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Chemisorption of atomic aluminum on Si(111): Evidence for an adsorbate-induced relaxation based on *ab initio* cluster-model calculations

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Interaction models of atomic Al with Si_4H_9, Si_4H_7, and Si_6H_9 clusters have been studied to simulate Al chemisorption on the Si(111) surface in the atop, fourfold atop, and open sites. Calculations were carried out using nonempirical pseudopotentials in the framework of the *ab initio* Hartree-Fock procedure. Equilibrium bond distances, binding energies for adsorption, and vibrational frequencies of the adatoms are calculated. Several basis sets were used in order to show the importance of polarization effects, especially in the binding energies. Final results show the importance of considering adatom-induced relaxation effects to specify the order of energy stabilities for the three different sites, the fourfold atop site being the preferred one, in agreement with experimental findings.

INTRODUCTION

When a metal is deposited on a Si surface, it reacts with Si producing a thin metallic film of metal silicide. The metal-semiconductor contact is an important part of the semiconductor technology, especially for determination of the microscopic nature of the Schottky-barrier formation.[1] Nevertheless, a full understanding has not been yet established. In this sense several surface-sensitive electron-spectroscopy techniques have been applied and an effort to compare experimental and theoretical results has also been done.

Lander and Morrison,[2] Hansson, Bachrach, Bauer, and Chiaradia,[3] Aiyama and Ino,[4] and Baba, Kawaji, and Kinbara[5] used low-energy electron diffraction (LEED) to study group-III metal overlayers on Si(111), showing the existence of different phases depending on metal-atom coverage and substrate temperature. The $(\sqrt{3}\times\sqrt{3})$ unit cell was found to be common for Al, Ga, and In overlayers on Si(111). It was obtained with $\frac{1}{3}$ monolayer coverage and attributed to metal chemisorption on the threefold sites. Hansson *et al.*[6] published an angle-resolved photoelectron spectroscopy (ARPES) study of the Si(111)$(\sqrt{3}\times\sqrt{3})$-Al and Si(111)$(\sqrt{3}\times\sqrt{3})$-In surfaces showing that both surfaces exhibit two occupied bands of surface states derived from the dangling-bond electrons of silicon surface atoms which are modified by the presence of the group-III atoms. Kinoshita, Kono, and Sagawa[7] and Uhrberg *et al.*[8] found another nondispersive surface state ($S1$) band not directly related to the $(\sqrt{3}\times\sqrt{3})$ surface which could be originated from defects on the $(\sqrt{3}\times\sqrt{3})$ reconstructed surface, although unambiguous interpretation was not possible from their data.

These results are in qualitative agreement with the theoretical study of Northrup[9] using first-principles pseudopotential total energy and force calculations to study the Si(111)$(\sqrt{3}\times\sqrt{3})$-Al surface and assuming $\frac{1}{3}$ monolayer coverage. Northrup found two geometries with low energy: The adatoms can rest in either the open sites (H_3) or in the fourfold atop sites above a second layer Si atom (T_4). The T_4 geometry was preferred by 0.3 eV/adatom when relaxation was taken into account. (Here H denotes a honeycomb structure and T a trimer.)

Chelikowsky,[10] Zhang and Schluter[11] performed band-structure calculations in order to determine the electronic local density of states (LDOS) for different sites using preselected Si—Al bond distances. The overall conclusion is that the open site along with the substitutional one are the most favorable for Al chemisorption on Si(111)(7×7) but no energetic data nor geometry optimizations are reported.

Likewise Xie Xide, Zhan Kai-Nung, and Yeh Ling[12] used a cluster model and the charge self-consistent iterative extended Hückel (IEHT) semiempirical approaches and concluded that the H_3 site is the most possible one. However, they did not exclude the atop site in the view of the relative binding energy for the two models explored.

Very recently, Dev *et al.*[13] explored all the high-symmetry sites by using the self-consistent-field (SCF) Hartree-Fock cluster method and minimal basis sets. They concluded that the adsorption of aluminum on the silicon (111) surface is possible at more than one site and proposed that at low temperature there is a coadsorption at the relaxed T_4 and atop sites.

As stated by Kobayashi *et al.*[14] Al chemisorption onto the Si(111)(2×1) surface is shown to take place in quite a different manner from that onto the Si(111)(7×7) surfaces. The chemisorption is most consistently interpreted by Al—Si covalent bond formation at the atop sites, in agreement with the Auger electron spectroscopic study (AES) of the same authors.

Additional information was obtained by Ping Chen *et al.*[15] by LEED, AES, and partial yield spectroscopy (PYS), confirming covalent bonding between Al atoms and the Si surface. They conclude that interface formation occurs in a three-step process, the first being the completion of an ordered layer where each Al atom is adsorbed into a hollow site due to the trivalence of Al. The last step shows the beginning of a metallic Al epitaxial layer. This epitaxial Al-Si interface has been studied by Legoues, Krakow, and Ho,[16] stating that two interfacial atomic configurations can coexist: one with each Al atom coupled to three Si atoms (substitutional model), and another one with the Al atoms in an atop position. It was concluded that the binding energy must be considered as an important factor.

Since no detailed structural nor energetic information exist, and since the adsorption sites are not fully ascertained, we present in this paper SCF *ab initio* calculations of increasing accuracy for the interaction of atomic Al with several cluster models simulating the Si(111) surface different sites. Three chemisorption sites are considered, named the atop, fourfold atop (T_4), and open (H_3) sites.

METHOD OF CALCULATION

Calculations have been carried out by using the PSHONDO program,[17] a version of the HONDO package,[18] including the possibility of using the nonempirical pseudopotentials developed by Durand and Barthelat[19] and Pelissier and Durand.[20] These pseudopotentials have proven to be a valuable tool in a wide range of chemical and physical situations involving heavy atoms containing systems and going from molecular structure to chemisorption and model surface phenomena.[21–31]

In particular, it has been shown[32,33] that good agreement is found between experimental results,[34] as well as with previous cluster model[35] or slab calculations,[36] for the chemisorption of halogens on the Si(111) and Ge(111) surfaces.

