

Chemisorption of group-III metals on the Si(111) and Ge(111) surfaces: An *ab initio* study

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Chemisorption of group-III metal adatoms on Si(111) and Ge(111) has been studied through the *ab initio* Hartree-Fock method including nonempirical pseudopotentials and using cluster models to simulate the surface. Three different high-symmetry sites (atop, eclipsed, and open) have been considered by using X_4H_9 , X_4H_7 , and X_6H_9 ($X = \text{Si, Ge}$) cluster models. In a first step, ideal surface geometries have been used. Metal-induced reconstruction upon chemisorption has also been taken into account. Equilibrium distances, binding energies, and vibrational frequencies have been obtained and compared with available experimental data. From binding-energy considerations, the atop and eclipsed sites seem to be the most favorable ones and thus a coadsorption picture may be suggested. Group-III metals exhibit a similar behavior and the same is true for Si(111) and Ge(111) surfaces when chemisorption is considered.

INTRODUCTION

The importance of metal-semiconductor interfaces has been reflected in a large number of experimental and theoretical investigations which seek to elucidate the structural and electronic properties of such systems. In particular, considerable attention has been devoted to the study of group-III metals on the Si(111) surface. Techniques such as low-energy electron diffraction (LEED),^{1,2} ultraviolet-photoemission spectroscopy (UPS),³ angle-resolved ultraviolet-photoemission spectroscopy (ARUPS),⁴⁻⁸ electron-energy-loss spectroscopy (EELS),⁹ high-resolution electron-energy-loss spectroscopy (HREELS),¹⁰ Auger-electron spectroscopy (AES),^{2,11} x-ray standing-wave interference spectrometry,^{12,13} partial-yield spectroscopy (PYS),^{2,7,14} k-resolved inverse-photoemission spectroscopy (KRIPES),¹⁵ polar-angle photoelectron diffraction (PPD),¹⁶ low-energy ion-scattering spectroscopy¹⁷ ISS, or scanning tunneling microscopy^{13,18,19} (STM) have all provided a considerable amount of valuable information. In particular it has been shown that Si(111)-($\sqrt{3} \times \sqrt{3}$)Al, ($\sqrt{3} \times \sqrt{3}$)Ga, and ($\sqrt{3} \times \sqrt{3}$)In surfaces have essentially the same electronic structure and hence the same surface atomic arrangement. With respect to surface-electronic structure, it is pointed out that there is a removal of clean-surface spectral features at an early stage of metal coverage and the appearance of new metal-related peaks.

Furthermore, threefold-hollow adatom models have been proposed from comparison of the experimental surface-electronic structures with those of theoretical calculations. However, no clear picture of the interfaces has been yet obtained. Nevertheless, the very recent works of Hamers¹⁹ and Daimon *et al.*,¹⁶ of Zegenhagen *et al.*,¹³ and of Izumi *et al.*,¹⁷ respectively for Al, Ga, and In on

Si(111)-($\sqrt{3} \times \sqrt{3}$) seem to be conclusive, showing that the adatoms sit in the threefold on-top sites of the second-layer Si atoms (T_4 site) when $\frac{1}{3}$ -monolayer coverages are considered.

Theoretical calculations for several high-symmetry adsorption sites have been reported using the empirical extended Hückel method (EHM) in the framework of cluster²⁰ and semi-infinite models,²¹ the self-consistent-pseudopotential model based on a slab geometry,^{13,15,22,23,24} and first-principles calculations using effective core potentials and cluster models.^{12,25,26} From these works, structural, energetic, and electronic-structure data are obtained. Nevertheless, among the several high-symmetry sites generally studied [substitutional, atop, open (H_3), and eclipsed (T_4)] only Dev *et al.*^{12,25} have studied and compared all of them without considering preselected M -Si ($M = \text{Al, Ga}$) distances. On the other hand, the eclipsed and open positions have been largely studied for Al, Ga, and In adatoms on the Si(111) surfaces by Northrup *et al.*^{5,13,15,24} Finally, the only data available for chemisorption on the Ge surface can be found in Ref. 20 in the framework of the EHM.

The most important feature that can be elucidated from all the previous theoretical works is that chemisorption of group-III metal adatoms on a Si(111) surface could take place in a multisite way, the atop and eclipsed positions being the most favorable ones from energy considerations, while the eclipsed and open threefold sites seem to be more consistent with UPS (Ref. 3) and ARUPS (Refs. 4-8) data. Moreover, it is believed that the adatoms induce a reconstruction of the ideal surface which changes the relative stabilization of the chemisorption bond of the sites considered with respect to the non-relaxed ideal surfaces.

