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Ab initio study of cesium chemisorption on the GaAs(110) surface

K. M. Song and A. K. Ray

Physics Department, P. O. Box 19059, University of Texas at Arlington, Arlington, Texas 76019

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Different possible adsorption sites of cesium atoms on a gallium arsenide (110) surface have been investigated using *ab initio* self-consistent unrestricted Hartree-Fock total-energy cluster calculations with Hay-Wadt effective-core potentials. The effects of electron correlation have been included by invoking the concepts of many-body perturbation theory and are found to be highly significant. We find that the Cs atom adsorption at a site modeled with a $CsGa_5As_4H_{12}$ cluster is most favored energetically followed by Cs adsorption at a site modeled with the $CsGa_4As_5H_{12}$ cluster. For molecular cesium, a site modeled by a $Cs_2Ga_6As_9H_{21}$ cluster is most favored energetically. However, here all four sites considered remain competitive energetically at the correlated levels of theory. The effects of charge transfer from Cs and Cs_2 to the GaAs surface and the possibilities of metallization are also analyzed and discussed.

I. INTRODUCTION

The phenomena of metal-semiconductor interfaces have been of major interest for scientists and engineers due to extensive industrial applications of semiconductor devices.[1,2] However, the physics of the Schottky barrier is not fully understood as yet. Metal-GaAs(110) has been considered as a prototype interface and a sizable amount of experimental data, e.g., by core-level photoelectron spectroscopy, scanning tunneling microscopy, electron-energy-loss spectroscopy, etc., on these systems have recently been acquired, which highlight the effects of band bending and the shift of the Fermi level, E_F.[3-13] Theoreticians have split the analysis of the band bending and the shift of the Fermi level in two groups, one for small metal coverage, θ ($\theta \leq 1$ ML), for which the Fermi-level movement exhibits a logarithmic dependence on θ, independent of the metal[14] and large metal coverages for which $\theta > 1$ and the final pinning position depends explicitly on the specific interactions at the metal-GaAs interface.[15] Even as one concentrates on the small-θ range, several methods are emerging which emphasize different aspects of the interface structure and dynamics. In this paper, we report the results of *ab initio* self-consistent electronic structure calculations for atomic and molecular cesium interactions with a GaAs(110) surface and we first comment on some relevant experimental and theoretical literature.

Kendelewicz *et al.*[16] studied chemisorption and Fermi-level pinning at the Cs/GaAs(110) and K/GaAs(110) interfaces by using soft-x-ray photoemission. They found that Cs and K overlayers deposited on the GaAs(110) surface produced band bending of 0.7 eV, comparable with band bendings produced by more electronegative metals. In particular, Cs chemisorbed in two sites on the GaAs(110) surface. Using photoemission, Cao *et al.*[17] studied Fermi-level movement and overlayer metallization at RT and 110-K low-temperature (LT) Cs/GaAs(110) interfaces. They found that 1 ML Cs was not metallic, whereas full metallicity was established with 2 ML Cs coverage. First *et al.*[18] investigated the adsorption morphologies of Cs atoms on GaAs(110) surfaces by scanning tunneling microscopy. For coverages as low as 0.03 ML, Cs formed one-dimensional zigzag chains of two elements on the GaAs(110) surface and for increased coverages, Cs adsorbates formed three element chains on the GaAs(110) surface. The formation of the extended chains with the increased coverages of Cs indicated an attractive interaction between Cs atoms. In the zigzag structure, the Cs-Cs nearest-neighbor distance was 6.9 Å, compared with bulk Cs value of 5.2 Å. Magnusson and Reihl[19] studied the change in the occupied states of K/GaAs(110) and Cs/GaAs(110) with ultraviolet photoelectron spectroscopy and in the unoccupied states with angle-resolved inverse photoemission. Beyond saturation coverage, the surface was found to be metallic. Heskett *et al.*[20] characterized the Cs/GaAs(110) interfaces by using angle-resolved ultraviolet photoemission spectroscopy and medium-energy ion-scattering spectroscopy. With coverages of Cs up to 1 ML at room temperature, the interface remained semiconducting but when the second alkali metal layer was formed, a metallic surface was observed. DiNardo, Maeda Wong, and Plummer[21] studied the Cs/GaAs(110) interface by electron-energy-loss spectroscopy. Up to one Cs layer, a semiconducting interface was observed and upon Cs multilayer growth, interfacial metallization was observed. Angle-resolved photoemission spectroscopy techniques have been used by Maeda Wong *et al.*[22] to study Cs adsorption on GaAs(110). A Cs-induced surface state was observed in the vicinity of the surface Brillouin-zone edge. Whitman *et al.*[23] studied the properties of Cs adsorbed on room-temperature GaAs and InSb(110) surfaces with scanning tunneling microscopy. With increasing coverage, the initial formation of one-dimensional (1D) Cs zigzag chains changed to a 2D overlayer consisting of five-atom Cs polygons arranged in a $c(4\times4)$ superlattice. Metallic characteristics were observed following saturation with a second Cs overlayer. Compañó, del Pennino, and Mariani[24] analyzed the Cs/GaAs(110) interface using high-resolution electron-energy-loss spectroscopy. The estimated band bending for the n-type doped GaAs(110) surface is 0.73

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eV at 1 ML Cs coverage. The Cs overlayer at 1 ML could be identified as not being uniformly metallic, but there could be metallic clusters with a mean size not larger than a few tens of Å.

As far as theoretical calculations are concerned, Manghi *et al.*[25] investigated the electronic properties of 1 ML of Cs/GaAs(110) ideal relaxed surfaces by a jellium slab model with self-consistent pseudopotential theory. A band of Cs-induced states was found in the gap which hybridized with the dangling- and back-bond states of the GaAs surface. The work function decreases with Cs deposition were 3.7 for the ideal and 3.8 eV for the relaxed surfaces, respectively. For the relaxed substrate, Cs was found to react mainly with As atoms at the surface. Self-consistent tight-binding calculations of Klepeis and Harrison[26] showed that at low coverages of less than 0.1 ML of Cs on the GaAs(110), the Ga site was preferred over the As site. Krauss and Stevens[27] examined Cs interactions with small clusters of GaAs(110) using self-consistent field (SCF) methods. Binding energies for two or three Cs atoms on GaAs were found to be less than 0.1 eV per Cs atom indicating only small binding contribution from charge transfer and polarization. Alkali valence charge was weakly bonded between the alkali atoms and polarized toward the Ga atom. Gao and Wang[28] studied adsorption of Cs on a GaAs(110) surface using first-principles linearized augmented-plane-waves method and a jellium-slab model. At low coverage, the interaction between the Cs overlayer and the GaAs(110) surface was dominated by hybridization between the 6*s* electrons and the arsenide-derived surface state in the band gap, leading to a strong polarization and substantial electron transfer to the substrate due to less screening in GaAs than in the metals. The work function decreased linearly for coverages less than half a monolayer and, at higher coverages, the work function remained almost flat with little increase, indicative of nonmetallicity up to 1 ML of Cs coverage. Using the Hubbard model, Gedik, Ciraci, and Batra[29] investigated the electronic structure of a Cs-covered GaAs(110) surface at submonolayer coverage. Estimates of electron hopping and electron repulsion energy indicated that the correlation effects were important and caused the metallic density of states in the band gap to split. Thus, the system became a Mott-Hubbard insulator with the absent density of states at the Fermi level up to monolayer coverage of Cs. Finally, Bechstedt and Scheffler[30] presented a review study of alkali adsorption, primarily Na and K, on GaAs(110).

The above summary indicates that, in spite of a large number of experimental data and some theoretical calculations, there exist significant controversies about Cs adsorption on GaAs(110). We use here *ab initio* unrestricted Hartree-Fock (UHF) theory to study the chemisorption of Cs and Cs_2 on GaAs by simulating the surface with finite hydrogen-bonded GaAs (GaAsH) clusters. We note that clusters are well suited for the study of semiconductor surfaces,[31] and in general can yield accurate results of such properties as the chemical nature of a bond, bond length, and other geometrical data.[32] In as much as the effects of electron correlation can be very significant, we have studied these by invoking the concepts of many-body perturbation theory, as in our previous works on chemisorption of alkali atoms on silicon surfaces,[33] on Na, K, and K_2 on a GaAs(110) surface,[34] and of hydrogen and oxygen atoms on lithium surfaces.[35]

This paper is organized as follows: In Sec. II we discuss the basic theory and the computational method used; the cluster models and results of cesium chemisorption on these clusters are presented in Sec. III.

