes on this important semiconductor surface and to compare their relative adhesion strength of these molecules on the substrate. Understanding their adsorption behavior on semiconductor surfaces should enable us to select the appropriate sizes of molecules for deposition with desired adhesion.

Fullerenes ($n \le 84$) are made of 12 pentagons and a certain number of hexagons with the most stable one being the well-known fullerene C₆₀.⁵⁴ In general, the stability of fullerenes varies with size and structural characteristics. The adjacent pentagons give rise to intermolecular stress with a higher curvature on the carbon atoms due to their geometric arrangement. It has been shown theoretically that C₂₈, C₃₂, C₅₀, C₆₀, and C₇₀ are relatively stable energetically.⁵⁵ Adhesion of fullerene layers on semiconductor surfaces should be associated with the relative stability. Several empirical rules



were proposed for predicting the stability based on topological considerations.^{56,57} It is anticipated that a less stable fullerene sticks to the substrate more tightly. Of course, the adhesion of fullerenes also depends on the surface structure, specific adsorption sites and the interplay between fullerenes and the substrates.

GaAs is one of the most well-studied semiconductor materials and has been widely utilized in a broad variety of electronic devices. The GaAs(001) surface undergoes substantial reconstructions and exhibits a variety of well-ordered phases under different preparation conditions. To make a consistent comparison with the results presented in our previous study, we select the arsenic-rich phase $c(4 \times 4)$ reconstructed GaAs(001) surface as the substrate, as shown in Fig. 1. The surface can be obtained upon annealing to room temperature and has been shown to be very stable.^{58,59} The surface structure was described in detail in our previous paper.53 Briefly, the top layer of the supercell is composed of three arsenic dimers along the [110] direction upon reconstruction. The dimers are formed through a single covalent bond. Each dimer atom connects with the second layer, composed of As atoms, with two single bonds, leaving an electron lone pair on its π orbital. This surface structural arrangement yields four possible adsorption sites [Fig. 1(c)] for the fullerenes: 1. the top layer single dimer for single [2+2] or [4+2] cycloaddition reaction with fullerenes, i.e., two C atoms of an ethene or four C atoms of a diene participating in the surface reaction with one As dimer (site S); 2. the top layer two adjacent dimers for double [2+2] and/or [4+2] cycloaddition reactions with fullerenes, i.e., 4-8 C atoms participating in the surface reaction with two As dimers (site **D**); 3. the trench formed by two opposite ends of nearest three-dimer units in the same row on one side and one three-dimer unit on another side (site **T**) and 4. the "bed" formed by four adjacent three-dimer units (site **B**).

We have performed extensive calculations in the previous study on the possible adsorption sites and orientations of C_{28} on the $c(4 \times 4)$ reconstructed GaAs(001) surface.⁵³ Although numerous stable configurations were found, the adsorption at the trench site (**T** site) with one hexagon of C_{28} facing down was identified to be energetically most favorable. In the present study, we assume that in most cases the deposition of other fullerene molecules on the surface follows the same adsorption pattern. To make certain that this is indeed the case, we calculated the adsorption energies at the above four surface sites for several selected fullerene molecules, which are also sampled for orientation preference. We found, without exception, that the trenches are always the preferred adFIG. 1. The reconstructed GaAs(001)- $c(4 \times 4)$ surface; The white middle size balls represent As atoms, the dark balls represent Ga atoms; the bottom microwhite balls denote the H atoms; and the top layer of As-As dimers are highlighted by larger white balls; (a) top view; (b) side view. (c) Four possible adsorption sites.

sorption site and, except for C_{32} , the energetically most favorable orientation of the fullerenes is the hexagonal ring of fullerenes facing downward the substrate. Therefore, we will focus our discussions mostly on adsorption at the surface trench site with the hexagon of fullerenes facing down as the preferred orientation.