In the present work, our previous study on the

Al/Si(111) system²⁶ is extended to group-III metal chemisorption on the Si(111) and Ge(111) surfaces. As before, the study is carried out at the *ab initio* Hartree-Fock (HF) level using nonempirical effective core potentials and considering three chemisorption sites (atop, open, and eclipsed) modeled by using the cluster-model approach to represent the surface. Nevertheless, some results for the Al/Si(111) system will be reported for purposes of comparison.

METHOD OF CALCULATION

The level of calculation used through this work corresponds to the well-known *ab initio* Hartree-Fock self-consistent-field (SCF) scheme using a monodeterminantal wave function build up by means of molecular orbitals (MO's) described by the linear combination of atomic orbitals (AO's), i.e., the LCAO method. To model adsorbate-substrate interactions by means of first-principles methods, in the framework of surface cluster models, is often faced with computational difficulties due to the large number of basis functions necessary to describe, with a minimum of accuracy, these relative large systems which usually contain several heavy atoms. In this case it is customary to represent the core electrons by means of a pseudopotential. In the present work the effect of the inner shells of Si, Ge, Al, Ga, In, and Tl ([Ne], [Ar+3*d*¹⁰], [Ne], [Ar+3*d*¹⁰], [Kr+4*d*¹⁰], and [Xe+5*d*¹⁰+4*f*¹⁴], respectively) are taken into account by means of the nonempirical pseudopotentials developed by Durand and Barthelat²⁷ and by Pelissier and Durand.²⁸ Then, Si and Ge are treated as four-electron pseudopotentials, and Al, Ga, In, and Tl as three-electron pseudopotentials. Relativistic corrections have been included for pseudopotentials corresponding to In and Tl atoms. For more details, see Ref. 26. These pseudopotentials have proven to be a valuable tool in a wide range of structural studies involving systems containing heavy atoms. In particular, it has been shown^{29,30} that good agreement is found between experimental results³¹ as well as with previous cluster models³² or slab calculations,³³ for the chemisorption of halogen atoms on the Si(111) and Ge(111) surfaces.

The valence shells are described by means of contracted Gaussian-type orbitals (CGTO's). Several basis sets were tested in Ref. 26 for Al chemisorption on the Si(111) surface, showing the correctness of a mixed basis set and strongly indicating the necessity of including polarization functions in the basis sets of atoms directly involved in the adatom-cluster interaction.

The basis set used throughout this work is of double- ζ -plus-polarization quality for the adatoms and first-layer Si and Ge atoms. The *ns* orbitals are described by four primitive Gaussian-type orbitals (GTO's) which are contracted by means of a 3+1 procedure. For the *np* orbitals an identical contraction scheme was used for Al, In, and Tl, but a 2+2 contraction procedure was used for Si, Ge, and Ga. A single *d*-polarization function was added to the adatoms and first-layer Si- and Ge-atom basis sets. Five components were always used to describe the *d* orbitals, the 3*s* combination of the Cartesian *d* or-

bitals being explicitly deleted. The exponents of these polarization functions being 0.15, 0.14, 0.09, 0.04, 0.45, and 0.15 for Al, Ga, In, Tl, Si, and Ge, respectively. The hydrogen basis set consists of four primitives GTO's contracted to minimum-basis-set quality. The effect of the minimum basis set on the embedding hydrogen atoms does not introduce significant differences with respect to the use of larger basis sets on these atoms, as shown previously.²⁶

Calculations have been carried out by using the PSHONDO program,³⁴ a version of the HONDO package,³⁵ including the possibility of using the nonempirical pseudopotentials quoted above. Two different kinds of systems have been treated: the cluster model plus an adatom, and the isolated cluster model. The former involves only closed shells, whereas the latter involves at least one open shell. The open shells have been treated through the variational restricted open-shell Hartree-Fock (ROHF) method by using a recent modification of the PSHONDO program³⁶ which uses the coupling-operator formalism of Carbó *et al.*^{37,38}

By using the above theoretical procedure, the total energy of the adatom-cluster-model systems has been computed as a function of the perpendicular distance to each one of the sites considered, giving potential-energy curves. From these curves, the equilibrium distance and binding energy for each system have been determined. Binding energies have been calculated using the expression

$$E_B = -\{E_{\text{tot}}(M-X_n H_m) - [E_{\text{tot}}(X_n H_m) + E_{\text{tot}}(M)]\},$$

where *M* refers to the metal adatom, *X*=Si,Ge, *n*=4,6, and *m*=7,9.