II. THEORY AND THE COMPUTATIONAL METHOD

Both the unrestricted Hartree-Fock theory and the many-body perturbation theory (MBPT), as used in this work, are well documented in the literature.[36–40] Here we present only a basic equation to define some terms. In the MBPT, the energy is given by the linked diagram expansion

$$\Delta E = E - E_0 = E_1 + E_{\text{corr}} = \sum_{n=0}^{\infty} \langle \Phi_0 | V[(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_L \,, \quad (1)$$

where Φ_0 is taken to be the UHF wave function, H_0 is the sum of one-electron Fock operators, E_0 is the sum of UHF orbital energies, and $V = H - H_0$ perturbation, where H is the usual electrostatic Hamiltonian. The subscript L indicates the limitation to linked diagrams. Though one can include various categories of infinite-order summations from Eq. (1), the method is usually limited by termination at some order of the perturbation theory. For most of the bare GaAs(110) clusters, we have previously carried out complete fourth-order calculations (MP4) which consist of all single-, double-, triple- and quadruple-excitation terms.[34] For the chemisorbed systems, due to severe demand on available computational resources, usually only MP2 (up to second-order perturbation theory) calculations have been carried out.

Now one of the primary considerations involved in *ab initio* HF/MBPT calculations is the determination of the type of basis set to be used.[41] Basis sets used in *ab initio* molecular orbital computations usually involve some compromise between computational cost and accuracy. Keeping in mind the tremendous cost of *ab initio* calculations, specifically for large systems like cesium, gallium, and arsenic, we have elected to represent them by effective-core potentials or pseudopotentials. In particular, we have used the Hay-Wadt (HW) effective-core potentials,[42,43] which are known to provide almost exact agreement with all electron results. However, to improve the accuracy of our calculations further, one *d* function was added to all the HW basis sets. The exponent of the *d* function was chosen to provide the minimum energy for the Cs_2, Ga_2, and As_2 dimers, with the bond lengths fixed at experimental values. The total energy versus the *d*-exponent values of the Ga_2, As_2, and Cs_2 dimers are shown in Fig. 1 and we find that $d_{\text{Ga}} = 0.17$, $d_{\text{As}} = 0.28$, and $d_{\text{Cs}} = 0.015$. The inclusion of *d* functions changes the GaAs optimized distance from 2.55 to 2.42 Å and the SCF binding energy per atom from −0.038 to 0.193 eV. For hydrogen, a (4*s*/1*p*) basis set was used. All computations were done using the programs GAUSSIAN92 (Ref.

44) and GAMESS (Ref. 45) on the Cray Y-MP8/864 at the University of Texas Center for High Performance Computing and on the Cray Y-MP C90 at the National Science Foundation Pittsburgh Supercomputing Center.

III. Cs AND Cs_2 ADATOM INTERACTIONS WITH THE GaAs(110) SURFACES

The basic clusters used to represent the GaAs(110) surface have been presented before[34] and will not be discussed, in detail, again. In brief, we studied GaAs clusters up to three layers and since, at the second-order many-body perturbation theory level, $Ga_5As_4H_{12}$ followed by $Ga_4As_5H_{11}$, has the most stable configuration, these units were chosen for chemisorption studies. For Cs adsorption on the GaAs(110) surface, we then considered the four sites used by Fong, Yang, and Batra[46] and in our studies of Na, K, and K_2 chemisorption on GaAs(110).[34] Top views of all these four Cs+GaAs systems are shown in Fig. 2 and the corresponding clusters are represented by $CsGa_4As_5H_{12}$, $CsGa_5As_4H_{12}$, $CsGa_5As_4H_{14}$, and $CsGa_4As_5H_{14}$, respectively. A single adatom Cs was then placed at all fixed sites, and, for each system, the total energy as a function of the vertical height z of the Cs atom from the GaAs(110) surface plane was calculated. The Hartree-Fock energy was then plotted against z (negative z representing position of the adatom below the surface) and the minimum energy z value, z_{eq}, was taken to be the equilibrium position at the adatom. Figure 3 shows a plot of E_{UHF} versus z for each site. A single-point MP2 calculation was then performed at the z_{eq} value. To examine the relative stability of chemisorption at the different sites, the chemisorption energies E_c are then calculated from

$$E_c(Cs/Ga_xAs_yH_z)=E(Cs)+E(Ga_xAs_yH_z) - E(CsGa_xAs_yH_z)\ , \qquad (2)$$

and Table I shows the values of E_c and z_{eq}. At this point, surface reconstruction possibilities are not allowed, based on some evidence that at low alkali-metal coverages, the reconstruction and relaxation of the GaAs(110) surfaces may be lifted.[47–49]

Before we discuss the results, we note first that, in spite of extensive experimental investigations, the stable atomic site of Cs on GaAs(110) is now known. From the results of Table I, we note first that all sites are stable at the MP2 level but, at the SCF level, sites III and IV have negative chemisorption energy. This again illustrates the importance of correlation for the alkali metal GaAs system.[34,50] Site II has the highest chemisorption energy both at the SCF and at the MP2 levels, followed by site I, and site IV has the lowest chemisorption energy. This is in good agreement with the results of Na-GaAs systems,[34] where sites I and II were found to be most stable with site II having significantly higher chemisorption energy. However, the results for K-GaAs systems are somewhat different in that site II is still the most stable but sites I and IV have nearly identical chemisorption energies at the MP2 level. Comparing our results to the bond lengths of Cs-Ga (4.11 Å) and Cs-As systems (3.62 Å), we find that the nearest-neighbor distance between Cs and Ga or As, in all four sites, increases as a result of the competition of all the neighboring atoms. For site II, the optimum vertical height of the Cs adatom from the topmost layer is found to be 3.87 Å.

In the next stage of the calculations, we studied the possibilities of surface reconstruction. The adatom was again allowed to approach the clusters and a simultaneous optimization of the adatom distance and the cluster lattice constant was carried out. Table II summarizes the results of such a total optimization process and Fig. 4 shows three-dimensional plots of the total energy versus lattice constant and adatom heights for all the four sites. If we compare the results in Table II to those in Table I, we first note that the atoms in the reconstructed surface move closer compared to an ideal surface but the adatom, in general, moves away from the surface except for site IV. The Cs-Ga and Cs-As distances, in general, decrease.

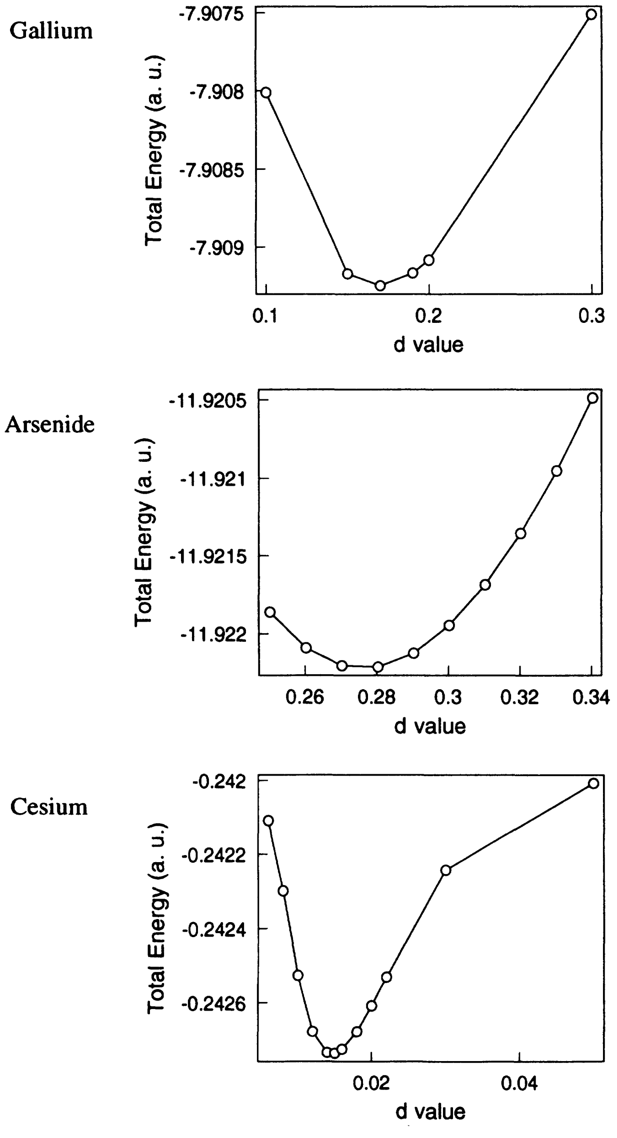

FIG. 1. Total energies (a.u.) vs d function value plots for Ga_2, As_2, and Cs_2 dimers.