II. COMPUTATIONAL DETAILS

In the present study, the $c(4 \times 4)$ reconstructed GaAs(001) surface was modeled as a slab. The supercell of the surface contains seven layers of GaAs as shown in Fig. 1. The bottom five layers alternate a gallium layer and an arsenic layer, respectively, and the top two layers are constituted only by As atoms. The bottom Ga layer is saturated with hydrogen atoms. The surface cell parameters were taken from the crystal structure of GaAs and the distance between adjacent slabs was chosen to be about 25 Å, large enough to prevent effective interaction between slabs. The unit cell contains 24 Ga atoms, 30 As atoms and 16 H atoms in addition to a fullerene molecule. The closest distance between two nearest neighboring fullerene molecules is in the range between 4.5 Å (for C₆₀) and 6.0 Å (for C₂₈) and thus the lateral interaction is relatively small compared with the adsorption energies.

All calculations were performed using ab initio density functional theory under the generalized gradient approxima-Perdew-Wang exchange-correlation tion with the functional.60-64 The method was implemented in the Siesta simulation code.^{65–68} Troullier and Martins' norm-conserving pseudopotentials were used to describe the core electrons and the localized numerical atomic orbitals of double ζ augmented with polarization functions as the basis set were employed to describe the valence electrons.^{69,70} An energy cutoff of 200 Ry was used to determine a boundary for the wave functions of atomic orbitals, beyond which the wave functions vanish,⁷¹ with good convergence in the calculated adsorption energies. The Brillouin zone integration was performed using a special k-point approach implemented with the Monkhorst and Pack scheme with $2 \times 2 \times 1$ k points. The present computational method has been widely utilized in a broad variety of studies on surface phenomena and shown to be highly accurate in providing reliable results on surface structures and energetics.53,63

Full structural relaxation for the top five layers of the surface together with the adsorbate was performed using the conjugate gradient algorithm without imposing symmetry constraints, while the bottom two layers as well as the hydrogen atoms were kept fixed. The adsorption energy of the fullerene is calculated using

TABLE I. The calculated structural parameters of various fullerene molecules.

Fullerene	Symmetry	Binding Energy (Å)
C ₂₈	T_d	-6.765
C ₃₂	D_{3d}	-6.936
C ₃₆	D_{6h}	-6.994
C_{40}	D_2	-7.063
C ₄₄	D_2	-7.128
C ₄₈	D_2	-7.169
C ₆₀	I_h	-7.330

$$\Delta E_{ads} = -\left[E_{sub+fullerene} - E_{sub} - E_{fullerene}\right],\tag{1}$$

where $E_{sub+fullerene}$, E_{sub} and $E_{fullerene}$ represent the total energies of $c(4 \times 4)$ reconstructed GaAs(001) surface with a fullerene molecule in the chosen unit cell, the surface itself and the fullerene molecule, respectively. The energy of the fullerene was calculated by first placing the molecule in a large cubic box with the dimension, 20 Å×20 Å×20 Å and then fully relaxing the atomic coordinates with the fixed box size and $2 \times 2 \times 2\mathbf{k}$ points.

III. RESULTS AND DISCUSSION

A. Structure and energetics of fullerenes

To gain insight into the adsorption mechanism of various sizes of fullerenes on the surface structure shown in Fig. 1, it is important to first understand the structures of these molecules and their relative stability. The fullerenes involved in the present study are C_{32} , C_{36} , C_{40} , C_{44} , C_{48} and C_{60} . For comparison purpose, we also include some of the results obtained previously on C_{28} . The main geometric characteristics of the fully optimized fullerene molecules and the calculated average binding energy per atom are shown in Table I. In particular, for C_{60} , the calculated bond lengths compare remarkably well with the experimental values (single bond: 1.446 Å; double bond: 1.406 Å).^{72–74} The calculated highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps are shown in Fig. 2, which are in good agreement with the available experimental data.⁷⁵ In



FIG. 2. The calculated HOMO-LUMO gap of fullerene molecules from C_{28} to C_{60} , comparing with the experimental results.

addition, the calculated binding energy per C atom for C_{60} is 7.33 eV, also in excellent agreement with the experimental value (7.4 eV).^{76,77} These results suggest that the present computational method is capable of providing accurate results for the fullerene systems.

B. Adsorption structures

We first tested the accuracy of the present computational method for describing the bulk GaAs structure against the experimental data by choosing a unit cell of GaAs containing four Ga atoms and four As atoms and then fully optimizing the structure including the cell parameters. Good agreement with the experimental values was achieved with the mean deviation of the cell parameters from the crystal structure of only 5.653 Å and maximum deviation of 5.750 Å. The calculated Ga-As bond distance is 2.486 Å, which compared well with the experimental value of 2.462 Å.