The vibrational frequency for the motion perpendicular to the surface has also been computed in the harmonic approximation by a quadratic fit and assuming infinite mass for the substrate. The computed vibrational frequency is then

$$\nu_e = (k/m_M)^{1/2},$$

where *k* is the force constant and *m_M* is the mass of the adatom. This procedure has been widely used in dealing with atomic chemisorption on cluster-model surfaces and the computed force constants are in error by less than 15%.^{29,39,40}

CLUSTER MODELS

The use of relatively small cluster models to represent a surface is imposed by the limited number of atoms that can be treated in the calculation and by the level of precision of the computation. Fortunately, the chemisorption of atoms on surfaces, especially when dealing with semiconductor surfaces, seems to be of local character, thus making it possible to use small clusters like *X₄H₉*, *X₄H₇*, and *X₆H₉* (*X*=Si,Ge) to simulate the three high-symmetry sites where group-III metal-atom chemisorption is expected to take place, as can be deduced from experimental information. The *X₄H₉* cluster model [Fig. 1(a)] is used to simulate the atop position, when an ada-

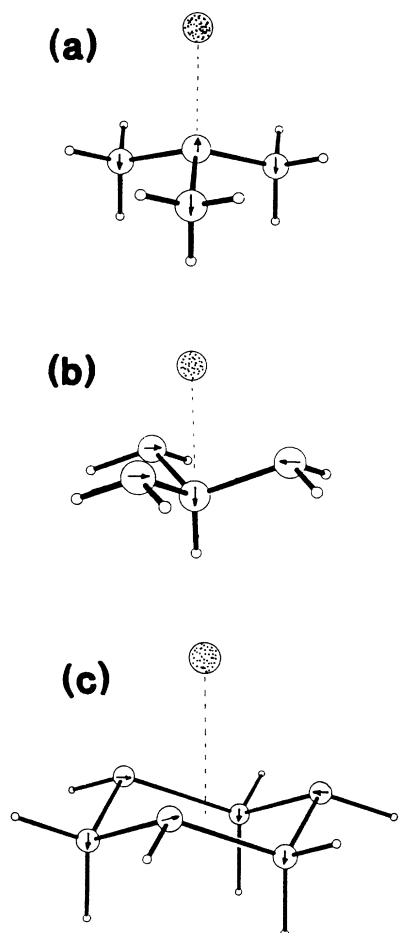


FIG. 1. Schematic representation of the systems used to model chemisorption of Al, Ga, In, and Tl atoms (dotted circles) on (a) the atop site, (b) eclipsed site, and (c) open site of the $X(111)$ ($X=\text{Si,Ge}$) surface. Arrows indicate displacements of atoms when relaxation upon chemisorption is taken into account.

tom stabilizes directly above a surface atom. The X_4H_7 [Fig. 1(b)] model contains three X atoms in the first layer (surface) and one in the second layer. This cluster simulates the threefold site in which the adatom is situated above a second-layer X atom. Finally, the X_6H_9 [Fig. 1(c)] model simulates the open site and has three X atoms in the first layer and three in the second. For more de-

tails, see Ref. 26. The use of embedding hydrogen atoms provides an adequate environment for the second-layer atoms, forces them to have the bulk sp^3 hybridization and minimizes edge effects.

Values of $d_{\text{Si-Si}}=4.44$ bohrs, $d_{\text{Ge-Ge}}=4.63$ bohrs, $d_{\text{Si-H}}=2.80$ bohrs, and $d_{\text{Ge-H}}=2.92$ bohrs have been used as a starting point to simulate the ideal (111) Si and Ge surfaces. The C_{3v} point-group symmetry has always been preserved.

The Si_nH_m clusters used in this work have been previously described in Ref. 26 at the same level of theory and with the same basis set (basis II in Ref. 26); consequently, no further comments will be added. Ge_nH_m clusters follow similar trends. A summary of results including binding energies, orbital-energy range for the valence levels, and singly occupied dangling-bond states is presented in Table I. It is shown that the computed orbital-energy range (0.389–0.427 a.u., depending on the system, for Si, and 0.410–0.434 a.u. for Ge) can be compared with the experimental bandwidths (0.455 and 0.463 a.u. for bulk Si and Ge, respectively). The singly occupied dangling-bond states lie above the valence levels and provide a satisfactory representation of the half-filled dangling-bond surface bond which lies in the energy gap between valence and conduction bands of the clean $X(111)$ ($X=\text{Si,Ge}$) surfaces.

The cluster binding energies were computed using the usual expression:

$$E_B = -[E_{\text{tot}}(X_nH_m) - nE_{\text{tot}}(X) - mE_{\text{tot}}(H)],$$

where $X=\text{Si,Ge}$, $n=4,6$, and $m=7,9$, depending on the cluster.

The energy of the isolated atoms are calculated at the SCF, restricted Hartree-Fock (RHF) open-shell level by using the PSATOM program, a modification of the ATOM-SCF program which permits the use of pseudopotentials at the atomic level as well as to optimization of basis sets to be used with these pseudopotentials.

