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A cluster study of Rb atom chemisorption on a GaAs(110) surface

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Abstract. Different possible adsorption sites of rubidium atoms on a GaAs(110) surface have been investigated using *ab-initio* self-consistent Hartree–Fock energy cluster calculations followed by detailed correlation investigations at the level of fourth-order many-body perturbation theory. The Hay–Wadt effective core potentials have been used to represent the cores of the rubidium, gallium and arsenic atoms. We find that the Rb atom adsorption at a site modelled with a $\text{RbGa}_5\text{As}_4\text{H}_{12}$ cluster is most favoured energetically followed by Rb adsorption at a site modelled with a $\text{RbGa}_4\text{As}_5\text{H}_{12}$ cluster. Significant charge transfer from the Rb atom to the GaAs surface is also found to occur, with Ga atoms losing charge and As atoms gaining charge. Finally, comparisons are made among different alkali atom adsorptions on the GaAs(110) surface.

1. Introduction

The physics of Schottky barrier formation at metal–semiconductor interfaces has been pursued with great intensity because of the extensive applications [1, 2]. Metal–GaAs(110) has been considered as a prototype interface and a sizeable amount of experimental data, e.g., obtained by core-level photoelectron spectroscopy, scanning tunnelling microscopy and electron energy loss spectroscopy, on these systems has recently been acquired, which highlight the effects of band bending and the shift of the Fermi level E_F [3–15]. Theoreticians have split the analysis of band bending and shift of the Fermi level into two groups, one for small metal coverage ($\theta \leq 1$ monolayer (ML)) for which the Fermi level movement exhibits a logarithmic dependence on θ , independent of the metal, and one for large metal coverages for which $\theta > 1$, and the final pinning position depends explicitly on the specific interactions at the metal–GaAs interface. Even if 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 rubidium interactions with a GaAs(110) surface and we first comment on the relevant literature.

To the best of our knowledge, no theoretical study exists in the literature of Rb chemisorption on a GaAs(110) surface. On the experimental side, Prietsch *et al* [16] studied detailed core-level photoemission spectra of interfaces between thin films of Rb and GaAs(110) surfaces at a temperature of 85 K. The local electronic structure of the As surface atoms remained almost unchanged upon Rb adsorption, while the Ga surface atoms attracted negative charge from the adsorbed Rb atoms. Their study also found that valence electrons in Rb films on GaAs(110) were less delocalized than in the metal. Cao *et al* [17]

studied interfaces of Cs and Rb on GaAs and InP(110) surfaces by using photoemission spectroscopy (PES) at 110 K to investigate overlayer metallization. By increasing the layers of Cs or Rb on the GaAs(110) surface, full metallizations were established at around 2 ML of Cs or Rb. Ortega and Miranda [18] studied work function changes of the n-GaAs(110) surface with different coverages of Rb. Using PES they identified three different phases in the adsorption geometry of up to 1 ML of Rb on GaAs(110). For the coverage range 0.06–0.2 ML, the Rb atoms adsorbed in the same corresponding positions inside the unit cell. For the second range 0.23–0.52 ML, an increasing quantity of Rb atoms adsorbed in a second adsorption site inside the unit cell. For more than 0.68 ML, the Rb atom was located at different sites from previous sites or in the second layer. At a coverage of 1 ML, the work function decreased to 3.03 eV.