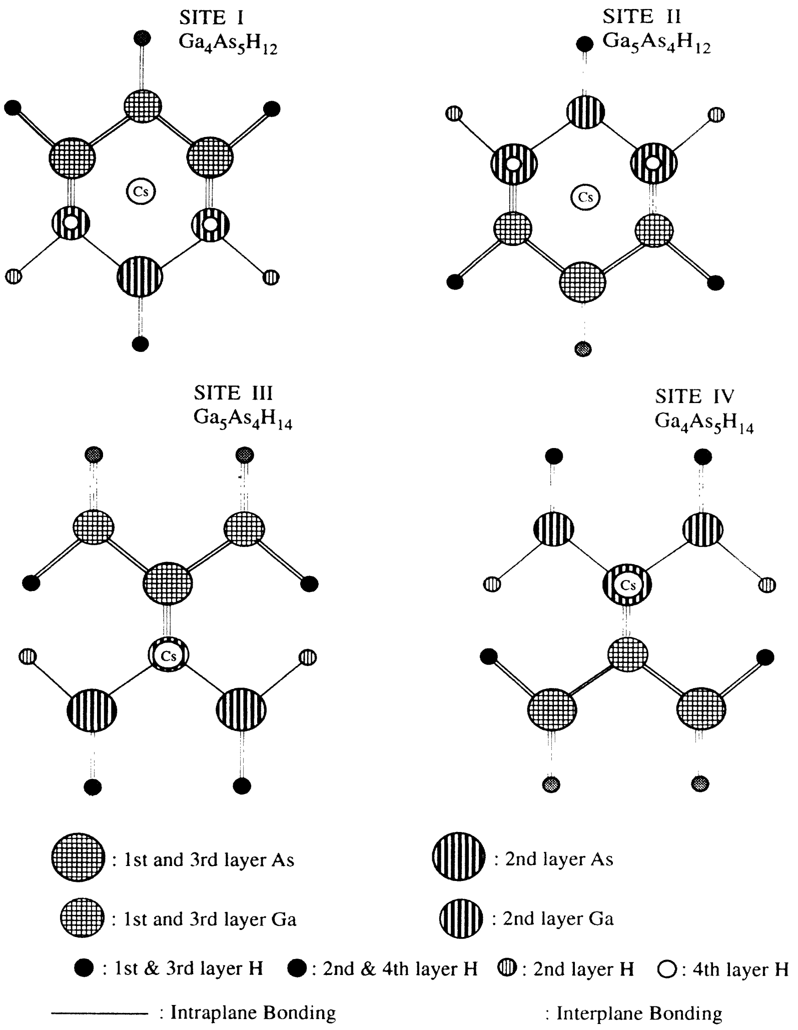

FIG. 2. Cs adatom locations on the GaAs(110) surface.

TABLE I. Optimum vertical heights of the Cs adatom from the ideal GaAs surface (lattice constant = 5.65 Å) and the total energies (a.u.) and the chemisorption energies (eV) of Cs + GaAs clusters.

Cluster	Site	Height (Å)	Bond length (Å) Cs-Ga	Bond length (Å) Cs-As	Total energy SCF	Total energy MP2	Chemisorption energy SCF	Chemisorption energy MP2
$CsGa_4As_5H_{12}$	I	2.45	4.29	3.81	−43.7618	−44.7451	1.01	2.32
$CsGa_5As_4H_{12}$	II	3.87	4.40	4.41	−39.8717	−40.7828	1.70	3.19
$CsGa_5As_4H_{14}$	III	3.50	4.91	3.77	−40.6783	−41.6837	−0.87	1.87
$CsGa_4As_5H_{14}$	IV	3.89	4.14	5.21	−44.4899	−45.5755	−1.73	0.56

TABLE II. Chemisorption energies from the results of total optimization of GaAs + Cs clusters.

Site	Height (Å)	Lattice constant (Å)	Bond length (Å) Cs-Ga	Bond length (Å) Cs-As	Total energy SCF	Total energy MP2	Chemisorption energy SCF	Chemisorption energy MP2
I	2.75	5.09	4.21	3.80	−43.9201	−44.8665	1.10	2.40
II	3.94	5.11	4.38	4.38	−40.0352	−40.9154	2.49	3.63
III	3.50	5.01	4.65	3.72	−40.8873	−41.8657	−1.17	1.87
IV	3.75	4.98	3.95	4.83	−44.7374	−45.7556	−1.05	0.45

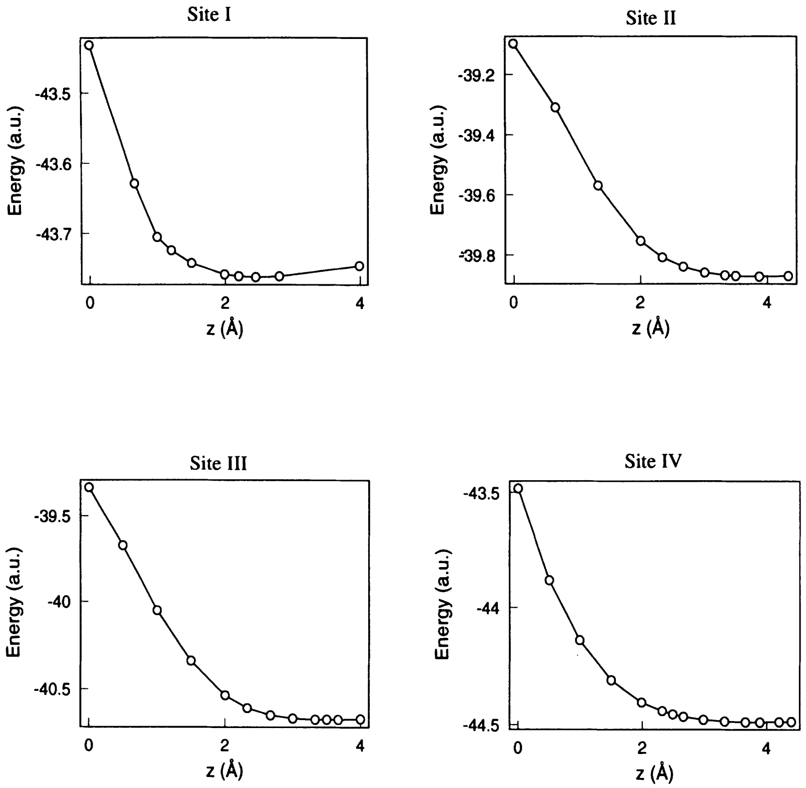

FIG. 3. UHF energies (a.u.) vs adatom vertical heights (Å) from the (110) surface plane for each site.