The level of calculation used through this work corresponds to the well-known *ab initio* Hartree-Fock SCF scheme using a monodeterminantal wave function built up by means of molecular orbitals (MO's) described by the linear combination of atomic orbitals (LCAO) method.

In the present work the effect of the inner shells of the Al and Si atoms is taken into account by means of the nonempirical pseudopotentials quoted above.[19,20] Pseudopotentials are derived in order to provide pseudoorbitals which reproduce the atomic SCF all electron double-ζ calculations of Clementi and Roetti[37] in the valence region, but in such a way that cancels out the orthogonality tails in the core region, and also to match the orbital energies calculated at that level. By using such a pseudopotential one ensures that the inner shells are treated effectively at the double-ζ level. (See Refs. 19, 20, and 32.) In this way the calculated energy depends only on the basis set chosen to construct the one-electron (MO's) functions used to define the Hartree-Fock determinant and on the choice of pseudopotentials. Pseudopotential parameters for Al and Si are reported in Table I.

The valence shells are described by means of contracted Gaussian-type orbitals (CGTO's) which constitute the atomic basis set. These basis sets are of mixed character and their usefulness has already been tested in related systems.[21,31] In particular, it has been shown that although a basis set of double-ζ quality is able to give a correct, qualitative and semiquantitative, description of the Cl/Si(111) system,[31] polarization functions are required to give an equilibrium distance comparable to the experimental one obtained through surface extended x-ray absorption fine-structure (SEXAFS) measurements.[34] The effect of the polarization functions in the geometrical parameters has already been shown in $\mathrm{Si}_n\mathrm{H}_{2n}$ compounds.[38] From the energetics viewpoint, polarization functions are also necessary as indicated by the calculations on the Cl/Si(111) system reported in Ref. 32, which were carried out using double-ζ plus polarization basis sets.[32] Thus it seems clear that a basis set of double-ζ plus polarization quality is required to obtain results accurate enough. Moreover, basis-set superposition errors (BSSE) are almost negligible when using basis sets of this quality, especially if the calculated binding energy is not of the order of the intermolecular interactions.

In this work several basis sets are used to show once again the importance of polarization functions to properly describe Si-containing compounds and, in particular, that it is accurate enough to consider polarization func-

TABLE I. Pseudopotential parameters for silicon and aluminum as taken from Ref. 54 according to the usual pseudopotential operator defined by $\hat{w}_l(r)=\exp(-\alpha_l r^2)\sum_{i=1}^{n} c_i r^{n_i}$.

l	α_l	c_1	n_1	c_2	n_2	c_3	n_3
			Aluminum				
0	2.780 95	15.036 55	0	24.491 14	2	0.000 12	4
1	1.521 96	5.037 33	−2	4.886 94	2	−1.314 80	4
2	1.130 22	−1.007 82	0				
			Silicon				
0	3.829 150	4.904 82	−1	−10.484 25	0	103.050 06	2
1	2.734 040	1.663 49	−2	16.009 87	2	6.435 28	4
2	1.554 080	−1.455 46	0				

tions only on the atoms which are directly involved in the interaction. Therefore, the basis sets I–IV have been used and are described in the following.

Basis I. This basis is of double-ζ quality in Si and Al valence shells. The *ns* orbitals are described by four primitive Gaussian-type orbitals (GTO's) which are contracted by means of a 3 + 1 procedure [i.e., the three first GTO's define the first basis function and the last GTO the second one. In this way each atomic orbital (AO) is represented by two basis functions]. For the *np* orbitals an identical contraction scheme was used for Al but a 2 + 2 contraction procedure was used for Si. The hydrogen basis set consists also of four primitive GTO's contracted to the minimum basis-set quality. Details concerning exponents and contraction coefficients are given in Table II.

Basis II. This basis is the same as the previous one but a single *d* polarization function was added to the previous Al and first-layer Si-atoms basis set, the exponents of the polarization functions being of 0.15 and 0.45 for Al and Si, respectively. It is worth noting that, as in Ref. 32, the effective $6d \rightarrow 5d$ recombination is carried out and all the computation was performed with the usual 5*d* atomic orbitals.

Basis III. This basis set differs only from the previous one in the hydrogen basis set, which here is treated at the double-ζ level. A 3 + 1 contraction procedure of the four primitive GTO's was used.

TABLE II. Valence Gaussian basis set.

Orbital	Exponent	Coefficient
	Silicon	
s	2.649 877	0.202 103
	1.637 220	−0.429 090
	0.236 353	0.671 680
	0.087 377	1.0
p	1.630 182	−0.023 793
	0.333 686	0.390 174
	0.122 415	0.545 199
	0.047 150	0.192 726
d	0.45	
	Aluminum	
s	2.589 324	0.075 385
	1.211 980	−0.292 680
	0.155 250	0.731 013
	0.056 606	1.0
p	1.221 033	−0.063 720
	0.349 691	0.155 701
	0.138 520	0.514 311
	0.047 128	1.0
d	0.15	
	Hydrogen	
s	13.247 9	0.019 255
	2.003 13	0.134 420
	0.458 67	0.469 565
	0.124 695	1.0

Basis IV. This basis set is used to obtain an estimate of the basis-set limit results and the extent of the BSSE introduced by the previous ones, as well as a test of the usefulness of the previous mixed basis sets. This basis set is then of extended quality, i.e., double-ζ plus polarization quality on all Al- and Si-atoms basis sets and double-ζ quality on the embedding H-atoms basis set. It is used only as a test in some selected system used through this work.