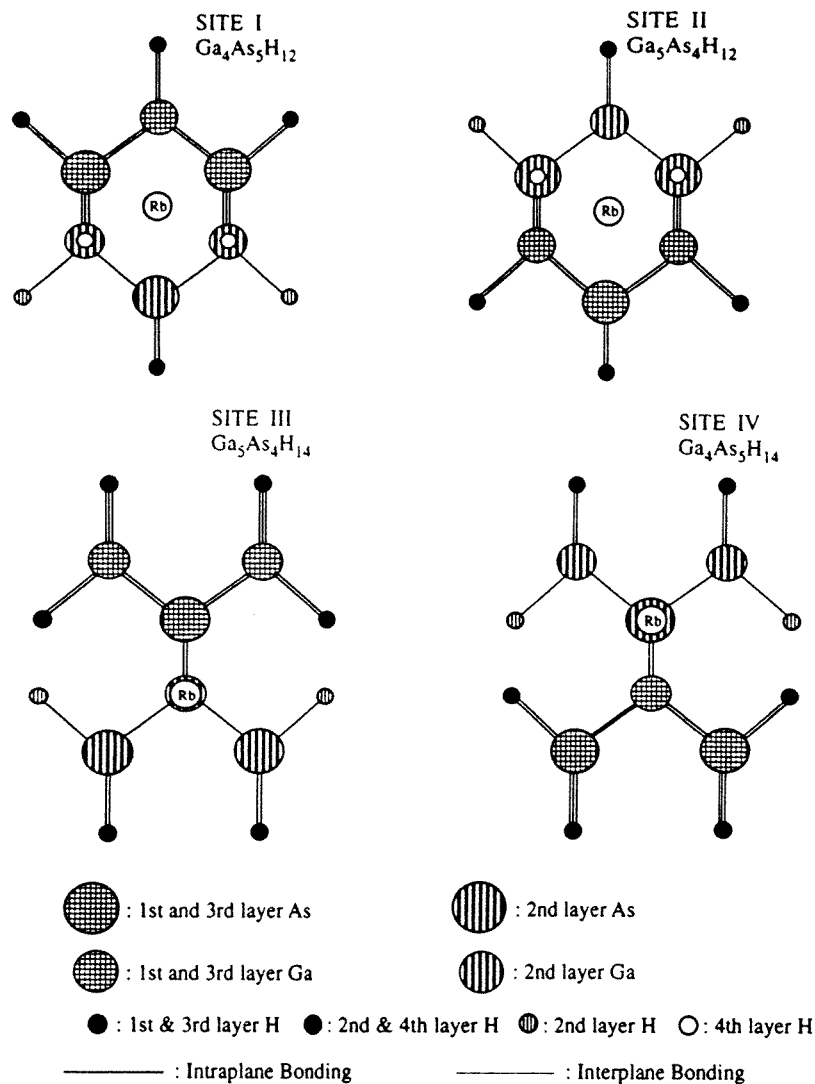


Figure 1. Rb adatom locations on the GaAs(110) surface.

As mentioned before, in this paper, we use *ab-initio* unrestricted Hartree–Fock (UHF) theory to study the chemisorption of Rb on GaAs by simulating the surface with finite hydrogen-bonded GaAs (GaAsH) clusters. It is well known that clusters are well suited to the study of semiconductor surfaces [19] and in general can yield accurate results of such properties as the chemical nature of a bond, the bond length and other geometrical data [20]. Inasmuch as the effects of electron correlation can be very significant, we have studied these by invoking the concepts of many-body perturbation theory (MBPT) up to fourth order, as in our previous work on the chemisorption of hydrogen and oxygen atoms on lithium surfaces [21], of alkali atoms on silicon surfaces [22, 23], and of Na, K and Cs on GaAs(110) surface [24].

This paper is organized as follows: in section 2 we discuss the basic theory and the computational method used; the cluster models and results of Rb chemisorption on these clusters are presented in section 3.

2. Theory and the computational method

Both the UHF theory and the MBPT, as used in this work, are well documented in the literature [25–29]. Here we present only a basic equation to define some terms. In the MBPT, the energy is given by the linked diagram expansion:

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

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

Table 1. Chemisorption energies from the results of optimization of the adatom distance from the ideal GaAs surface.