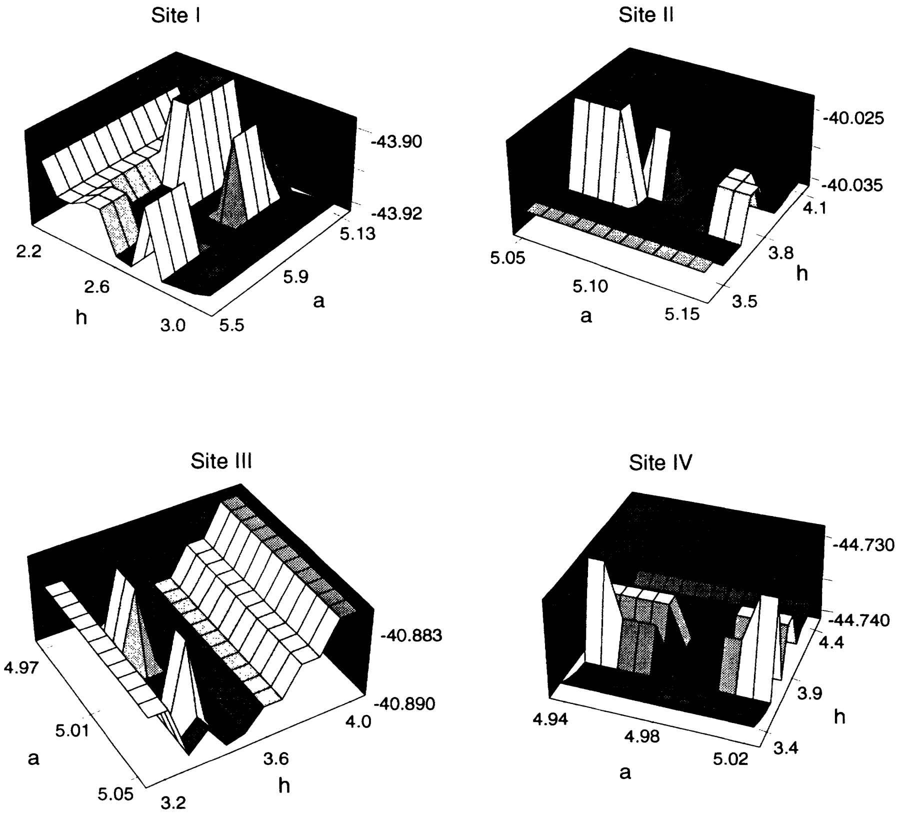

FIG. 4. Total energies (a.u.) vs lattice constant (Å) and adatom height (Å) from the (110) surface for each site.

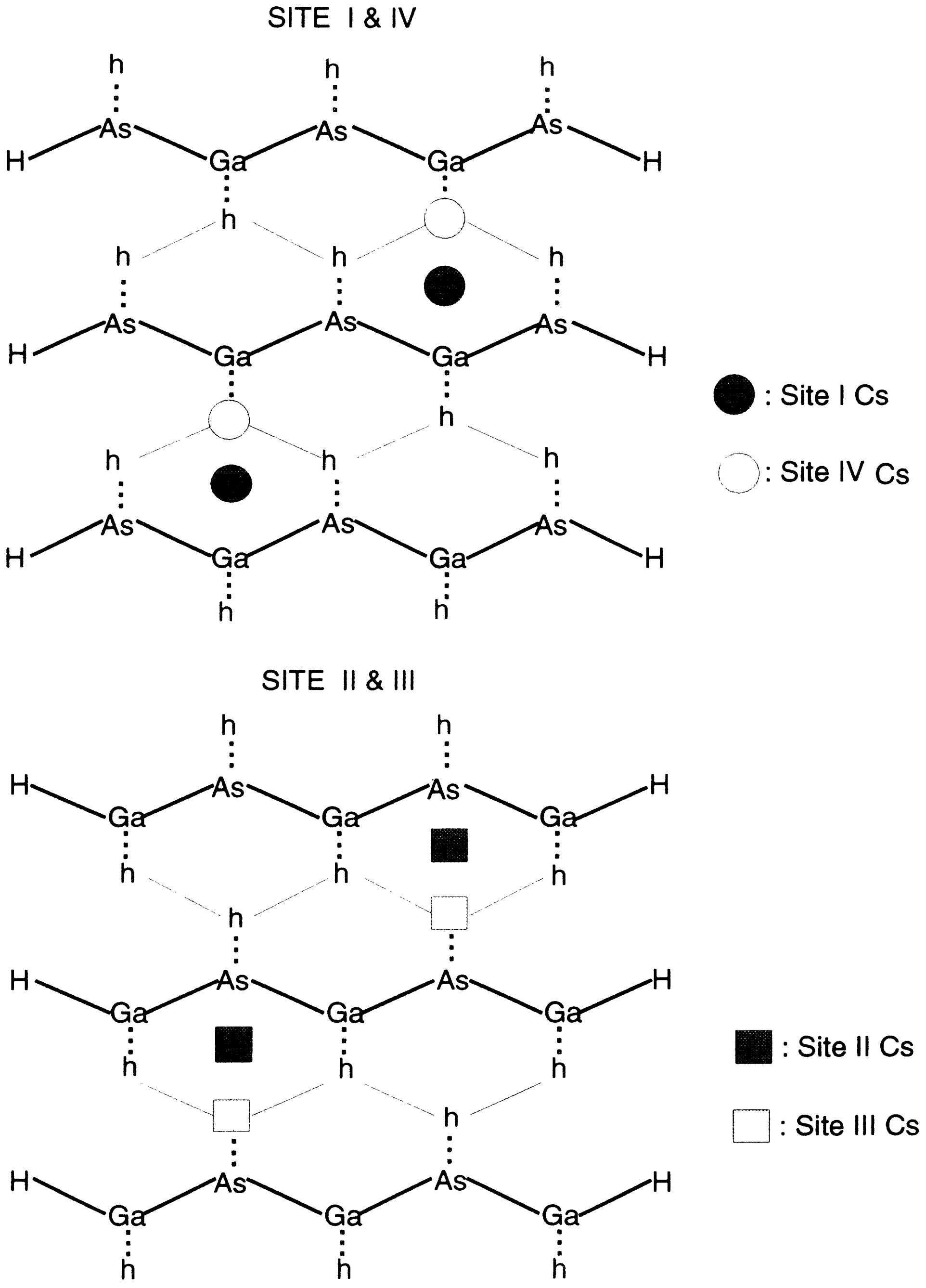

FIG. 5. Schematic drawings of GaAs(110)/Cs_2 for all sites.

TABLE III. Chemisorption energies from the results of optimization of GaAs+Cs_2 clusters.

Cluster	Site	Height (Å) h_1	h_2	Bond length (Å) Cs-Ga	Cs-As	Total energy SCF	MP2	Chemisorption energy SCF	MP2
$Cs_2Ga_6As_9H_{21}$	I	3.20	3.50	3.84	3.83	−75.6870	−77.4544	3.58	4.95
$Cs_2Ga_9As_6H_{21}$	II	3.40	3.50	4.00	4.00	−64.0261	−65.5480	2.77	4.71
$Cs_2Ga_9As_6H_{21}$	III	3.50	3.60	4.91	3.77	−64.0247	−65.5504	2.73	4.78
$Cs_2Ga_6As_9H_{21}$	IV	3.40	3.80	3.68	4.84	−75.6728	−77.4387	3.19	4.52

The same general conclusions prevailed also for sodium and potassium. The total energies of the chemisorbed clusters also decrease, as expected, after optimization but, as for sodium and potassium, the chemisorption energies do not indicate any consistent pattern. At the self-consistent-field level, compared to the ideal surface, E_c increased for sites I, II, and IV but decreased for site III; at the MP2 level, E_c increased for sites I and II but decreased for site IV. Site II still remains the most preferred site followed by sites I and III, respectively. The SCF calculations of Krauss and Stevens[27] found a binding of ~ 0.35 eV to a $Ga_3As_4H_9$ cluster with a Cs distance from the reconstructed surface of ~ 3.4 Å. Our value for the largest chemisorption energy is 3.63 eV for the cluster $CsGa_5As_4H_{12}$, with a Cs distance from the surface of 3.94 Å. Though the sizes of Cs, K, and Na atoms are different, site II remains the most preferred site for chemisorption for all the elements. However, the Cs atom is at a larger distance (3.87 Å) from the surface compared to the distances of K and Na. Also, the distances between the Cs atom and the nearest-neighbor Ga and As atoms are larger compared to the corresponding distances for K and Na. This trend is continued for the values of the chemisorption energy.