Two different kinds of systems are treated: the cluster model plus Al-adatom contributions and the isolated cluster model. The former involves closed shells; the latter involves then at least one open shell. The open shells are treated through the Nesbet method[39,40] and also through the variational restricted open-shell Hartree-Fock (ROHF) method. In this work, the ROHF energy was obtained by using a recent modification of the PSHONDO program by Caballol and Daudey[41] which uses the coupling operator formalism of Caballol *et al.*[42] and Carbó *et al.*[43]

In order to analyze the bonding of the Al atom with the Si cluster model substrate, the corresponding orbital transformation of Amos and Hall[44] has been used following the work of Seel and Bagus on the F/Si(111) and Cl/Si(111) systems.[35]

This transformation serves basically to compare the bare substrate MO's with those of the cluster + adatom supermolecule. Overall, the technique leads to molecular orbitals which have extremal values of overlap between the two sets.

Thus, if $|v_i^1\rangle$ are the n_1 isolated cluster canonical MO's and $|v_i^2\rangle$ are the n_2 ones of the supersystem, the corresponding orbitals $|w_i^1\rangle$ and $|w_i^2\rangle$ are solutions of the eigenvalue equations

$$\begin{aligned} \underline{S}\,\underline{S}^{\dagger}\,|w_i^1\rangle &= \lambda_i^1\,|w_i^1\rangle \;, \\ \underline{S}^{\dagger}\underline{S}\,|w_i^2\rangle &= \lambda_i^2\,|w_i^2\rangle \;, \end{aligned} \tag{1}$$

$\underline{S}$ being the overlap matrix between the two sets of canonical molecular orbitals, i.e., $\underline{S}_{ij} = \langle v_i^1 \mid v_j^2 \rangle$.

From Eq. (1) it is clear that $0 \le \lambda_i^1 = \lambda_i^2 \le 1$, $i = 1, \ldots, n_1$ and that $\lambda_i = 0$ for $i = n_1 + 1, \ldots, n_2$. Hence those corresponding orbitals with λ_i values near the unity correspond to MO's that have not been changed after interaction with the adsorbate, those with a zero value for λ_i are the purely adatom atomic orbitals, and those with intermediate values are the ones that have changed most during adsorption.

From the chemical point of view, another kind of useful information can be obtained by simply drawing schematically the MO's. As the SCF wave function is invariant under unitary transformation one can choose to draw the interactions arising from different kind of MO's, from the various localized MO's obtained through the known localization procedures, to the canonical delocalized ones, i.e., the ones providing a diagonal representation of the Fock operator when self-consistency is achieved. In this work the later option will be used for interpretative purposes in the line described in Ref. 45.

By using the above theoretical procedure the total energy of the Al-cluster model system has been computed as a function of the perpendicular distance to each one of the considered sites, giving the equilibrium distance and the potential energy curves. The vibrational frequency for the perpendicular motion to the surface has been computed from this curve, in the harmonic approximation, by a quadratic fit and assuming infinite mass for the substrate. The computed vibrational frequency is then

$$\nu_e=(k/m_{\mathrm{Al}})^{1/2}\,, \tag{2}$$

where k is the force constant and m_{Al} is the mass of the Al atom.

The use of such a procedure has been widely used in dealing with atomic chemisorption on cluster model surfaces and the computed force constants are in error by about 15%.[32,34,46–48] Moreover, corrections for a nonharmonic behavior would be smaller than the error introduced by assuming a rigid cluster or infinite mass (as shown in Table V), where the harmonic frequencies are compared with those obtained using a polynomial fit of fourth order. Moreover, the higher terms in the quartic expansion are reasonably small.

At this point it is worthwhile to point out that a very recent study, similar to the present one, has been reported by Dev *et al.*[13] However, while the theoretical procedure used in Ref. 13 is close to the present one, there are some points that must be clarified.

The first one concerns the effective core potential procedure used in Ref. 13, which being of a nonempirical nature, uses a somewhat different fit of the pseudoorbitals (i.e., the procedure fits the matrix elements of the potential to obtain the analytic form but uses an earlier form of the pseudoorbital which did not maintain necessarily the same electron density in the valence region.[49]

Secondly, and more important, the results reported in Ref. 13 have been obtained through a minimal basis-set calculation. The authors argue that this procedure yields accurate results for the adatom-surface equilibrium distance by comparison of their previous minimal basis-set results on the Cl/Si(111) system with the available experimental results. However, the double-ζ quality calculations of Seel and Bagus[35] give an equilibrium distance larger than the experimental value,[34] and only when polarization functions were introduced in the double-ζ quality basis set was the calculated distance comparable to the experimental result.[32] Thus, although the overall description achieved by the recent work of Dev *et al.*[13] fairly agrees with the present one, it is clear that it is somewhat affected by the BSSE, as can be easily deduced by comparison between the binding energies reported in this work at the basis III level and those reported in Ref. 13.

Finally, the description of the open-shell systems described in Ref. 13 uses the unrestricted Hartree-Fock (UHF) formalism which introduces a small quantity of correlation and spin-polarization energy leading to a result that cannot be exactly, in a size consistent way, compared to the restricted Hartree-Fock (RHF) closed-shell description of the adatom-cluster supersystem. For those reasons we feel that the present work, which uses reasonably large basis sets, can give additional information of the Al/Si(111) system.