From Fig. 1, it is seen that the $c(4 \times 4)$ GaAs(001) surface is reconstructed to yield a structure covered by units of three As dimers in the top layer followed by layers alternating with a layer of As atoms and a layer of Ga atoms. Except the atoms in the top two layers, the atoms all adopt a tetrahedral bonding configuration. In the second layer constituted entirely by As atoms, the valence of the atoms fully covered by the top layer dimers is also fully saturated with four covalent bonds. The rest of atoms are only partially covered by the side As dimers and thus each of the atoms has a dangling bond. This unique electronic structure makes this local area of the surface highly reactive. In the present study, we will focus only on adsorption at the trench site since adsorption of C₂₈ at this site was shown in our previous study to be energetically most favorable.⁵³ To ensure this is also the case for larger fullerenes, we selected several fullerene molecules to test the adsorption strength at other surface sites. But, without exception, the trench site always gave the lowest energy adsorption structures and thus we will discuss adsorption of fullerenes only at this site. As shown in Fig. 1(c), the **T** site is roughly 5.25 Å in width and 7.8 Å in length. It is in fact part of the **B** site, which is of a dimension of 8.0 Å \times 7.8 Å. With the current range of the fullerenes, the **T** site is capable of providing one As dimer in the middle of a three-dimer unit on one side and two opposite ends of two three-dimer units in the same row to interact with the fullerenes. In addition, the two As atoms with dangling bonds in the second layer at this site also give a strong anchoring force for the molecules.

To simplify the description of the adsorption structures, we first label the atoms of the As dimers as As^S for the two side dimers, As^M for the dimer atoms in the middle and As^U for the unsaturated As atoms in the second layer. The covalent bonds formed between a fullerene and the two As^S atoms of both sides are denoted by α and δ , respectively, and the bond formed between a fullerene and the As^M atom is labeled as ξ . Finally, the covalent bonds between a fullerene and the As^U atoms are labeled as β and γ , respectively. Here, α , β , γ , δ and ξ represent not only bonds but also the close contacts. The labeling scheme is shown in Fig. 3.

For C_{28} , we already presented a detailed description of adsorption structures and associated energetics in our previ-



FIG. 3. (Color online) The labeling scheme of geometric parameters.

ous work⁵³ and will not describe them here. We now concentrate only on the adsorption of C_{32} through C_{60} at the T site.

Among the fullerene molecules, C₃₂ is rather special. It was shown to be much more stable as an individual molecule than other small fullerene molecules. In fact, the time-flight mass spectrum of fullerene anions has shown a great abundance of this species and its ultraviolet photoelectron spectrum exhibits an unusually large HOMO-LUMO gap, 1.30 eV.⁷⁵ Our calculated HOMO-LUMO gas is 1.40 eV, in good agreement with the experimental result. The most stable adsorption configuration is that the molecule orients itself with two adjacent five-membered rings facing downward the **T** site upon adsorption (Fig. 4). It forms two strong covalent bonds with two As^U atoms in the second layer with bond lengths of 2.173 Å(β) and 2.103 Å(γ), respectively. The bonding with the As^S atoms is relatively weak with the bond distances of 3.084 Å(α) and 3.214 Å(δ), respectively, and the bondlength with the As^M atom is 2.880 Å(ξ). This result indicates that C₃₂ is anchored mainly by the unsaturated As atoms in the second layer and the interaction between C₃₂ and top layer dimers is relatively weak. As a consequence, the dimers are elongated only slightly upon C_{32} adsorption (approximately 0.05 Å) and the substrate relaxation is also very small. The calculated adsorption energy of 2.38 eV, which is much smaller than that of C_{28} of 3.02 eV mainly due to the exceptional stability of C32, suggests that C₃₂ can stick to the surface quite strongly. Mulliken population analysis indicates that the adsorption is facilitated by a partial charge transfer mechanism from the substrate to C_{32} (0.226 e). The charge transfer results mostly from electronsharing between C₃₂ and the dangling bonds of the second layer As atoms to form two covalent bonds.