We now discuss some preliminary results on molecular cesium adsorption on GaAs(110). Noting again that no precise information on site preferences is available, we tried the same approach positions as mentioned above for molecular cesium. Due to computational limits, only one layer of GaAs(110) clusters was considered and Fig. 5 shows schematic drawings of the GaAs(110)/Cs_2 systems for the four sites. To simulate experimental conditions, a zigzag pattern of Cs atoms was constructed, with the two Cs atoms occupying same type of sites. The corresponding clusters are represented by $Cs_2Ga_6As_9H_{21}$, $Cs_2Ga_9As_6H_{21}$, $Cs_2Ga_9As_6H_{21}$, and $Cs_2Ga_6As_9H_{21}$, respectively, and a three-dimensional optimization of the total energy versus the heights of the first and second adatom from the GaAs(110) surface were carried out. Figure 6 shows the plots of the total energy versus both adatom heights for all four sites and Table III gives the chemisorption energies. Here h_1 is the height of the first adatom from the surface and h_2 the height of the second adatom from the surface. The chemisorption energies are calculated from

$$E_c(Cs_2/Ga_xAs_yH_z)=E(Cs_2)+E(Ga_xAs_yH_z)-E(Cs_2Ga_xAs_yH_z)\ . \qquad (3)$$

Here $E(Cs_2)$ is the total energy of the cesium dimer at the optimized interatomic distance. At the SCF level, site I has the highest chemisorption energy and site IV has second-highest chemisorption energy compared to the other sites. However, when correlation is included, all sites become rather competitive, with E_c ranging from

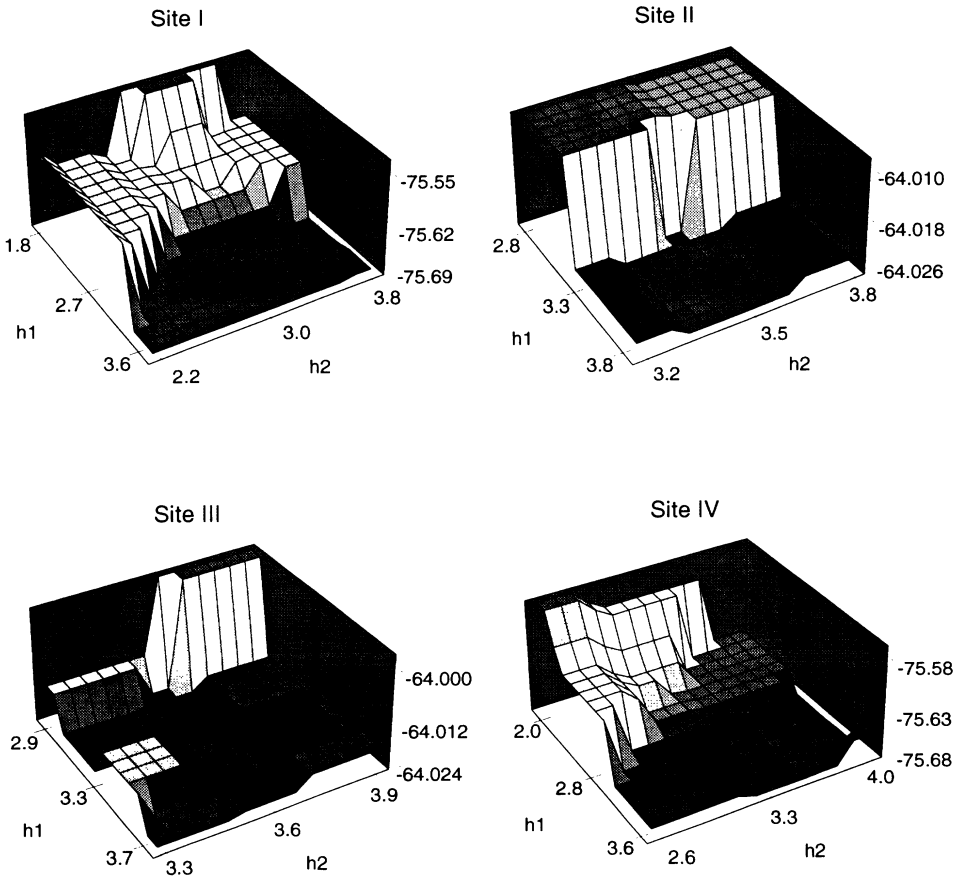

FIG. 6. Total energies (a.u.) vs adatom heights (Å) of Cs_2 from the (110) surface for each site.

TABLE IV. Atomic charge distributions for the ideal clusters of GaAs(110)+Cs.

Cluster	Adatom charges	First layer atom charges		Second layer atom charges		Third layer atom charges		Fourth layer atom charges	
$Ga_4As_5H_{12}Cs$	0.78	Ga	0.36	Ga	0.19	Ga	0.24	H	0.09
(Site I)		As	−0.29	Ga	0.19	As	−0.07	H	0.09
		As	−0.29	As	−0.29	As	−0.07	H	−0.23
		H	−0.01	H	−0.15	H	−0.24		
		H	−0.01	H	−0.04	H	0.04		
		H	−0.15	H	−0.04	H	−0.12		
$Ga_5As_4H_{12}Cs$	0.80	Ga	0.14	Ga	0.10	Ga	0.10	H	−0.11
(Site II)		Ga	0.14	As	−0.10	Ga	0.10	H	−0.10
		As	−0.29	As	−0.10	As	−0.06	H	−0.10
		H	−0.09	H	0.02	H	0.05		
		H	−0.09	H	−0.15	H	0.07		
		H	0.02	H	−0.15	H	−0.22		
$Ga_5As_4H_{14}Cs$	0.84	Ga	0.11	Ga	0.40	Ga	0.10	H	−0.14
(Site III)		Ga	0.30	As	−0.15	Ga	0.18	H	−0.10
		As	−0.46	As	−0.12	As	−0.10		
		H	−0.03	H	−0.04	H	−0.08		
		H	−0.14	H	−0.12	H	−0.08		
		H	−0.05	H	−0.12	H	0.06		
		H	−0.00	H	−0.23	H	−0.03		
$Ga_4As_5H_{14}Cs$	0.67	Ga	0.16	Ga	0.18	Ga	0.25	H	−0.06
(Site IV)		As	−0.22	Ga	0.18	As	−0.04	H	−0.06
		As	−0.22	As	−0.19	As	−0.04		
		H	−0.07	H	0.04	H	−0.06		
		H	−0.07	H	0.04	H	−0.06		
		H	−0.11	H	0.07	H	−0.30		
		H	−0.11	H	0.07	H	−0.08		

TABLE V. Atomic charge distributions for the optimized clusters of GaAs(110)+Cs.

Cluster	Adatom charges	First layer atom charges		Second layer atom charges		Third layer atom charges		Fourth layer atom charges	
$Ga_4As_5H_{12}Cs$	0.82	Ga	0.34	Ga	0.11	Ga	0.22	H	0.11
(Site I)		As	−0.26	Ga	0.11	As	−0.25	H	0.11
		As	−0.26	As	−0.26	As	−0.02	H	−0.30
		H	−0.01	H	−0.16	H	−0.24		
		H	−0.01	H	−0.04	H	0.08		
		H	−0.16	H	−0.04	H	−0.13		
$Ga_5As_4H_{12}Cs$	0.86	Ga	0.09	Ga	0.02	Ga	0.05	H	−0.11
(Site II)		Ga	0.09	As	0.00	Ga	0.05	H	−0.10
		As	−0.28	As	0.00	As	−0.03	H	−0.10
		H	−0.10	H	0.02	H	0.06		
		H	−0.10	H	−0.16	H	0.08		
		H	0.02	H	−0.16	H	−0.22		
$Ga_5As_4H_{14}Cs$	0.86	Ga	0.04	Ga	0.26	Ga	0.05	H	−0.14
(Site III)		Ga	0.31	As	−0.17	Ga	0.15	H	−0.12
		As	−0.34	As	−0.14	As	0.02		
		H	−0.04	H	0.02	H	−0.22		
		H	−0.12	H	−0.05	H	−0.05		
		H	−0.01	H	−0.14	H	0.10		
		H	−0.01	H	−0.14	H	−0.09		
$Ga_4As_5H_{14}Cs$	0.67	Ga	0.03	Ga	0.11	Ga	0.20	H	−0.03
(Site IV)		As	−0.29	Ga	0.11	As	−0.06	H	− 0.03
		As	−0.29	As	0.11	As	−0.06		
		H	−0.04	H	0.09	H	−0.08		
		H	−0.04	H	0.09	H	−0.08		
		H	−0.14	H	0.12	H	−0.30		
		H	−0.14	H	0.12	H	−0.06		

4.52 to 4.95 eV. Site I remains most preferable both at the SCF and at the MP2 levels. This agrees with the results of Klepeis and Harrison,[26] since their Ga site is similar to our site I. First *et al.*[18] showed profiles of primary and secondary Cs on GaAs(110) which have heights of ~2.2 and ~2.8 Å, with a Cs-As distance of ~4.0 Å. For our site I, the height of the closest Cs is 3.2 Å, followed by 3.5 Å for the second Cs. The Cs-Cs distance for this site is 6.93 Å. Cs-Ga and Cs-As distances are 3.84 and 3.83 Å. Thus the results compare well with experimental values. Krauss and Stevens[27] found a binding of 0.18 eV for Cs_2 adsorption on a $Ga_3As_4H_9$ cluster. The energy minimum was obtained for a Cs-Ga distances of 3.7 Å. Thus our chemisorption energies are considerably higher but the distances compare well with these results.