Cluster ground states are 2A_1 , 4A_2 , and 4A_2 for X_4H_9 , X_4H_7 , and X_6H_9 , respectively, arising from open-shell configurations a_1^1 , $a_1^1e^2$, and $a_1^1e^2$ in the same order. When the group-III metal adatoms interact with all these cluster models, they always lead a closed-shell ground state of 1A_1 symmetry.

TABLE I. Binding energy and orbital-energy range for the valence levels in the three unrelaxed clusters considered. The energy of the lowest (highest doubly occupied valence molecular orbital is denoted E_l (E_h)). The range is denoted ΔE . The e_d are the energy values corresponding to dangling bonds (a_1 and e refer to its symmetry in the C_{3v} point group). Energies are in hartrees.

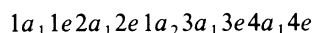
	E_B	E_l	E_h	ΔE	e_d	
Si_4H_9	0.90	-0.801	-0.397	0.404	-0.351	
Si_4H_7	0.75	-0.788	-0.399	0.389	-0.357 (a_1)	-0.357 (e)
Si_6H_9	1.03	-0.812	-0.385	0.427	-0.358 (a_1)	-0.355 (e)
Ge_4H_9	0.81	-0.786	-0.376	0.410	-0.332	
Ge_4H_7	0.64	-0.779	-0.383	0.396	-0.345 (a_1)	-0.343 (e)
Ge_6H_9	0.90	-0.797	-0.363	0.434	-0.341 (a_1)	-0.336 (e)

RESULTS FOR CHEMISORPTION ON IDEAL UNRELAXED SURFACES

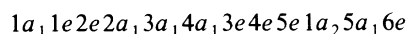
It is known that clean (111) semiconductor surfaces reconstruct into (2×1) and (7×7) structures. Then, the use of an ideal (1×1) unreconstructed surface as a model for chemisorption seems to be unrealistic for the purpose of making comparisons with experimental data. Nevertheless, as the interactions involved in chemisorption are competing with the reconstructions, and as the binding energies of metal atoms on a Si(111) surface are markedly larger than the energy gained by the surface reconstruction, it seems that the final geometry can be imposed by the adatoms, leading to an adatom-induced reconstruction. These considerations make possible the use of the ideal unreconstructed surface as a model, but possible substrate-geometric optimization must be explored upon chemisorption.

Results for group-III metal-atom chemisorption on ideal unreconstructed Si(111) and Ge(111) cluster-model surfaces are shown in Tables II, III, and IV for the atop, eclipsed, and open positions, respectively. Unfortunately, structural experimental data are practically nonexistent and it is difficult to assess how reliable our data are. However, they should be quite accurate, provided the results obtained for similar systems using the same methodology as the study of halogen chemisorption on Si(111) and Ge(111) surfaces.²⁹

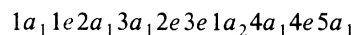
Configurations of the 1A_1 closed-shell $M-X_nH_m$ clusters are



for $M-X_4H_7$,



for $M-X_6H_9$, and



for $M-X_4H_9$, with all the molecular orbitals (MO's) fully occupied.

Results for Al chemisorption and a theoretical interpretation in terms of MO's and their interactions were already discussed in Ref. 26, and similar behavior is found for the other adatoms. In the case of atop chemisorption the open-shell (dangling-bond) a_1 orbital of the bare cluster forms a bonding combination with an sp_z -hybridized adatom orbital. In the case of the open position, the a_1 and e dangling bonds of the substrate form bonding combinations with the $a_1(s)$ and $e(p_x, p_y)$ metal orbitals. It is interesting to note that for the eclipsed site there is an antibonding interaction between the $3s(4s)$ atomic orbital (AO) of the second-layer Si(Ge) atom and that the main interactions arise from the $e(p_x, p_y)$ AO's of the metal atom and the a_1 and e cluster dangling bonds.

The preferred site for Al, Ga, In, and Tl is the atop one in view of binding energies that are practically the same for Al, Ga, In, and Tl over both Si(111) and Ge(111) surfaces (33–40 kcal/mol). Bond distances increase monotonically from Al to Tl, and they are 0.2 Å greater than the sum of covalent radii (2.35, 2.43, 2.61, and 2.65 Å for (Al, Ga, In, Tl)/Si, and 2.40, 2.48, 2.66, and 2.70 Å for (Al, Ga, In, Tl)/Ge.