 C_{36} has a geometry of a highly symmetric spheroid. Its equator consists of six fused six-membered rings and each of its poles is composed of one six-membered ring. The equator and the poles are connected by 12 five-membered rings. The



FIG. 5. (Color online) Optimized structure of C_{36} on GaAs(001)- $c(4 \times 4)$ surface. (a) Top view and (b) local side view.

height of the spheroid is 5.31 Å and its width is 4.34 Å. Therefore, C₃₆ can interact with the substrate with one of the hexagons either vertically or horizontally. Our calculations suggest that the horizontal adsorption configuration is energetically more favorable, as shown in Fig. 5. This is chiefly because the horizontal configuration allows more bonding sites to interact with the surface. One of the equator hexagons is anchored at the T site with the C atoms forming two covalent bonds with the As^U atoms. The calculated bond distances are 2.129 Å(β) and 2.133 Å(γ), respectively, suggesting that the bonding is rather strong. The adsorption results in a slight compression of the anchoring As atoms of the second layer, pushing them downward. In addition, there is one C atom on each of the poles forming a relatively weaker bond with the As^S atom with the bond distances of 2.673 Å(α) and 2.681 Å(δ), respectively. The relaxation of the side dimers is rather small. The calculated adsorption energy is 2.691 eV. The charge transfer from the substrate to C_{36} of 0.118 electron is small, which results mainly from the formation of the covalent bonds between C36 and the unsaturated As atoms in the second layer.

Unlike C₃₆, C₄₀ is much less symmetric. Of several optimized stable adsorption configurations, the structure with one of the six-membered rings, which has most of the sharp corners, is most stable. At these sharp corners, the C atoms adopt a quasi- sp^2 electronic configuration and thus are more reactive than those flat carbons. The optimized structure is shown in Fig. 6. The bonding structure of C₄₀ with the substrate is similar to that of C_{36} but the bond distances differ slightly. The less symmetric geometry of C₄₀ results in significant twist of the six-membered ring upon adhesion at the **T** site; the C atoms forming covalent bonds with the As^U atoms are pulled out of the plane toward the second layer. A small bond relaxation occurs at the side dimers participating the bonding with C_{40} , resulting in a marginal stretch of the dimer bonds by approximately 0.012 Å. The calculated adsorption energy is 2.464 eV with a small charge transfer of 0.086 e from the substrate to C_{40} .



FIG. 4. Optimized structure of C_{32} on GaAs(001)- $c(4 \times 4)$ surface. (a) Top view and (b) local side view.



FIG. 6. (Color online) Optimized structure of C_{40} on GaAs(001)- $c(4 \times 4)$ surface. (a) Top view and (b) local side view.



FIG. 7. (Color online) Optimized structure of C_{44} on GaAs(001)- $c(4 \times 4)$ surface. (a) Top view and (b) local side view.

The structure of C₄₄ is also of low symmetry. One of its six-membered rings with most acute C atoms forms covalent bonds with the substrate, as shown in Fig. 7. Unlike the other smaller fullerenes, there is only one C atom in C44 forming a covalent bond with the As^U atom with a bond length of 2.191 Å. The C atom is pulled out from the fullerene considerably. The structural distortion mainly results from the ill fit of C_{44} at the **T** site due to the larger size of the molecule. Another atom in C₄₄ also forms a strong covalent bond with the As^M atom with a bondlength of 2.216 Å. Significant deformation of the six-membered ring participating in the surface bonding occurs and the dimer formed by As^M atoms stretches considerably by 0.121 Å. Slight bond elongations for other dimers and a marginal lattice relaxation take place upon the fullerene deposition. The calculated adsorption energy is 1.842 eV and the electron transfer from the substrate to C₄₄ is 0.071.

Like C_{40} and C_{44} , C_{48} is also of low symmetry with a similar adsorption configuration (Fig. 8). On one side of the fullerene, two C atoms form a C-As^{*U*} bond and a C-As^{*S*} bond with bond distances of 2.178 and 2.393 Å, respectively. On another side, it also forms additional two relatively weaker bonds with bond distances of 2.945 and 2.996 Å. Consequently, the six-membered ring becomes severely distorted. Very little surface relaxation is observed. The calculated adsorption energy is 1.598 eV with a charge transfer of 0.11 from the substrate to C₄₈.