To analyze the nature of the bond and the charge transfer, we show, in Table IV, the atomic charge distributions for the ideal cluster and we find that there is significant charge transfer from the Cs atom. Ga atoms lose charge whereas the As atoms gain charge. This is true for all the sites as expected; however, the charges on the particular atoms vary. Table V shows the charge distributions for the optimized clusters and, again, there is a significant charge transfer, Δq, of 0.82 and 0.86*e* for sites I and II, respectively. The differences in charge densities

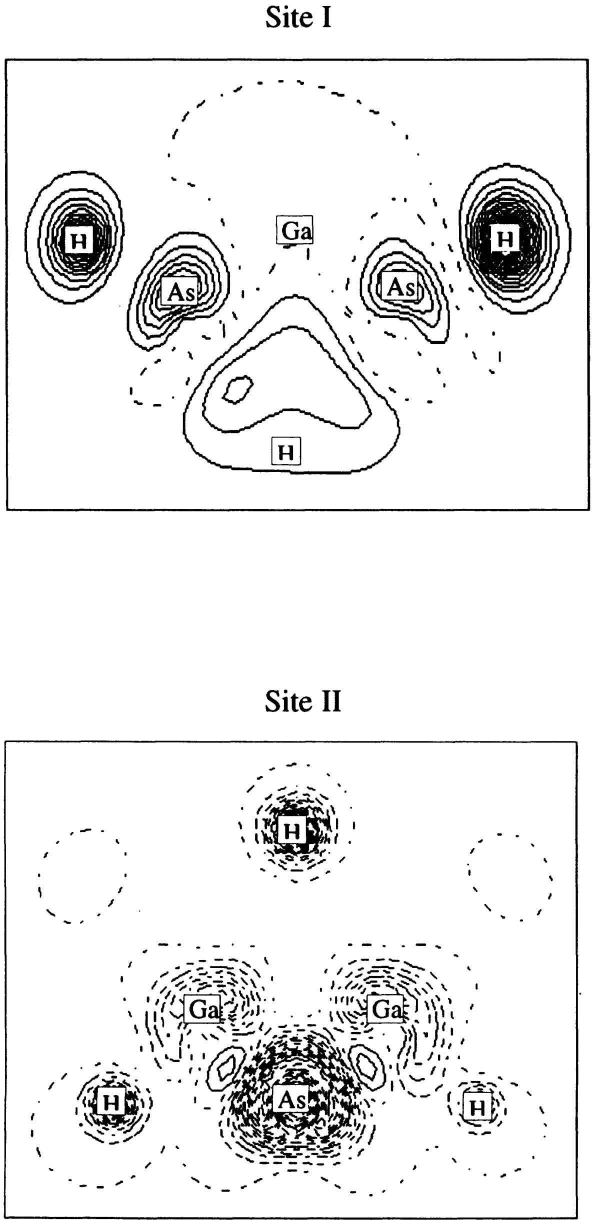

FIG. 7. Plot of difference charge density of Cs+GaAs and GaAs for the (110) surface.

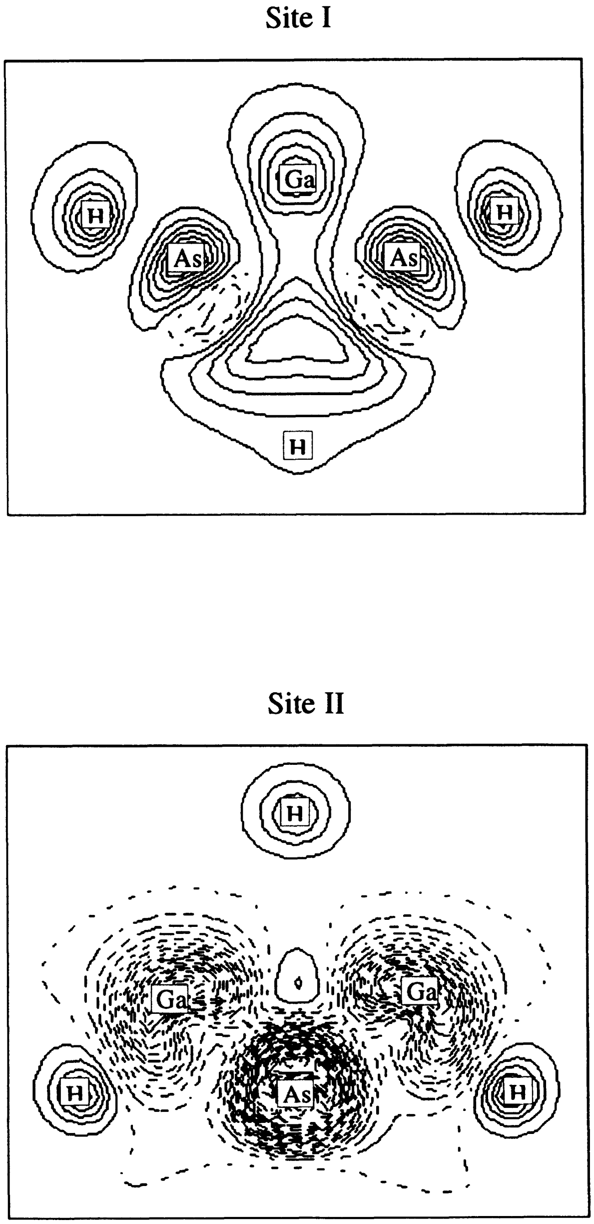

FIG. 8. Plot of difference charge density of Cs+GaAs and GaAs for the optimized (110) surface.

of GaAs and Cs+GaAs for the ideal and optimized surfaces are plotted in Figs. 7 and 8. These plots clearly indicate the excess charges on the As atom compared to the Ga atom. Table VI shows the charge distributions for the Cs_2/GaAs(110) clusters and again, in general, Ga atoms lose charge and the As atoms gain charge. For site II, for Cs adsorption, an analysis of the wave-function coefficients shows that the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) states of the surface layer atoms of the cluster before Cs adsorption consist principally of *s* and *p* states. Upon the adsorption of Cs, the GaAs HOMO-LUMO states retain their characteristics and the Cs states are basically *s* and *p*. Also, the HOMO states are pushed up in energy ($\Delta E = 1.33$ eV) and the HOMO-LUMO gap decreases significantly, from 6.99 to 6.21 eV. Thus, the gap decreases by 0.78 eV. Similar analysis shows a general reduction of HOMO-LUMO gaps for Cs and Cs_2 adsorption (Table VII), indicating the possibilities of eventual metallization.

In summary, different possible adsorption sites of cesium atoms on a gallium arsenide (110) surface have been investigated using *ab initio* self-consistent unrestricted Hartree-Fock total-energy cluster calculations with Hay-

TABLE VI. Atomic charge distributions for the ideal clusters of GaAs(110)+Cs_2.