Cluster	Site	Height	Bond length (Å)		Total energy		Chemisorption energy	
			Rb–Ga	Rb–As	SCF	MP2	SCF	MP2
Ga ₄ As ₅ H ₁₂	I	2.50	4.33	3.85	–43.7640	–44.7476	0.75	2.08
Ga ₅ As ₄ H ₁₂	II	3.67	4.23	4.24	–39.8732	–40.7849	1.43	2.93
Ga ₅ As ₄ H ₁₄	III	3.33	4.79	3.62	–40.6815	–41.6871	–1.10	1.65
Ga ₄ As ₅ H ₁₄	IV	3.66	3.92	5.04	–44.4890	–45.5913	–2.07	0.67

Now one of the primary considerations involved in *ab-initio* Hartree–Fock MBPT calculations is the determination of the type of basis set to be used [30]. 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 such as sodium, gallium and arsenic, we have elected to represent them by effective core potentials or pseudopotentials. In particular, we have used the Hay–Wadt effective core potential [31], which is known to provide almost exact agreement with all electron results. However, to improve the accuracy of our calculation further, one d function was added to all the Hay–Wadt basis sets. The exponent of the d function was chosen to provide the minimum energy for the Rb₂, Ga₂ and As₂ dimers, with the bond lengths fixed at experimental values. For hydrogen, a (4s/1p) basis set was used. All computations were done using the programs GAMESS (which stands for general atomic and molecular structure system) [32] and Gaussian 92 [33] on the Cray Y-MP8/864 at the University of Texas Center for High Performance Computing, and the Cray C90 at the National Science Foundation Pittsburgh Supercomputing Center.

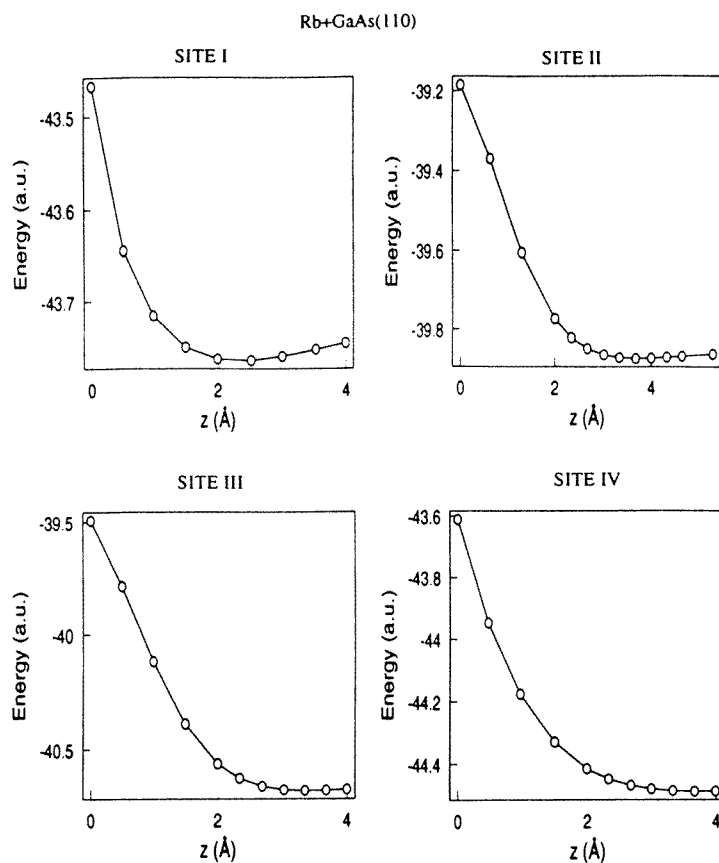


Figure 2. SCF energy versus vertical heights of adatoms from the surface plane for each site.