CLUSTER MODELS

As the nature of the chemisorption of atoms on surfaces is provided to be in general of local character, the different high-symmetry sites of the Si(111) unreconstructed and unrelaxed surface may be properly simulated by cluster models.[22,32,33,35,13,50,51] Thus, the atop position, in which chemisorption of the adatom takes place directly over a surface Si atom, is simulated by a Si_4H_9 cluster model (Fig. 1) containing a surface atom and its three nearest neighbors on the second layer. H atoms are used as embedding atoms to provide an adequate environment for the second layer Si atoms. This model has been previously used to study chemisorption of F and Cl on Si(111) by Seel and Bagus,[35] which indeed show that the

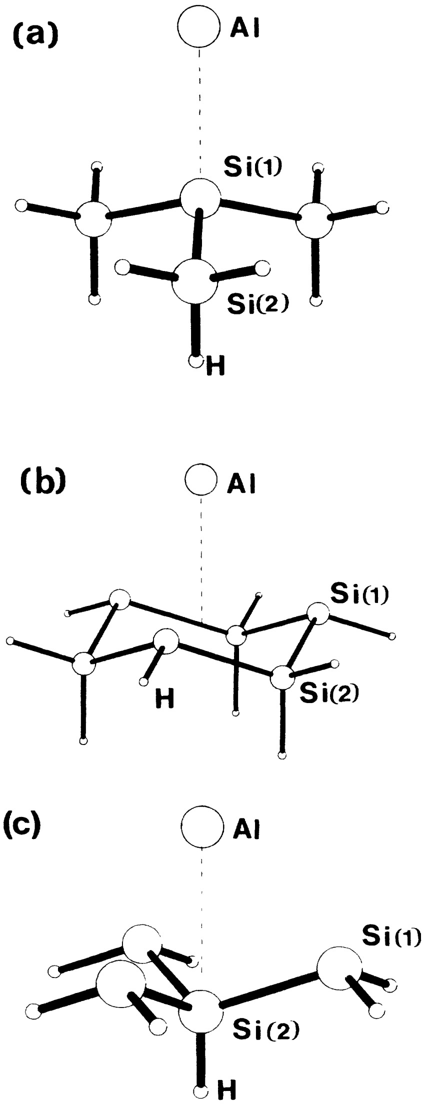

FIG. 1. (a) The Si_4H_9-Al cluster model used to model the atop site. (b) The Si_6H_9-Al cluster model used to model the H_3 site. (c) The Si_4H_7-Al cluster model used to model the T_4 site.

equilibrium distance to the surface and vibrational frequency for the normal motion to the surface have reasonably well converged properties with respect to the cluster size and the binding energy exhibiting small changes. It is worth pointing out that such a behavior with respect to the cluster size is not general. Thus, while the chemisorption properties on Si(111) and Ge(111) surfaces show little variation with the cluster size, a qualitative change occurs when dealing with metal surfaces as recently shown by Hermann, Bagus, and Nelin[52] in dealing with CO on Cu(100). However, there is a clear difference between semiconductor or metal surfaces. In particular, it has been shown[53] that the near degeneracy of several electronic states appearing when dealing with a metal cluster model may be a key to understand the behavior reported in Ref. 52.

The open-shell configuration for Si_4H_9 is a_1^1 leading to a $^2A_1$ electronic state which provides a closed-shell system corresponding to a $^1A_1$ electronic state when coupled with the ^2P electronic state of the Al adatom.

For the fourfold atop site (T_4), the Si_4H_7 cluster model has been used (see Fig. 1). This cluster model was also previously used by Seel and Bagus in Ref. 35. As in Ref. 35, an $a_1^2e^2$ open-shell configuration was found. The a_1 and e canonical molecular orbitals are always different combinations of the sp_z dangling bonds (z being the C_3 symmetry axis) as expected from intuitive arguments. The different coupling possibilities between the a_1^1 and the e^2 open shells lead to several possible electronic states,[35] among which the $^4A_2$ is the stablest one and the one used in this work. When the Al atom interacts with this cluster model it leads also to a closed-shell ground state of $^1A_1$ symmetry.

Finally, the Si_6H_9 cluster model has been used to simulate the H_3 site. This cluster is a somewhat reduced model of the $Si_{10}H_{13}$ used in Ref. 35, but it maintains the main characteristics of such a site and thus enables the use of a more extended basis set. In this case the ground-state open-shell occupation is also $a_1^1e^2$, and $^4A_2$ is the electronic state used through this work. The electronic ground state is again a closed shell of $^1A_1$ symmetry when interacting with atomic Al.

The geometric parameters for the cluster models described above are the ones previously used by different authors.[22,32,33,35,48] Thus, values of $d(\text{Si—Si})=4.44$ bohr and $d(\text{Si—H})=2.80$ bohr have been used through this work for the nonrelaxed cluster models.

Finally, it is important to point out that all the present calculations concerning the isolated clusters, as well as those of the supersystem, have been carried out by imposing the C_{3v} symmetry to the calculated wave functions and hence the notation used to describe the MO's.

Results for the Si_4H_9 cluster model were reported in Ref. 32 but they are included here for comparative purposes. Moreover, the treatment of the open shells in Ref. 32 was done by means of the Nesbet method,[39,40] whereas in this paper the ROHF results are also presented.

The cluster binding energies are computed in the usual way as

$$D=-[E_{\text{tot}}(\text{Si}_n\text{H}_m)-nE_{\text{tot}}(\text{Si})-mE_{\text{tot}}(\text{H})]\ , \tag{3}$$

with $n=4,6$ and $m=9,7$. The energy of the isolated atoms is calculated at the SCF RHF open-shell level using the PSATOM program,[54] a modification of the ATOM program[55] including the nonempirical pseudopotentials of Durand *et al.*,[19,20] and using the basis sets described in the previous section.

Values obtained for the cluster binding energies are reported in Table III and compared with the available results of Seel and Bagus[35] and Hermann and Bagus[56] obtained at the all-electron level and using basis sets of double-ζ quality on the valence shells.

As it can be seen, the difference between the results arising from the basis II or III is very small and enables the use of basis II in the chemisorption calculations. An additional evidence for the stability of the results with respect to the basis-set size is provided by the results obtained for Si_4H_7 and Si_4H_9 using basis IV which is of extended quality. These results show that the overall calculations presented in this work are not affected by the BSSE. Moreover, calculations concerning the cluster-adatom interaction always show the same features as it will be shown in the next sections.