Finally, we calculated the adsorption structure of C_{60} on the surface. Because of its large size and relatively flat sp^2 configuration, its interaction with the substrate is relatively weak with the calculated adsorption energy to be only 1.123 eV. Its calculated closest distances from the surface are 3.156, 3.194, 3.273, and 3.227 Å, respectively, much longer than the other smaller fullerenes. No appreciable bonding with the top layer dimers was found. Consequently, the dimer structure remains nearly unchanged. We have systematically examined the adsorption structures at other sites



FIG. 8. (Color online) Optimized structure of C_{48} on GaAs(001)- $c(4 \times 4)$ surface. (a) Top view and (b) local side view.



FIG. 9. (Color online) Optimized structure of C_{60} on GaAs(001)- $c(4 \times 4)$ surface. (a) Top view and (b) local side view.

and found that none of the optimized structures is energetically more favorable than the one reported here. The optimized adsorption structure at the **T** site is shown in Fig. 9. The fundamental difference between C_{60} and the small fullerenes is that the large size of C_{60} does not allow it to interact directly with the second layer As atoms with dangling bonds, while the small fullerene molecules can fit well in the trench site of the substrate and thus are capable of effectively forming covalent bonds with these As atoms. As a consequence, C_{60} has the smallest adsorption energy among the fullerenes on the GaAs(001)- $c(4 \times 4)$ reconstructed surface.

C. Bonding analysis

Our extensive search for stable adsorption structures for the above fullerenes indicates that the surface trench site combined with the facedown six-membered ring of fullerenes with the most acute C atoms gives the energetically most stable adsorption configurations. Covalent bonds can be formed between the fullerenes and the substrates. The unsaturated As atoms with a dangling bond in the second layer play a key role in anchoring the fullerene molecules. As the size of fullerenes increases, the distances of the covalent bonds increase and it becomes increasingly difficult for the fullerenes to fit in the T site, suggesting that the bonding in general becomes weaker in the adsorption structures from C28 to C60. Indeed, the calculated adsorption energy decreases monotonically, except for C32, as the size of fullerenes increases, as shown in Fig. 10. The unusually small adsorption energy for C₃₂ is attributed to the exceptional stability of the molecule in the gas phase.

Two factors dictate the relative bonding strength of fullerenes on the substrate. The first one is the local curva-



FIG. 10. The calculated fullerene adsorption energies.

ture of the hexagon in the fullerene participating in the bonding with the substrate. The carbon atoms adopt a quasi- sp^2 hybridization forced by curvature. A large curvature gives rise to a higher strain on the atoms; formation of covalent bonds with the surface would relax the stress on the C atoms as their orbital hybridization changes from sp^2 to sp^3 . Therefore, the adsorption energy of a fullerene in general increases with curvature. Qualitatively, the relative adsorption strength of fullerenes can also be understood based on their relative gas phase binding energies. It can be seen from Table I that the calculated average binding energies of the fullerenes increase monotonically from C28 to C60 as their curvatures decrease. An energetically stable structure tends to be less reactive. Thus one would expect that the adsorption energy decreases as the average binding energy increases. However, the binding energy of C₃₂ cannot explain the unusually small adsorption energy. This is due to the fact that partial electron transfer from the substrate to C_{32} is needed in order to form stable covalent bonds between C_{32} and the surface. With a large HOMO-LUMO gap of C₃₂, partial electron attachment to the fullerene is difficult, leading to relatively weaker bonding.