3. Rb adatom interaction on the GaAs(110) surface

The basis clusters used to represent the GaAs(110) surface have been presented before and will not be discussed in detail again [24]. In brief, we studied GaAs clusters up to three layers and, since, at the second-order MBPT level, Ga₅As₄H₁₂ followed by Ga₄As₅H₁₁

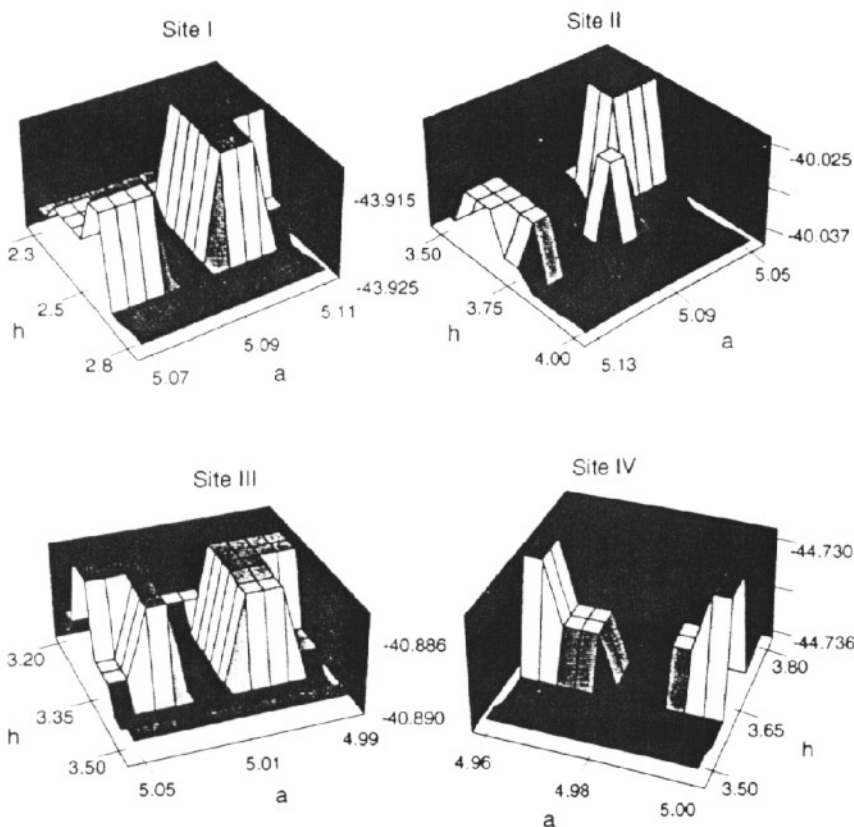


Figure 3. Total energies versus lattice constant and adatom height from the surface for each site.

has the most stable configurations, these units were chosen for chemisorption studies. The difference between the binding energies of these two clusters was 0.06 eV, reasonably well converged within the limits of accuracy. For Rb adsorption on a GaAs(110) surface, we then considered the four sites used by Fong *et al* [34] and in our studies of Na, K, K₂, Cs and Cs₂ chemisorption of GaAs(110). Top views of all four sites are shown in figure 1 and the corresponding clusters are represented by RbGa₄As₅H₁₂, RbGa₅As₄H₁₂, RbGa₅As₄H₁₄ and RbGa₄As₅H₁₄, respectively. A single adatom Rb was then placed at all fixed sites, and for each system the total energy as a function of the vertical height z of the Rb atom from the surface plane was calculated. The Hartree–Fock energy was then plotted against z (negative z representing the position of the adatom below the surface) and the minimum energy z -value z_{eq} was taken to be the equilibrium position of the adatom. Figure 2 shows a plot of E_{HF} 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

$$E_c(\text{Rb}/\text{Ga}_x\text{As}_y\text{H}_z) = E(\text{Rb}) + E(\text{Ga}_x\text{As}_y\text{H}_z) - E(\text{RbGa}_x\text{As}_y\text{H}_z) \quad (2)$$

and table 1 shows the values of E_c and z_{eq} . At this point, surface reconstruction possibilities are not allowed, on the basis that, from some experimental evidence at low alkali-metal

coverages, the reconstruction and relaxation of the GaAs(110) surfaces may be lifted [35–37].