Table II shows that charge transfer from the adatom to the substrate is about $0.4e$, indicating a partial ionic bond. This charge transfer is similar in all the cases. Inspection of the Mulliken population analysis seem to suggest a rather large bond ionicity. This is larger than the one expected from the difference of electronegativities of the substrate atoms and the adatoms. The Mulliken

TABLE II. Results for group-III metal-atom chemisorption on the atop site. d_c is the distance (in Å) from the adatom to the nearest X ($X = \text{Si, Ge}$) surface atom, ν_c (in cm^{-1}) is the harmonic vibrational frequency perpendicular to the surface, E_B is the binding energy (in kcal/mol) calculated with respect to the isolated systems, and q is the net charge on the adatom. Both unrelaxed and metal-induced relaxed substrates are considered.

M	Unrelaxed				Relaxed			
	d_c	ν_c	E_B	q	d_c	ν_c	E_B	q
	Silicon							
Al	2.62 2.37 ^a	241.9	39.6 90.8 ^a	0.47	2.61	237.2	40.05	0.49
Ga	2.64 2.57 ^b	137.5	36.2 139.5 ^b	0.45	2.64	139.5	36.67	0.47
In	2.81	105.7	36.1	0.48	2.81	104.6	36.84	0.50
Tl	2.90	72.7	32.93	0.46	2.89	72.7	33.84	0.48
	Germanium							
Al	2.68	220.4	40.07	0.42	2.68	227.7	41.67	0.45
Ga	2.71	136.5	36.92	0.40	2.71	141.5	38.54	0.43
In	2.86	103.6	36.73	0.44	2.86	103.7	39.14	0.47
Tl	2.95	70.4	34.42	0.43	2.95	70.5	36.69	0.47

^aData from Ref. 22.

^bData from Ref. 12.

TABLE III. Same as Table II for the eclipsed site.

<i>M</i>	d_e	Unrelaxed			Relaxed			
		ν_e	E_B	q	d_e	ν_e	E_B	q
				Silicon				
Al	2.76 2.68 ^a 2.73 ^b	297.0	15.75 13.6 ^a	0.37	2.44 2.44 ^a 2.50 ^b	313.0	54.80 97.1 ^a	0.35
Ga	2.82 2.78 ^c	167.2	-2.03 154.2 ^c	0.25	2.46 2.61 ^c 2.46 ^d	198.4	32.69 178.9 ^c	0.25
In	2.92	135.6	0.42	0.37	2.64 2.63 ^c	156.6	24.88	0.36
Tl	2.98	88.8	-21.65	0.28	2.72	108.6	4.50	0.23
				Germanium				
Al	2.87	274.4	9.21	0.25	2.50	300.2	53.87	0.24
Ga	2.93	158.9	-5.73	0.14	2.53	185.3	33.50	0.12
In	3.02	127.1	-0.89	0.28	2.69	148.5	28.42	0.27
Tl	3.13	85.7	-20.48	0.23	2.76	104.8	0.93	0.15

^aReference 22.^bReference 12.^cReference 21.^dReference 13.^eReference 5.

analysis⁴¹ is known to suffer basis-set dependence. Moreover, the arbitrary partition of the overlap population tends to give net charges that are too large. The ionicity of the bond on this system is of importance on the understanding of the leading physical interactions and merits a deeper insight using more quantitative methods. Such

study is now being carried out in our laboratory.⁴²

The open position is slightly stable for Al, Ga, and In, and the eclipsed position is practically unstable for Ga and In, and clearly unstable for Tl at the SCF level of calculation.

From Table III it is seen that the charge transfer for

TABLE IV. Same as Table II for the open site.

<i>M</i>	d_e	Unrelaxed			Relaxed			
		ν_e	E_B	q	d_e	ν_e	E_B	q
				Silicon				
Al	2.68 2.55 ^a	241.4	21.54 45.2 ^a	0.67	2.54 2.53 ^b	273.3	34.83	0.73
Ga	2.72 2.68 ^c	152.9	6.03 46.1 ^c	0.48	2.58 2.44 ^d	172.5	17.93	0.55
In	2.82	122.0	8.57	0.59	2.71 2.62 ^c	135.3	16.90	0.64
Tl	2.90	85.8	-12.93	0.42	2.80	98.1	-8.41	0.44
				Germanium				
Al	2.70	225.7	18.37	0.53	2.60	254.7	36.94	0.59
Ga	2.83	141.3	5.01	0.36	2.65	160.5	19.91	0.43
In	2.90	114.5	9.57	0.49	2.76	127.0	21.37	0.55
Tl	3.00	79.4	-9.48	0.36	2.87	92.21	-2.17	0.38

^aReference 22.^bReference 21.^cReference 12.^dReference 13.^eReference 5.

the eclipsed position is about $0.37e$, lower than the value for the atop site, and that, according only to population analysis, the more ionic bond is found for the open position. Vibrational frequencies are slightly larger for the eclipsed site and decrease from Al to Tl.

It can also be seen that the open site is slightly more stable than the eclipsed one for all the adatoms, in agreement with the first-principles pseudopotential total energy and force calculations of Northrup *et al.*²⁴ when unrelaxed systems were considered. As will be shown, this situation is reversed when relaxation is taken into account.