Table IV shows the energy of the lowest and highest doubly occupied valence orbitals. The difference between them can be compared with the experimental and calcu-

TABLE III. Binding energies (in hartrees) for the three unrelaxed clusters considered in this work.

	Si_4H_7		Si_4H_9		Si_6H_9	
Basis set	ROHF	Nesbet	ROHF	Nesbet	ROHF	Nesbet
I	0.66	0.65	0.87	0.86	0.95	0.93
II	0.75	0.73	0.90	0.90	1.03	1.02
III	0.77	0.75	0.92	0.92	1.06	1.04
IV		0.78		1.04[c]		
All electron *DZ*[a]		0.56[b]		0.91		
All electron *DZ*+*P*[a]				1.05		

[a] *DZ* denotes a double-ζ basis set (Ref. 35) whereas *DZ*+*P* denotes double-ζ plus polarization quality (Ref. 56).

[b] Average of configurations result (Ref. 35).

[c] Reference 32.

TABLE IV. 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. Energies are in hartrees.

		E_l		E_h		ΔE	
Cluster	Basis	ROHF	Nesbet	ROHF	Nesbet	ROHF	Nesbet
Si_4H_7	I	−0.798	−0.805	−0.397	−0.404	0.401	0.401
	II	−0.788	−0.796	−0.399	−0.406	0.389	0.389
	III	−0.780	−0.787	−0.388	−0.395	0.392	0.392
	IV		−0.788		0.408		0.380
	DZ[a]		−0.792		−0.387		0.405
Si_4H_9	I	−0.807	−0.810	−0.394	−0.396	0.413	0.414
	II	−0.801	−0.803	−0.397	−0.399	0.404	0.404
	III	−0.793	−0.795	−0.388	−0.387	0.408	0.408
	IV[b]		−0.782		0.387		0.395
	DZ[a]		−0.801		−0.383		0.418
	DZP[c]		−0.776		−0.332		0.440
Si_6H_9	I	−0.822	−0.827	−0.385	−0.390	0.437	0.437
	II	−0.812	−0.817	−0.385	−0.389	0.427	0.428
	III	−0.803	−0.807	−0.373	−0.377	0.430	0.430

[a] Reference 35.
[b] Reference 32.
[c] Reference 56.

lated bandwidths of silicon which are 0.46 a.u. (Ref. 57) and 0.44 a.u. (Ref. 58), respectively.

Finally, it is worth comparing the variational results arising from the ROHF treatment for open shells with those obtained by using the Nesbet procedure. For Si_4H_9, which contains only one open shell, the differences between the two procedures is very small and the use of ROHF does not introduce appreciable changes. However, for Si_4H_7 and Si_6H_9, which contain three open shells, the differences are somewhat larger stabilizing the cluster models by about 12 kcal/mol, which is an average of 4 kcal/mol for open-shell clusters. The main consequence will then be to favor the atop site by comparison with the H_3 or T_4 sites when using ROHF instead of the approximate Nesbet method since all the Al-Si_nH_m supersystems are closed shells. Likewise, the bandwidth values reported in Table IV are almost unaffected by the method used to deal with open shells. This is logical since only the double occupied levels are involved. As it will be shown in the following sections, there is no qualitative change, in which model chemisorption occurs, when using either ROHF or Nesbet procedures for open shells.

RESULTS FOR THE NONRELAXED Al-Si CLUSTER SYSTEMS

As stated previously, the total energy for the Al-Si cluster models was computed as a function of the perpendicular distance of the Al atom to the surface, and the binding energy for the interaction was calculated using the expression

$$E_B = E_{\mathrm{tot}}(\mathrm{Si}_n\mathrm{H}_m\text{-Al}) - [E_{\mathrm{tot}}(\mathrm{Si}_n\mathrm{H}_m) + E_{\mathrm{tot}}(\mathrm{Al})] \quad (4)$$

with $n = 4, 6$ and $m = 7, 9$.

All the results reported in this section have been obtained by using the bulk geometry for the cluster model and both ROHF and Nesbet energies for the isolated cluster models. The vibrational frequencies for the perpendicular motion to the surface were calculated as described previously. Finally, the equilibrium bond distances and binding energy for adsorption were calculated and compared with available results.

Results are summarized in Table V. As it can be seen the preferred site for Al chemisorption is the atop one. These data are in contradiction with the results of Xie Xide *et al.*,[12] who found the H_3 site to be the most stable at the iterative extended Hückel level (IEHT). With respect to the work of Zhang and Schluter[11] it must be pointed out that the distances assumed by these authors (2.34 Å and 0.78–0.97 Å for the atop site and H_3 sites, respectively) are not very well selected. However, the present results are in good agreement with the data obtained by Northrup[9] for the T_4 and H_3 sites when considering the unrelaxed substrate. In fact, the distances from the Al adatom to the plane containing the second-layer Si atoms are 2.30 and 2.43 Å for the H_3 and T_4 models, respectively, to be compared with 2.01 and 2.45 Å as reported by Northrup. Likewise, the present binding-energy difference between the two sites is 5.8 kcal/mol (the H_3 site being the stablest one) to be compared with a value of 8.5 kcal/mol reported by Northrup.[9]

With respect to the recent calculations of Dev *et al.*[13] it is worth realizing that although they agree qualitatively with the present ones, the bond distance values reported in Ref. 13 are too short and the binding energies are too large. The differences between the present calculations and those reported in Ref. 13 arise mainly from the use of a minimal basis set in Ref. 13. In fact, if minimal basis-set results for the Si_4H_9-H system[22] are compared with those obtained at the double-ζ and double-ζ plus polar-

TABLE V. Results for the Al chemisorption over the ideal Si_nH_m clusters. r_e is the equilibrium perpendicular distance (in Å) from Al adatom to the surface, $d_{\mathrm{Al\text{-}Si}}$ is the distance (in Å) from the adatom to its nearest surface Si atom, ν_e (in cm^{-1}) is the harmonic vibrational frequency perpendicular to the surface and the values in parentheses refer to the same quantity obtained through a quartic polynomial fit. BE is the binding energy (in kcal/mol) calculated with respect to the isolated systems and using both ROHF and Nesbet energies for the cluster models.