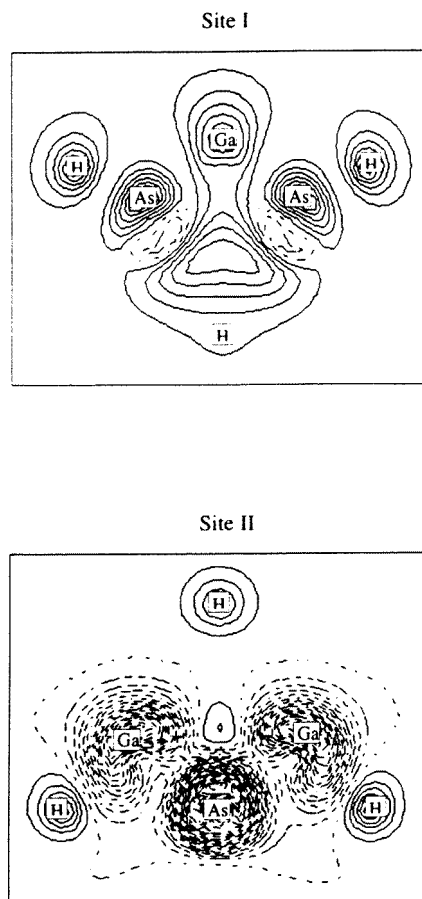


Figure 4. Plot of difference charge density of Rb + GaAs and GaAs for the optimized (110) surface.

Table 2. Chemisorption energies from the results of optimization, of both the adatom distances and the interatomic distances in GaAs.

Site	Height	Lattice constant	Bond length (Å)		Total energy		Chemisorption energy	
			Rb–Ga	Rb–As	SCF	MP2	SCF	MP2
I	2.60	5.09	4.11	3.69	–43.9237	–44.8706	0.88	2.19
II	3.73	5.11	4.19	4.20	–40.0370	–40.9176	2.23	3.37
III	3.42	5.01	4.59	3.64	–40.8905	–41.8689	–1.40	1.64
IV	3.66	4.98	3.87	4.77	–44.7367	–45.7587	–1.38	0.22

Table 3. Atomic charge distances for the optimized clusters of adatom+GaAs(110).

Cluster	Adatom charges	First layer		Second layer		Third layer		Fourth layer	
		Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
Ga ₄ As ₅ H ₁₂ Rb (Site I)	0.83	Ga	0.35	Ga	0.10	Ga	0.21	H	0.11
		As	-0.26	Ga	0.10	As	-0.02	H	0.11
		As	-0.26	As	-0.25	As	-0.02	H	-0.31
		H	-0.01	H	-0.16	H	-0.25		
		H	-0.01	H	-0.04	H	0.08		
		H	-0.16	H	-0.04	H	-0.13		
Ga ₅ As ₄ H ₁₂ Rb (Site II)	0.83	Ga	0.11	Ga	0.02	Ga	0.05	H	-0.11
		Ga	0.11	As	0.00	Ga	0.05	H	-0.10
		As	-0.29	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 ₅ As ₄ H ₁₄ Rb (Site III)	0.85	Ga	0.05	Ga	0.27	Ga	0.05	H	-0.13
		Ga	0.31	As	-0.18	Ga	0.15	H	-0.12
		As	-0.33	As	-0.15	As	0.02		
		H	-0.04	H	-0.05	H	-0.05		
		H	-0.12	H	-0.14	H	-0.06		
		H	-0.01	H	-0.14	H	0.10		
		H	0.03	H	-0.22	H	-0.09		
Ga ₄ As ₅ H ₁₄ Rb (Site IV)	0.67	Ga	0.09	Ga	0.09	Ga	0.20	H	-0.03
		As	-0.30	Ga	0.09	As	-0.06	H	-0.03
		As	-0.30	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	-0.31		
		H	-0.14	H	0.12	H	-0.06		