Cluster	Adatom charges	First layer atom charges		First layer atom charges		Second layer atom charges		Second layer atom charges	
$Ga_6As_9H_{21}Cs_2$	0.62	Ga	0.33	As	−0.05	H	−0.01	H	0.14
(Site I)	0.45	Ga	0.16	As	−0.21	H	−0.04	H	0.08
		Ga	0.26	As	−0.39	H	−0.08	H	− 0.13
		Ga	0.20	As	−0.06	H	−0.19	H	−0.14
		Ga	0.18	H	−0.08	H	−0.06		
		Ga	0.24	H	−0.09	H	0.08		
		As	−0.04	H	−0.06	H	0.17		
		As	−0.17	H	−0.11	H	−0.08		
		As	−0.08	H	−0.06	H	−0.15		
		As	−0.12	H	−0.10	H	−0.16		
		As	−0.34			H	0.09		
$Ga_9As_6H_{21}Cs_2$	0.62	Ga	0.20	As	−0.27	H	−0.06	H	0.15
(Site II)	0.47	Ga	0.13	As	−0.24	H	−0.08	H	−0.09
		Ga	0.14	As	−0.29	H	−0.16	H	−0.12
		Ga	0.14	As	−0.25	H	−0.14	H	−0.10
		Ga	0.20	H	−0.13	H	−0.15		
		Ga	0.21	H	−0.14	H	0.14		
		Ga	0.21	H	−0.10	H	0.14		
		Ga	0.27	H	−0.10	H	−0.13		
		Ga	0.20	H	−0.11	H	−0.18		
		As	−0.13	H	−0.11	H	−0.14		
		As	−0.18			H	0.18		
$Ga_9As_6H_{21}Cs_2$	0.57	Ga	0.20	As	−0.20	H	−0.03	H	0.17
(Site III)	0.50	Ga	0.22	As	−0.30	H	−0.04	H	−0.08
		Ga	0.18	As	−0.37	H	−0.13	H	− 0.11
		Ga	0.18	As	−0.25	H	−0.09	H	− 0.10
		Ga	0.17	H	−0.13	H	−0.11		
		Ga	0.20	H	−0.14	H	0.05		
		Ga	0.18	H	−0.11	H	0.06		
		Ga	0.24	H	−0.12	H	−0.15		
		Ga	0.18	H	−0.11	H	−0.19		
		As	−0.15	H	−0.11	H	−0.13		
		As	−0.16			H	0.22		
$Ga_6As_9H_{21}Cs_2$	0.57	Ga	0.31	As	−0.02	H	−0.01	H	0.14
(Site IV)	0.50	Ga	0.09	As	−0.15	H	−0.06	H	0.08
		Ga	0.18	As	−0.33	H	−0.07	H	−0.13
		Ga	0.20	As	−0.05	H	−0.19	H	−0.15
		Ga	0.24	H	−0.09	H	−0.06		
		Ga	0.24	H	−0.09	H	0.10		
		As	−0.04	H	−0.05	H	0.13		
		As	−0.18	H	−0.15	H	0.01		
		As	−0.09	H	−0.08	H	−0.12		
		As	−0.14	H	−0.11	H	−0.19		
		As	−0.30			H	0.05		

TABLE VII. HOMO-LUMO gaps for $Ga_xAs_yH_z$ and $Cs_mGa_xAs_yH_z$ clusters.

Clusters	Site	Gap (eV)
Ideal surface		
$Ga_5As_4H_{12}$	II	4.98
Ideal surface		
$CsGa_5As_4H_{12}$	II	5.45
Ideal surface		
$Ga_6As_9H_{21}$	I	3.19
$Ga_9As_6H_{21}$	II	4.93
$Ga_9As_6H_{21}$	III	4.93
$Ga_6As_9H_{21}$	IV	3.19
Ideal surface		
$Cs_2Ga_6As_9H_{21}$	I	2.94
$Cs_2Ga_9As_6H_{21}$	IV	2.97
$Cs_2Ga_9As_6H_{21}$	IV	2.68
$Cs_2Ga_6As_9H_{21}$	IV	2.69
Optimized surface		
$Ga_5As_4H_{12}$	II	6.99
Optimized surface/Cs		
$CsGa_5As_4H_{12}$	II	6.21

Wadt effective-core potentials. The effects of electron correlation have been included by invoking the concepts of many-body perturbation theory and are found to be highly significant. We find that the Cs atom adsorption at a site modeled with a $CsGa_5As_4H_{12}$ cluster is most favored energetically followed by Cs adsorption at the site modeled with a $CsGa_4As_5H_{12}$ cluster. For molecular cesium, a site modeled by a $Cs_2Ga_6As_9H_{21}$ cluster is most favored energetically. However, for molecular case, all four sites considered remain competitive energetically at the correlated levels of theory. We also find significant charge transfers from Cs and Cs_2 to the GaAs(110) surface. This coupled with a general reduction of HOMO-LUMO gaps for all the systems studied indicate definite possibilities of metallization. Finally, though computational cost considerations limited the cluster size and the level of perturbation theory, we believe that higher level of calculations should not change the basic conclusions of this paper with regard to geometry and relative energetics of adsorption sites and the possibilities of metallization.

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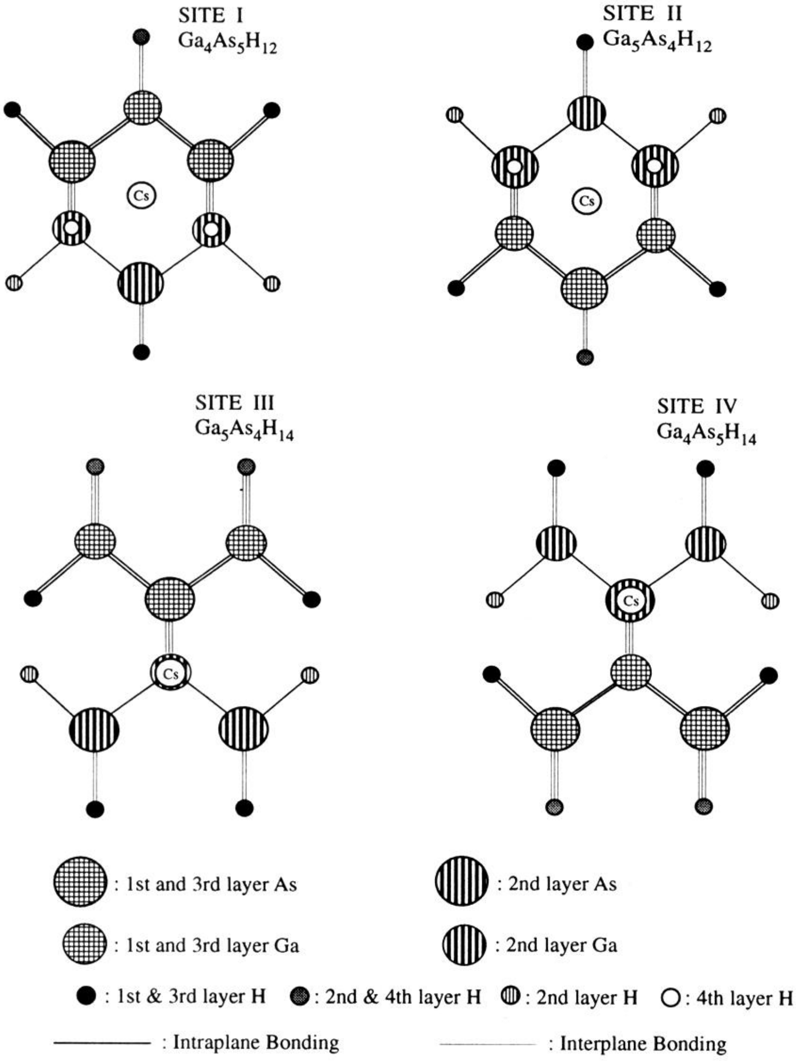

FIG. 2. Cs adatom locations on the GaAs(110) surface.