					BE		
Site	Basis set	r_e	$d_{\mathrm{Al\text{-}Si}}$	ν_e	ROHF	Nesbet	Others
Atop	I	2.64	2.64	226.0(228.5)	−37.3	−40.7	
	II	2.62	2.62	241.9(233.4)	−39.6	−43.5	
	III	2.62	2.62	240.3	−38.9	−42.7	
	STO-3G[a]	2.37	2.37	377.4			−90.8(UHF)
	IEHT[b]	2.43	2.43				−43.8
H_3	I	1.63	2.75	245.9(246.0)	−8.0	−17.3	
	II	1.51	2.68	241.4(240.5)	−21.6	−33.3	
	III	1.50	2.67	240.3	−22.0	−34.1	
	STO-3G[a]		2.55	304.0			−45.2(UHF)
	IEHT[b]	1.69					−34.1
	MSF[c]	1.23					−60.9
T_4	I	1.77	2.83	277.5(270.4)	−3.1	−9.4	
	II	1.65	2.76	298.1(296.4)	−14.9	−27.5	
	III	1.65	2.76	297.0	−15.5	−28.1	
	IV	1.65	2.76	297.0	−15.5	−28.1	
	STO-3G[a]		2.68	375.0			−13.6(UHF)
	MSF[c]	1.60					−52.4

[a] Reference 13 (STO-3G refers to minimal basis set).

[b] Reference 12.

[c] Reference 9 (MSF refers to momentum-space formalism).

ization levels, including or not nonempirical pseudopotentials, one can see that minimal basis-set bond lengths are too short and minimal basis-set binding energies are too large (by about 25 kcal/mol). When Al is considered instead of H as an adatom, the BSSE should be even larger, as shown by comparison between results reported in Ref. 13 and the present ones obtained using a basis set of near double-ζ quality (basis I in Table V). It is also important to point out that the result for the T_4 fourfold atop site reported by Dev *et al.*[13] is very close to the results reported here with basis sets of double-ζ plus polarization quality and clearly shows that cancellation errors may give minimal basis-set results that lie near the ones obtained by using extended basis sets. Unfortunately this is not always true.

Before going on with the interpretation of the chemisorption bond, let us point out that for the atop site the effect of the basis-set quality is very small, although for the other cases the inclusion of a polarization function to the basis set of Al adatom and to the Si first-layer atoms appear to be necessary. This effect may be understood by looking at the Mulliken population analysis, which shows that in the atop case the d population is 0.07 and 0.08 for the Al and first-layer Si atoms, respectively. However, if a tricoordinate site, as the T_4 one, is considered, these values are 0.28 and 0.11, respectively. These values clearly indicate that the need for the d polarization functions is in this case more important. This appears because d orbitals contribute more effectively to the bond formation, allowing a better overlap, and hence an appropriate directionality to the chemisorption bond.

As stated previously, the electronic ground state for the atop interaction, when using the Si_4H_9 model, corresponds to a closed shell. From the corresponding orbital transformation it can be concluded that the $4a_1$ cluster orbital forms a bonding combination with a sp_z hybridized Al orbital (see Fig. 2 and Table VI). This result shows that only the Si sp_z dangling bond is strongly affected after Al adsorption.

Likewise, Fig. 3 shows the basic interactions for the open H_3 site. In this case the $5a_1^1$ and $6e^2$ dangling bonds of the cluster model interact with the s and the p_x,p_y Al AO's, respectively, producing two states per adatom below the occupied levels of the Si bulk, and an unoccupied level in the gap. Finally, Fig. 4 and Table VI show similar results for the T_4 site. In this case it is interesting to note that there is an antibonding interaction between the second-layer Si atom 2s AO and that the main interactions arise from the p_x and p_y AO's of the Al atom and the p_z Si surface atoms dangling bonds.

The electronic structure results for the tricoordinate sites may be directly compared with the results of band calculations for the Si(111)($\sqrt{3}\times\sqrt{3}$)-Al or

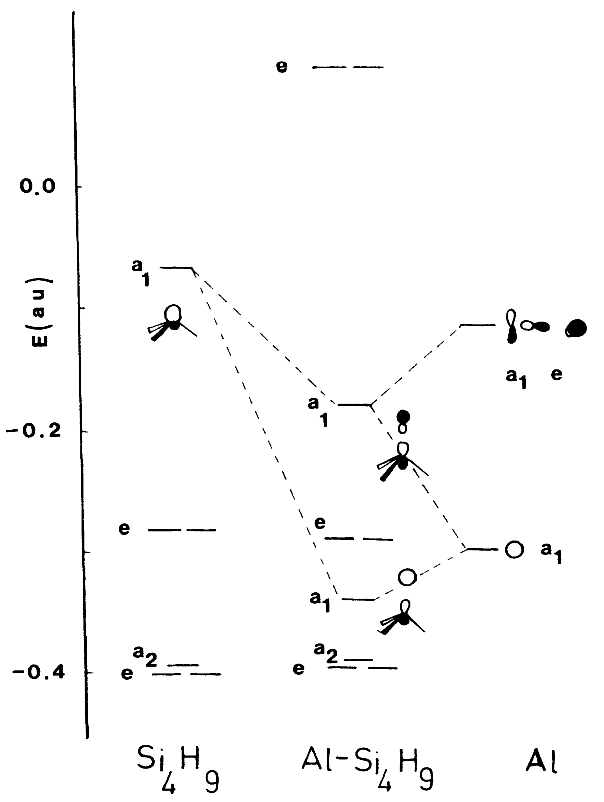

FIG. 2. Molecular orbital interaction diagram for the Al-Si_4H_9 system. A schematic representation of the cluster and supersystem MO's is included in order to show the origin of the main orbital interactions.