The second factor controlling the fullerene adhesion process is whether the molecule can fit well in the narrow size of the \mathbf{T} site to be anchored by the unsaturated As atoms in the second layer. As the fullerene size increases, it becomes increasingly difficult for the molecule to fit in this site. As a result, the distance between a fullerene and the substrate increases with the molecular size, leading to incrementally weaker bonding for large fullerenes. The major driving force for anchoring fullerenes comes from the unsaturated As atoms in the second layer. The As atoms with a dangling bond are in a meta stable state and ready to form σ bonds with carbon atoms upon fullerene deposition. This is the primary reason why the surface trenches are the preferred sites for fullerenes adsorption. Bond formation between a large fullerene and the substrate requires substantial structural deformations of the six-membered ring, leading to a smaller adsorption energy. The top layer As dimers also contribute to the adsorption but its interaction with fullerenes is much weaker. Each atom of the dimers forms two σ bonds with the second layer As atoms with a bond distance approximately 2.46 Å, while the distance of the dimer bond itself is about 2.60 Å. This implies that the two As atoms of the dimer form only a single σ bond and there is no π bonding between them. Therefore, there is an electron lone pair on each of the dimer atoms. This electronic structure does not facilitate formation of a covalent σ bond with a fullerene. As a consequence, surface dimers interact with fullerenes rather weakly. This is remarkably different from the deposition of fullerenes and small unsaturated organic molecules on silicon surfaces, which has been shown extensively to be capable of reacting strongly with the C-C π bonds via a cycloaddition process with the π bonds of Si-Si dimers.^{5–25,43}

Adsorption of fullerenes on the GaAs(001) surface directly results in formation of covalent bonds at the interface, facilitated by a partial charge transfer process. Due to the covalent nature of the bonding, the transfer is very small and the charges are largely shared between the fullerenes and the substrate. The calculated Mulliken charges can only partially



FIG. 11. The calculated charge transfer.

reflect the relative strength of adsorption. Figure 11 displays the calculated charge transfer from the surface to the fullerenes, which generally decays as the curvature of the fullerenes decreases. The trend of the charge transfer is qualitatively consistent with the calculated adsorption energies.

D. Electronic structure analysis

Figure 12 displays the calculated density of states (DOS) for the $c(4 \times 4)$ reconstructed GaAs(001) surface. The DOS spectra for the fullerenes and the adsorption systems are shown in Figs. 13 and 14, respectively. The DOS spectrum of the substrate exhibits a typical semiconductor band gap of about 1.5 eV. Detailed analysis on the spectrum projected to individual atoms suggests that As atoms contribute mostly to both the conduction band and the valence band. The band near the Fermi level comes from the surface states dominated by the As dimers and, in particular, the As atoms with a dangling band in the second layer. The detailed features of the DOS spectra of fullerenes differ significantly. The band gaps range approximately from 0.3 to slightly above 1.7 eV and these materials exhibit considerable metallic or semiconductor characteristics. The dominant contribution to the valence band and conduction band comes from the π orbitals. The overlap of these orbitals varies with curvature of the



FIG. 12. The calculated density of states of $c(4 \times 4)$ GaAs(001) reconstructed surface.



FIG. 13. The calculated density of states of fullerenes.

molecule. A large curvature forces the π electrons to localize around nuclei and thus gives rise to a poor overlap. Consequently, these orbitals more likely participate in the surface reaction. The conduction band of fullerenes is to accept partial electron transfer from surface. We also note that the DOS spectrum of C₃₂ displays a relatively large band gap, which explains why it is somewhat resistant to the surface reaction. Figure 14 indicates strong orbital mixing between fullerenes and the substrate and band features of the DOS spectra near the Fermi level change considerably. In all cases, the energy bands of fullerenes move slightly downward, reflecting the partial charge transfer from the substrate to the fullerenes. The downshift results in a shoulder band at the Fermi level, which is contributed by the C and As atoms involved in the bond formation. As adsorption becomes weaker with molecular size, the band mixing becomes less accordingly. The shoulder band gradually overlaps with the rest of the valence band and the DOS spectrum of an adsorption system more resembles that of the substrate.

E. Effect of fullerene isomers

There are numerous isomers for each fullerene molecule. The structures chosen in the present study are among the