Before we discuss the results, we note that the stable atomic site of Rb on GaAs(110) is not known experimentally. From the results in table 1, we note first that all sites, are stable at the MP2 level but, at the SCF level, sites III and IV have negative chemisorption energies. This again illustrates the importance of including a correlation for AM (AM =alkali metal)–GaAs systems [24]. Site II has the highest chemisorption energy at both the SCF and the MP2 levels, followed by site I. This is in agreement with the results for Na–GaAs systems and Cs–GaAs systems [23] where sites I and II were found to be most stable. For the K–GaAs system, site II is also the most stable site, but sites I and IV have nearly identical chemisorption energies at the MP2 level. Comparing our results with the optimized bond lengths of Rb–Ga (4.15 Å) and Rb–As systems (4.05 Å), we find that the nearest-neighbour distances between Rb and Ga, in general, increase as a result of the competition of all the neighbouring atoms but no definite pattern is indicated for the distances between Rb and As. For site II, the optimum vertical height of the Rb adatom from the top layer is found to be 3.67 Å.

In the next stage of the calculations, we studied the possibilities of surface reconstruction. For this purpose, the adatom was again allowed to approach the clusters and simultaneous optimization of the adatom distance and the cluster lattice constant was carried out. Table 2 summarizes the results of such an optimization process and figure 3 shows three-dimensional

Table 4. Comparisons of adatom heights and chemisorption energies from optimizations of GaAs(110)+alkali metal clusters. The third to fifth columns refer to optimization of only the adatom distance from the ideal GaAs surface; the sixth to eighth refer to simultaneous optimizations of the adatom distance and the interatomic distance in GaAs.

Site	Alkali metal	Lattice constant (Å)	Height (Å)	Chemisorption energy (eV)	Lattice constant (Å)	Height (Å)	Chemisorption energy (eV)
I	Na	5.65	1.50	1.68	5.09	1.70	1.85
	K	5.65	0.99	1.50	5.09	1.20	1.76
	Rb	5.65	2.50	2.08	5.09	2.60	2.19
	Cs	5.65	2.45	2.32	5.09	2.75	2.40
II	Na	5.65	3.01	2.26	5.11	3.00	2.71
	K	5.65	2.67	2.02	5.11	2.72	2.48
	Rb	5.65	3.67	2.93	5.11	3.73	3.37
	Cs	5.65	3.87	3.19	5.11	3.94	3.63
III	Na	5.65	2.67	1.07	5.01	2.70	1.05
	K	5.65	2.33	1.02	5.01	2.42	1.00
	Rb	5.65	3.33	1.65	5.01	3.42	1.64
	Cs	5.65	3.50	1.87	5.01	3.50	1.87
IV	Na	5.65	2.98	1.38	4.98	3.00	-0.25
	K	5.65	2.66	1.49	4.98	2.80	-0.43
	Rb	5.65	3.66	0.67	4.98	3.66	0.22
	Cs	5.65	3.89	0.56	4.98	3.75	0.45

plots of the total energy versus lattice constants and adatom heights for all the four sites. If we compare the results in table 2 with those in table 1, we first note that the atoms in the reconstructed surface move closer to an ideal surface but the adatom, in general, moves away from the surface except for site IV. The Rb–Ga and Rb–As distances, in general, decrease. The same general conclusions prevailed also for Na, K and Cs. The total energies of the chemisorbed clusters also decreased, as expected, after optimization and the chemisorption energies of sites I and II increased and those of sites III and IV decreased after optimization. However, sites I and II still remain preferred sites for chemisorption, with site II having the highest chemisorption energy after surface reconstruction. Although the sizes of the K, Na, Cs and Rb atoms are different, site II remains the most preferred site for chemisorption for all the elements. The Rb atom is a distance of 3.73 Å from the surface, which is smaller than the corresponding distance (3.87 Å) of the Cs atom but larger than the distances of K and Na atoms.