With respect to the eclipsed and open sites, Tables III and IV show that a negative binding energy is found in some cases. This is due to the fact that the closed-shell SCF wave functions for the threefold-coordinated sites do not correctly dissociate into open-shell fragments.

We compared²⁶ our results for Al-Si(111) systems with those obtained by Dev *et al.*²⁵; qualitative agreement was found, but the bond-distance values reported in Ref. 25 were too short and the binding energies were too large, the differences arising mainly from the use of a minimal basis set in Ref. 25, as stated in Ref. 26. The same trends could be expected for the Ga-Si(111) results of the same authors,¹² but in this case the differences are even more important. In fact, Ga chemisorption seems more favorable than Al chemisorption,^{12,25} contrary to our findings (Tables II–IV). Furthermore, the binding energy for the eclipsed position seems to be overestimated in Ref. 12 and the situation is very different from our results, which predicts a negative binding energy, i.e., 139.5 kcal/mol ¹² to be compared with 36.2 kcal/mol for the atop site, and 154.2 kcal/mol ¹² to be compared with -2.03 kcal/mol for the eclipsed one. As the main difference from our calculations and those performed by Dev *et al.*^{12,25} is the quality of the basis set employed, it seems that their results are less accurate than the present ones. On the other hand, it is important to stress once again the importance of adding polarization functions in the atomic basis set of the interacting atoms to obtain results of sufficient accuracy. Nevertheless, it must be remembered that the present work lacks the effect of electronic correlation, which tends to reduce the bond lengths slightly and to increase the binding energy.

METAL-INDUCED SURFACE RELAXATION

As in Refs. 12, 13, and 24–26, we consider the possibility of a surface relaxation upon chemisorption. As already discussed in Ref. 26, the relaxation introduces important physical effects because it allows one to maximize the bonding interactions and, thus, to obtain shorter metal-adatom–surface-atom distances, while still keeping the antibonding interaction unchanged. The effect of the relaxation on the position of the cluster atoms was schematically shown in Fig. 1. Calculations for the relaxed systems have been carried out by simultaneously allowing variation in M -surface and Si-Si or Ge-Ge distances, always maintaining C_{3v} symmetry. Such optimization has been carried out in several steps. First, the metal-surface and vertical distances between the first- and second-layer semiconductor atoms has been optimized as

in Ref. 26. Second, the first-layer semiconductor atoms have been displaced with respect to the axis containing the adatom by simultaneously allowing variation in the metal-surface distance. These two steps were repeated until consistent data were obtained. In each case a quadratic interpolation procedure has been used to locate the new minima.

The isolated clusters are also allowed to relax, as in Ref. 26, but the stability recovered is always less than 0.5 kcal/mol , showing that the relaxation is very small. Anyway the binding energies for the relaxed $M-X_nH_m$ systems will be referred to the relaxed isolated cluster energies.

Numerical results are shown in Tables II–IV and displayed in Figs. 2–4. It can be seen that the bond distances are reduced with respect to the nonrelaxed systems, particularly for the eclipsed position. The new equilibrium bond distances are very close to the sum of covalent radii (see Figs. 3 and 4), but the most spectacular result is the increase in the binding energy for the eclipsed site. The effect is also important for the open position, while the atop one is practically unaffected. The gain in binding energy due to reconstruction decreases in the order Al, Ga, In, and Tl. It is also seen that the binding energy for the eclipsed and atop sites are quite close and larger than the binding energy for the open position. In particular, for Si(111)-Al, -Ga, and -In surfaces, the resulting total energy for the eclipsed model is 19.97 , 14.76 , and 7.98 kcal/mol lower, respectively, than for the open position. These results are rather close to those reported by Northrup *et al.*^{5,24} 6.92 , 8.76 , and 7.98 kcal/mol , respectively.