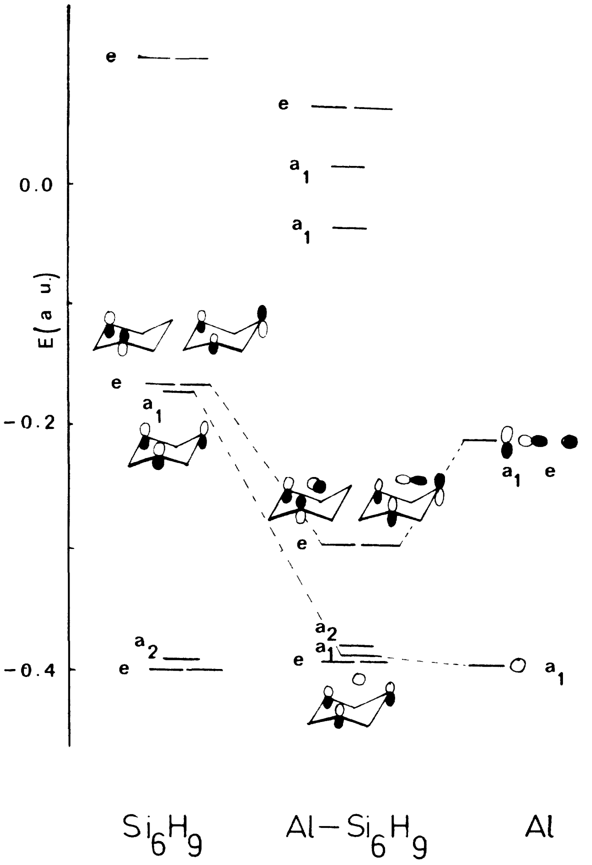

FIG. 3. Same as Fig. 2 for the Al-Si_6H_9 system.

Si(111)(7×7)-Al at the Γ point of the Brillouin zone[11] which indeed are in agreement with experimental data reported in Refs. 6 and 7. At this point it is worth noting that the electronic configuration arising from the interaction between the Al adatom and the cluster model simulating the atop position does not fit the experimental results quoted above. On the other hand, our results for the atop position seem to be in agreement with the experimental findings of Kobayashi *et al.*[14] using Al and Si $L_1L_{2,3}V$ Auger transition for an Al-Si(111)(2×1) interface electronic structure, assuming that the reconstruction which occurs upon cleavage is only a small perturbation of the ideal unreconstructed surface.

Thus, from electronic structure considerations, the T_4

TABLE VI. Eigenvalues of the cluster corresponding orbitals [see Eq. (1)] for the three chemisorption sites using the unrelaxed cluster models. These values have been obtained using basis I at the r_e distance.

Al-Si_4H_7		Al-Si_6H_9		Al-Si_4H_9	
λ_i^1	Orbital	λ_i^1	Orbital	λ_i^1	Orbital
0.9997	$1a_1$	0.9998	$1a_1$	1.0000	$1a_1$
1.0000	$1e$	0.9999	$1e$	1.0000	$1e$
0.9999	$2a_1$	1.0000	$2e$	0.9957	$2a_1$
0.9999	$2e$	1.0000	$2a_1$	0.9999	$3a_1$
1.0000	$1a_2$	0.9999	$3a_1$	0.9999	$2e$
0.9709	$3a_1$	0.9841	$4a_1$	0.9999	$3e$
0.9983	$3e$	1.0000	$3e$	0.9999	$1a_2$
0.5553	$4a_1$	0.9984	$4e$	0.9982	$4e$
0.8970	$4e$	0.9989	$5e$	0.5527	$4a_1$
		0.9998	$1a_2$		
		0.5787	$5a_1$		
		0.8960	$6e$		

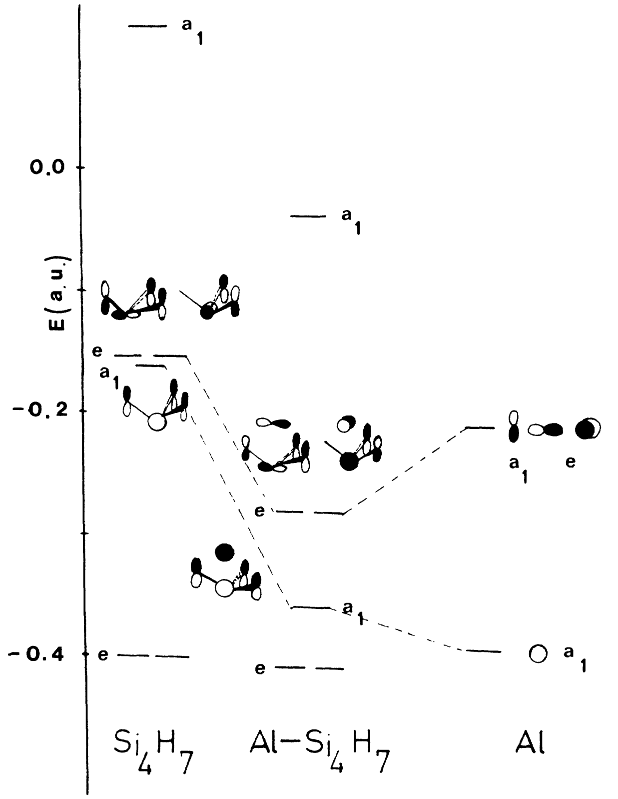

FIG. 4. Same as Fig. 2 for the Al-Si_4H_7 system.

or H_3 sites seem to be favored while the total energy criterium favors the atop position. In the view of the present results and those of Northrup[9] we found it necessary to explore the effects of surface relaxation.