To analyse the nature of the charge transfer, we show, in table 3, the atomic charge distributions for the optimized clusters. Mulliken population analysis [29, 38] was used to determine the gross atomic populations from

$$q_A = \sum_{\mu}^A q_{\mu}. \quad (3)$$

Here the summation is carried out for all functions ϕ_{μ} on a particular atom A . Assuming all basis functions to be atom centred, it follows that the sum of gross atomic populations is equal to the total electron count. Finally, a total atomic charge on A is defined as $Z_A - q_A$, where Z_A is the atomic number of A . As indicated, there are significant charge transfers

Table 5. Comparisons of HOMO–LUMO gaps from optimizations of GaAs(110)+alkali metal clusters.

Site	Alkali metal	Gap (eV)
I	Pure surface	6.17
	Na	4.61
	K	4.62
	Rb	4.53
	Cs	4.52
II	Pure surface	6.99
	Na	6.05
	K	5.93
	Rb	6.14
	Cs	6.21
III	Pure surface	5.37
	Na	3.02
	K	3.01
	Rb	3.00
	Cs	3.00
IV	Pure surface	5.14
	Na	2.96
	K	2.76
	Rb	3.36
	Cs	3.46

from the adatom to the Ga and As atoms. In general, 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. For the optimized clusters, for example, there are identical charge transfers Δ_q of $0.83e$ for sites I and II, respectively. The difference between the charge densities of GaAs and Rb + GaAs for the optimized surface is plotted in figure 4. This plot clearly indicates the excess charges on the As atom compared with the Ga atom. For site I, the highest occupied molecular orbital (HOMO) states of Rb adsorption are pushed up in energy ($\Delta E = 0.69$ eV) and the HOMO–lowest unoccupied molecular orbital (LUMO) gap decreases significantly, from 0.2270 to 0.1667 au. Thus, the gap decreases by 1.64 eV. For site II, the gap decreases by 0.85 eV. We note that the large deviations of the HOMO–LUMO gaps for the pure surfaces from the experimental value are characteristic of Hartree–Fock-based cluster calculations. The upward shift in energy of the HOMO states on adatom adsorption implies that an interface electronic state may be induced by the alkali metal atom and the reduction in the HOMO–LUMO gap points to the possibilities of metallization.

We now make some comparative statements about different alkali atom adsorptions on a GaAs(110) surface. Table 4 shows comparisons of chemisorption energies and adatom heights from the two types of optimization for alkali GaAs(110). For the first type of optimization the potassium atom approaches closest to the ideal surface for all sites and all alkali atoms are closer to the GaAs(110) surface in site I, compared with all other sites. Site III has the second lowest and sites II and IV have almost identical heights for different atoms. As far as the chemisorption energy is concerned, site II is preferred by all alkali atoms, followed by site I. However, preferences between sites III and IV appear to be

mixed. Na and K atoms prefer site IV, whereas Rb and Cs atoms prefer site III. For the case of simultaneous optimization, the same comments apply as far as adatom heights are concerned; in regard to the chemisorption energy, site II is again preferred followed by site I and site III, respectively. Na and K atoms do not appear to bind to the surface at all in site IV while Rb and Cs atoms have rather small chemisorption energies. Also, Cs has the highest chemisorption energy for all sites and, in general, E_c increases with increasing atomic number. As far as the HOMO–LUMO gap is concerned, there is a general tendency of gap reduction upon alkali atom adsorption (table 5). This points to eventual metallization upon increase in the amount of alkali adsorption atoms. We also note that site II, which had the highest chemisorption energy, has the highest HOMO–LUMO gaps. In general, Site II also has the highest adatom heights. Thus, for alkali atom adsorption, there appears to be an approximate linear relationship between adatom heights, HOMO–LUMO gaps and chemisorption energies.

Acknowledgments

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