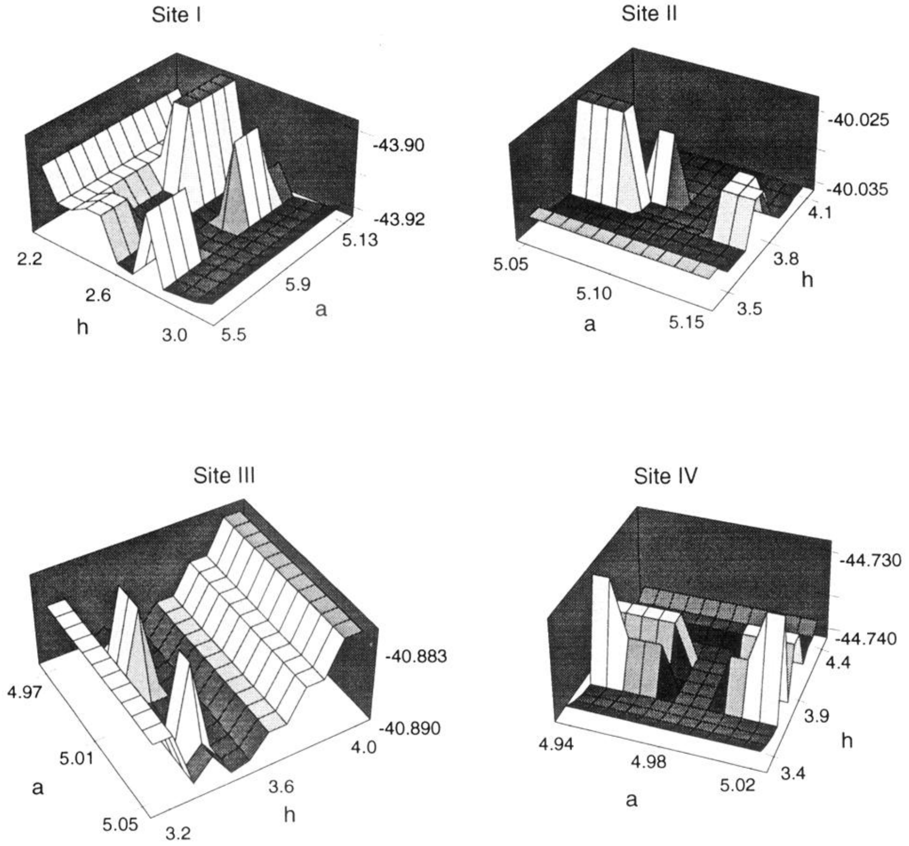

FIG. 4. Total energies (a.u.) vs lattice constant (Å) and adatom height (Å) from the (110) surface for each site.

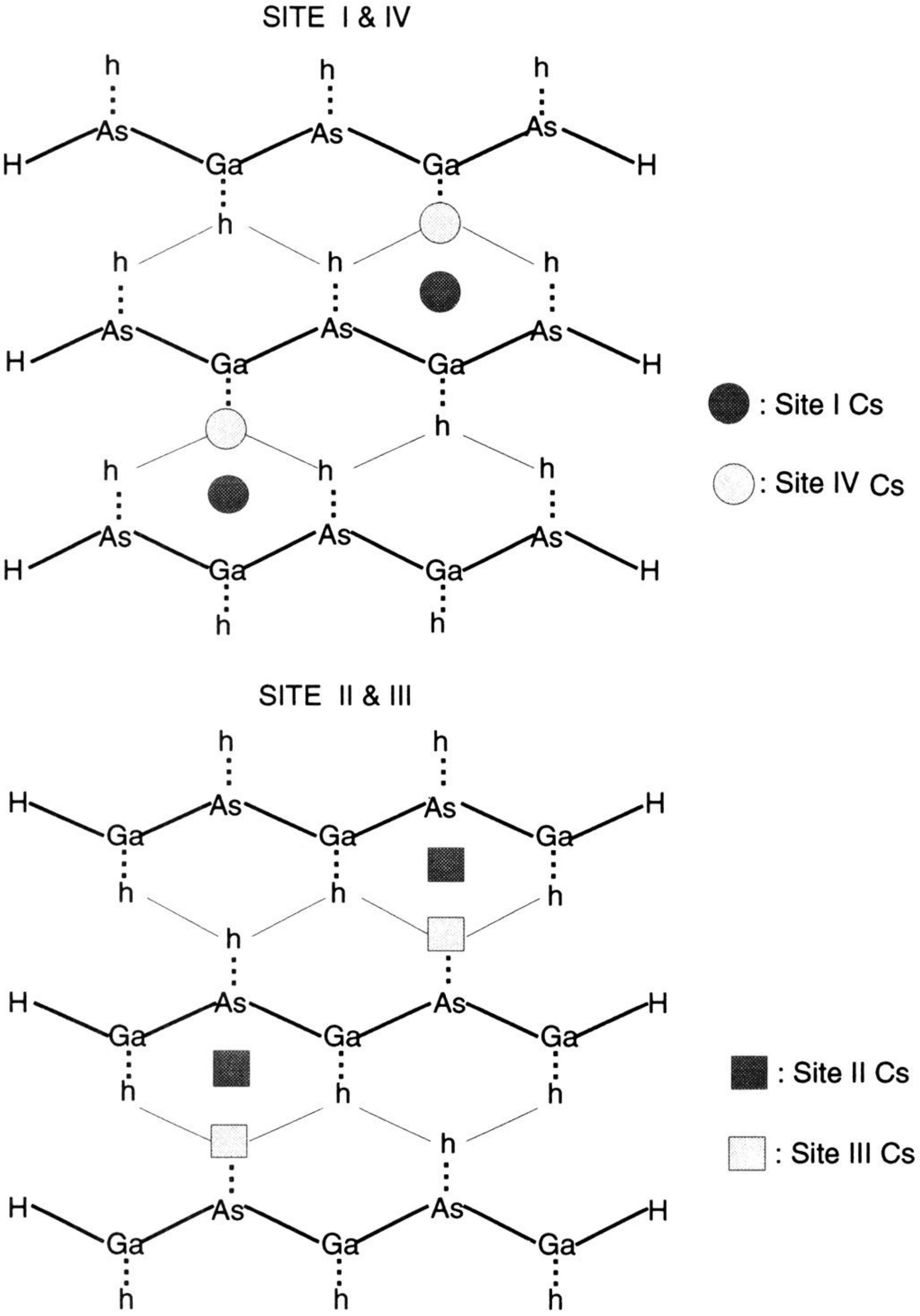

FIG. 5. Schematic drawings of GaAs(110)/Cs_2 for all sites.

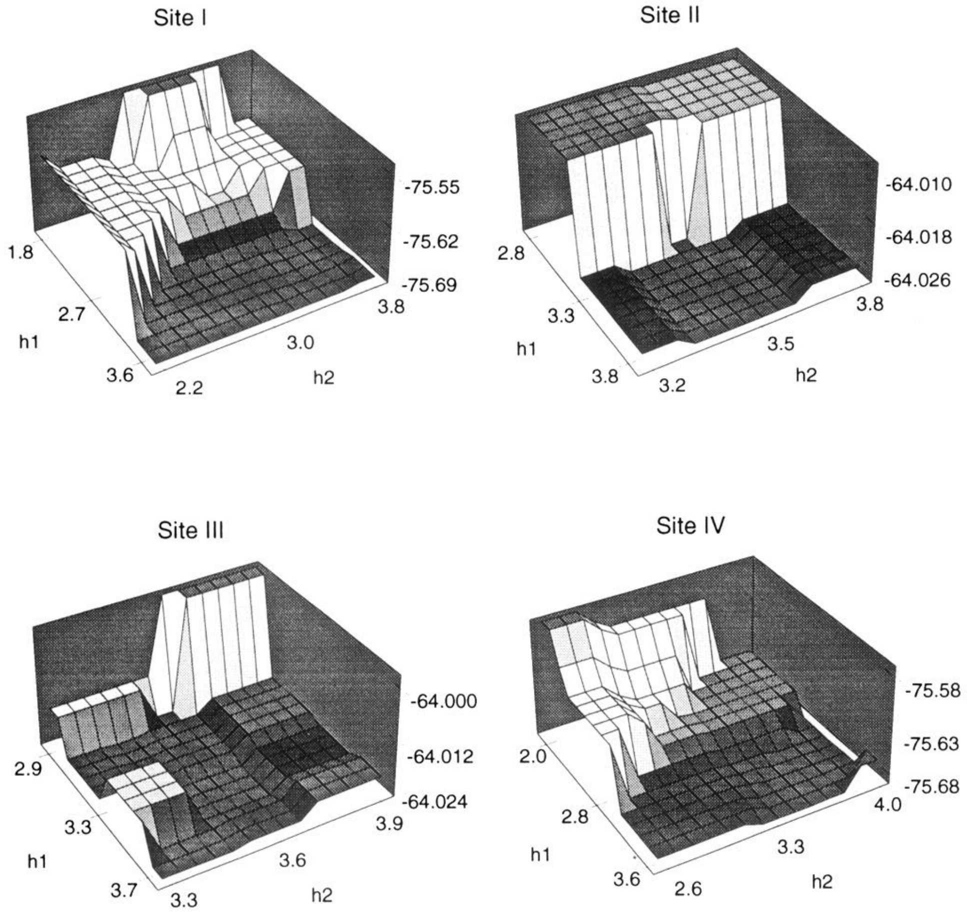

FIG. 6. Total energies (a.u.) vs adatom heights (Å) of Cs_2 from the (110) surface for each site.