lowest energy isomers. To examine whether a different isomer would result in a radically different adsorption configuration, we chose an isomer of C₃₆ with a comparable total energy with the one described in the above to compare the adsorption properties on the $c(4 \times 4)$ GaAs(001) surface. This isomer of C_{36} is with a D_{2d} symmetry and thus more "spherical" than the one with D_{6h} symmetry.^{78,79} Their optimized structures are shown in Fig. 15. The calculated total energies of these two isomers are -5539.2760 eV for $C_{36}(D_{2d})$ and -5539.1666 eV for $C_{36}(D_{6h})$, respectively, with the former being slightly more stable. We sampled eight different possible adsorption configurations on the GaAs(001) surface for each of the isomers and found that adsorption at the trench site is energetically more favorable, as expected. Furthermore, the calculated adsorption energy for $C_{36}(D_{2d})$ is 1.80 eV, much smaller than the calculated adsorption for $C_{36}(D_{6h})$ of 2.69 eV reported in the above. The reason for the latter to be more stable is that the D_{6h} structure adopts a horizontal adsorption configuration at the trench site to maximize the interaction with the substrate, while the bulkier D_{2d} structure does not allow the molecule to fit well at this site. Therefore, we conclude that adsorption behavior of different fullerene isomers could vary significantly on the surface.



FIG. 14. The calculated density of states of the adsorption systems.



FIG. 15. The C_{36} isomers: (a) D_{2d} (b) D_{6h} .

IV. SUMMARY

As size of semiconductor devices continues the reduction trend, there is increasing demand for developing new chemistries on important semiconductor materials such as GaAs. Fullerenes represent one of the most novel materials in the past few years and their physicochemical properties have been extensively studied. Because of the inherent curvature and the highly delocalized π orbitals, fullerenes are capable of reacting with a wide variety of substances. A large size variation of these molecules provides an excellent opportunity to design and develop materials for a broad range of applications. In the present study, we have attempted to explore the adsorption properties of a range of fullerenes on the $c(4 \times 4)$ reconstructed GaAs(001) surface. We show that these molecules can be adsorbed on the surface strongly by forming covalent bonds. The calculation yields physical insight into the adsorption mechanism and provides useful information on the properties of the materials.

We found that the As atoms in the second layer of the surface with a dangling bond play a critical role in anchoring fullerenes by forming covalent bonds and the top layer As-As dimers are less important in determining the adsorption process although they can also form relatively weak bonding with these molecules. This is significantly different from the adsorption of fullerenes and small unsaturated organic molecules on reconstructed silicon surfaces covered by dimers on their top layers, where the C-C double bonds are capable of reacting strongly with the surface dimers via a cycloaddition process. The presence of the dangling bonds in the second layer makes the trench sites most reactive toward fullerenes. Since the trench site is relatively narrow, it becomes increasingly difficult to place a large fullerene at this site to take advantage of the dangling bond. As a consequence, the bonding between fullerenes and the surface gradually becomes weaker as the size of fullerenes increases. The calculated adsorption energies reflect this trend of bonding, except for C_{32} due to its unique stability in its electronic structure. However, in all cases, the calculated adsorption energies are well above 1.0 eV, suggesting rather strong bonding. It is expected that as the size of fullerenes continues increasing, the nature of adsorption will change from the chemisorption to physisorption.

We have sampled numerous orientations of fullerenes upon adsorption and found that the energetically most preferred one is for one of the hexagons with a large local curvature to interact with the surface. Again, C₃₂ is an exception, which interacts with the substrate with its shared bond of two adjacent pentagons instead. Of course, the orientational preference is subject to the number of binding sites available; the adsorption strength increases with the number of available binding sites. The curvature of fullerenes near the adsorption sites dictates the local bonding strength between molecules and the surface; a large curvature gives rise to a stronger bonding by relaxing the stress of the carbon atoms imposed by the quasi- sp^2 electronic configuration. We have also found that adsorption structures and energies can vary significantly with different fullerene isomers. This again underscores the importance of fullerene curvature and geometry near the adsorption sites in determining the local bonding strength.

GaAs with surfaces covered by fullerenes via chemisorption represents a class of materials that may exhibit novel physicochemical properties. By depositing fullerene molecules with a selected size on surfaces, these materials can be tailored to achieve the desired properties, such as low dielectric constant.^{53,80} We anticipate excellent adhesion for fullerenes with a small size on these surfaces. There have been active research activities in recent years to develop functionalized fullerene derivatives via novel chemical processes. It can be envisaged that these functionalized fullerene derivatives can further enrich the properties of fullerene films on semiconductor surfaces and provide a great opportunity for developing a rich variety of materials.

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- *Electronic address: cgzhou@cug.edu.cn; URL: http:// unit.cug.edu.cn/chxy/itccms/temp/fu_coor.tar.gz
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