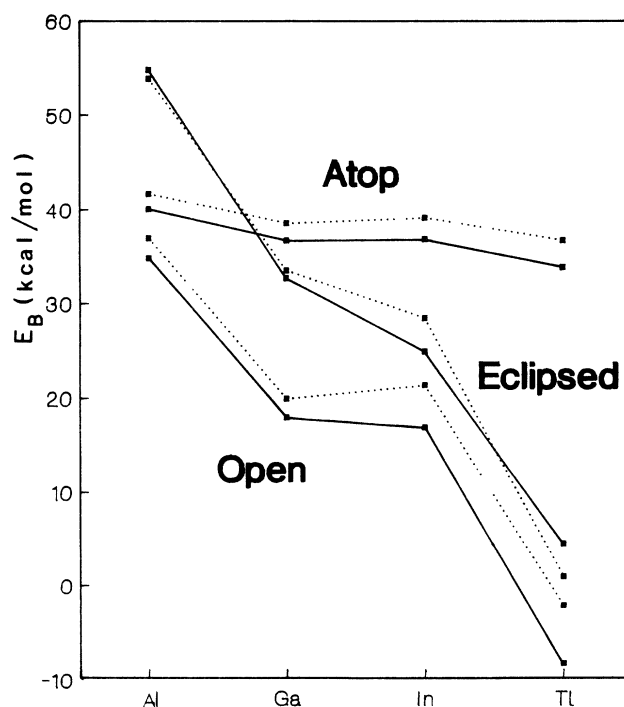


FIG. 2. Binding energies of the metal-relaxed substrate systems (—, Si surface; · · ·, Ge surface).

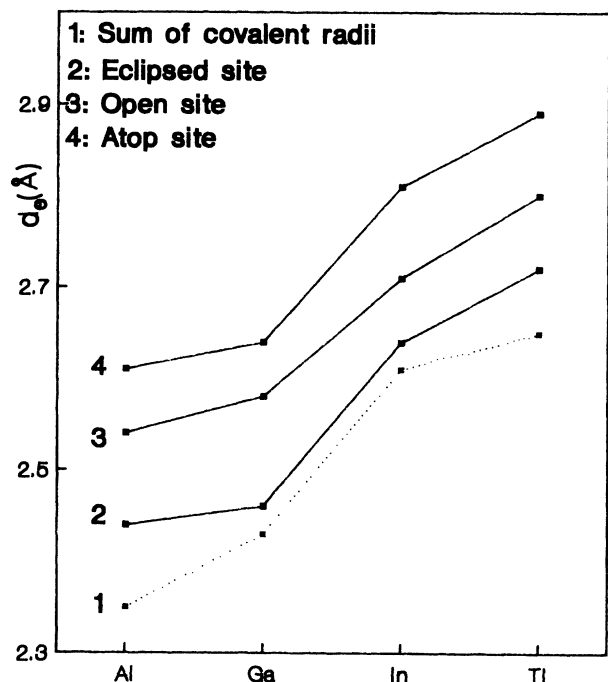


FIG. 3. Equilibrium distances between adatoms and surface atoms for M -Si systems.

Qualitative results are in agreement with the previous calculations of Dev *et al.*²⁵ for Al-Si(111) and of Thundat *et al.*¹² for Ga-Si(111), supporting the possibility of coadsorption at the eclipsed and atop sites from binding-energy considerations. On the other hand, it is worth noting that the behavior of Al, Ga, and In as adatoms

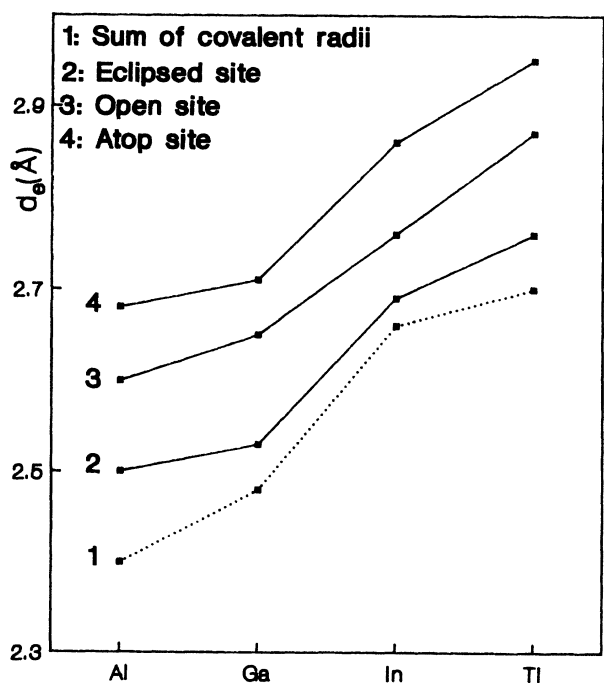


FIG. 4. Equilibrium distances between adatoms and surface atoms for M -Ge systems.

and Si and Ge as substrates is very similar, and that the gain in binding energy due to the reconstruction decreases in the order Al, Ga, In, and Tl. According to the present SCF results, Tl could be adsorbed in the atop position, but not in the others.

In view of the present results, it can be concluded that binding-energy considerations favor the eclipsed position for Al, although similar binding energies for Al and Ga on the atop and eclipsed sites, after relaxation effects have been accounted for, suggest the possibility of a multisite adsorption. On the other hand, present results suggest that In and Tl will prefer the atop position, and one is tempted to relate this to the well-known fact of the stabilization of smaller valencies when going down a column of the Periodic Table.

With respect to the vibrational frequencies, it is shown that reconstruction leads to an increase of about 20 cm^{-1} for the eclipsed and open sites, while for the atop site there are no significant differences.

In Table V we collect the variations on the bulk structure: the new X - X distances, the vertical distances between the first and second layers, and the new distances from the axis containing the adatom. In the case of M - X_4H_9 , only the vertical relaxation was considered: An enlargement of the first-layer-second-layer vertical distance of 0.08 Å for the silicon surface and of 0.1 Å for the germanium surface was found for all the adatoms. The adatom-induced reconstruction for eclipsed and open sites is more important. It can be seen that X - X ($X = \text{Si, Ge}$) distances increase, this effect being more important when considering the eclipsed position. The vertical distance between the two substrate layers increases, and finally the substrate surface atoms approach the axis containing the chemisorbed metal.

These results are in very good agreement with those from Northrup²⁴ and Zegenhagen *et al.*¹³ when considering Al and Ga chemisorption over the Si(111) surface. Nevertheless, it is shown (Table V) that the increase in the vertical distance between the two silicon layers is somewhat exaggerated for the eclipsed model due to the limited cluster size, but the important thing is to see that reconstruction effects are qualitatively important. The calculated values have to be considered at least from a semiquantitative point of view. In fact, preliminary calculations using a larger model for the eclipsed position indicate a somewhat smaller relaxation for the interlayer Si distance, but do not affect the remaining structural parameters.

On the other hand, the effect of the Si-H or Ge-H has not been investigated in the present work, but a related one⁴³ dealing with graphite models has shown that there are no appreciable changes when using either the experimental C-H distances or the C-O distance for the C-H bond, although in the latter case convergence was more difficult. Similar results were reported in Ref. 25.

In the case of Ga on Si(111), the perpendicular distance from the adatom to the surface for the eclipsed site is 1.38 Å , in good agreement with the very recently determined experimental distance of 1.49 Å (Ref. 13) above the bulk extrapolated surface (111) plane above the filled threefold silicon surface sites, and close to the calculated

TABLE V. New parameters for the reconstructed substrate clusters. d_{X-X} is the $X-X$ ($X=Si,Ge$) distance, Z_{X-X} is the distance between the first- and second-layer substrate atoms, d_a is the distance of first X atoms to the axis containing the adatom. All the distances are in Å.

	Silicon			Germanium		
	d_{X-X}	Z_{X-X}	d_a	d_{X-X}	Z_{X-X}	d_a
			Eclipsed			
Al	2.42	1.28 (1.09) ^a	2.06 (2.09) ^a	2.56	1.39	2.15
Ga	2.39	1.26 (1.09) ^b	2.03 (2.06) ^b	2.54	1.38	2.13
In	2.40	1.20	2.08	2.54	1.31	2.17
Tl	2.38	1.16	2.08	2.52	1.28	2.17
			Open			
Al	2.37	0.98	2.10	2.50	1.07	2.19
Ga	2.36	0.95 (0.82) ^b	2.10 (2.14) ^b	2.48	1.04	2.19
In	2.37	0.94	2.13	2.49	1.03	2.17
Tl	2.36	0.91	2.15	2.49	0.90	2.25
NR ^c	2.35	0.78	2.21	2.45	0.82	2.31

^aReference 21.

^bReference 13.

^cNR: nonrelaxed substrate.

distance of 1.34 Å, computed by Zegenhagen *et al.*¹³ using total-energy calculations.

It is also shown that displacements decrease when going from Al to Tl, as does the binding energy, indicating that they are in relation with the chemisorption binding energy and also with the relative size of the adatom. We can then conclude that, effectively, the relaxation is adatom induced. Finally, the similar behavior of Si and Ge surfaces must be pointed out when considering group-III metal chemisorption.

CONCLUSIONS

Ab initio Hartree-Fock calculations in the framework of the cluster approximation have been carried out to study the interaction of group-III metal atoms (Al, Ga, In, and Tl) with both Si(111) and Ge(111) surfaces. Three high-symmetry chemisorption sites—denoted atop, eclipsed, and open—have been considered. While the atop site seems the most favorable for all the adatoms when an ideal surface is considered, the situation is very different when adatom-induced reconstruction of the sub-

strate is taken into account.

Final results show that the eclipsed position is the most probable from binding-energy considerations for Al as the adatom, while for Ga the atop and eclipsed positions show similar binding energies, and for In and Tl the atop position remains the most favorable. A multisite chemisorption could be established in view of the relative binding energies.

The present results give further support to the adatom-induced relaxation suggested earlier by Northrup,²⁴ and in the case of Ga on Si(111) good agreement is found when considering the position of the adatom on the surface, proving the ability of the methodology used here in dealing with chemisorption phenomena.

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