EFFECT OF THE SURFACE RELAXATION

As is well known the Si(111) surface relaxes and reconstructs; i.e., the positions of the surface atoms in the first few layers of the crystal change from their position in the bulk[57] although there is evidence that the displacements of the surface Si atoms on Si(111) are reasonably small.[50,51,58] However, as far as finite cluster models are used to investigate the effect of surface relaxation when an adsorbate is considered, a preliminary search for the relaxation of the naked cluster models seems necessary.

In the view of results reported in Table V, relaxation effects have been considered only by using basis II. For the isolated clusters only the vertical distance between the two first silicon layers has been optimized. Both Nesbet and ROHF wave functions have been used.

In all cases (see Table VII) the direction of the relaxation is in toward the bulk (lowering the interlayer distance by about 0.04 Å) in agreement with the previous results of Goddard *et al.*[50,51] The stability increase recovered by allowing such an inward relaxation is always less than 0.5 kcal/mol. These results show that this effect is really small. Anyway the binding energies for the relaxed Al-Si_nH_m systems will be referred to the relaxed isolated cluster energies.

Calculations for the relaxed Al-Si_nH_m systems have been carried out by simultaneously allowing variation in both Al-surface and second-layer first-layer distances. There are then two parameters to be optimized and a quadratic two-dimensional interpolation was used to locate the new minima. In this case the vibrational frequencies were calculated as in the unrelaxed case. The substrate was then kept fixed at the relaxed optimum geometry. Results are presented in Table VIII.

First of all it is worthwhile to note that the direction of the relaxation, with respect to the unrelaxed cluster model, is always out towards the bulk, tending to increase the interlayer distance contrarily to the case of the isolated clusters. While the atop situation after relaxation is very similar to the nonrelaxed one, the effect in the T_4 site is really large and to a lesser extent it also affects the H_3 structure. As a result the new order of stabilities is now T_4, atop, H_3, with T_4 the most stable.

The results reported in Table VIII show good agreement with the earlier study of Northrup.[9] In particular, the Al to first-layer Si atoms and Al to second-layer Si atoms distances for the T_4 site are 2.51 and 2.49 Å, respectively, to be compared with the values of 2.49 and 2.45 Å reported by Northrup.

As stated by Northrup[9] such a relaxation allows the Al atom to move closer to the Si surface atoms while still maintaining an optimum distance from the second layer. This fact can be easily interpreted in terms of the orbital interactions depicted in Fig. 4. Thus, the observed displacements do not modify the antibonding interaction of the 2*s* AO of Si and the sp_z hybrid orbital of the second-layer Si atoms but enforce the bonding interaction between the Al p_x and p_y AO's with the dangling bonds of the Si surface atoms.

Likewise, the general trends discussed above are in agreement with those reported by the recent study of Dev *et al.*[13] However, while the relaxation and Al-Si distances for the relaxed T_4 model site are close to the present ones, the binding energy they report differs from the present one by a factor of about 2.5 and has to be attributed to the use of a minimal basis set.

TABLE VII. Vertical relaxation (Δz) in Å for the naked cluster models used in this work. ΔE refers to the energy increment (in kcal/mol) with respect to the unrelaxed clusters.

	Si_4H_7		Si_6H_9		Si_4H_9	
	ROHF	Nesbet	ROHF	Nesbet	ROHF	Nesbet
Δz	−0.050	−0.069	−0.035	−0.050	−0.039	−0.053
ΔE	−0.20	−0.40	−0.25	−0.46	−0.14	−0.25

TABLE VIII. Results for substrate relaxations. d_v(Si(1)-Si(2)) is the percentage change in vertical distance from the first to the second layer referred to the bulk. ΔE is the energy difference (in kcal/mol) between the relaxed and nonrelaxed Al-Si_nH_m energies at the minima. Symbols have the same meaning as that in Table V.

	Atop	H_3	T_4
d_v(Si(1)-Si(2)) (%)	10	13	60 (40)[a]
r_e	2.60	1.37 (1.23)	1.17 (1.15)[a]
$d_{\text{Al-Si}}$	2.60	2.60 (2.53)[a]	2.51 (2.49)[a] (2.44)[b]
ν_e	237.2	244.6	300.8 (430.6)[b]
BE ROHF	−39.9	−29.8	−43.4 (−108.6)[b]
Nesbet	−43.8	−41.5	−55.8
ΔE	0.65	8.0 (3.3)[a]	28.7(20)[a] (98.5)[b]

[a] Reference 9.

[b] Reference 13.

CONCLUSIONS

The interaction of atomic Al with cluster models simulating the atop, H_3, and T_4 structures has been studied at the *ab initio* SCF level.

From the computational point of view it is evidenced again that inclusion of polarization functions in the atomic basis set of the interacting atoms is necessary to properly describe the bond distances. This gives further support to the use of mixed basis sets as already indicated in Ref. 32.

The most favorable interaction, when the cluster geometry is unrelaxed, is the atop one. However, this is at variance with some earlier experimental and theoretical works that suggest a three-coordinated geometry.

The situation is reversed if the interlayer distance of the clusters models are allowed to vary. Thus, in the atop site the effect of relaxation is very small, but in the three coordinated positions the effect is considerable and becomes dramatically important in the fourfold T_4 position. The effect is due to a maximization of the bonding interactions between the adsorbate and the surface Si atoms as clearly appears from the schematic orbital representation depicted in Fig. 4.

It is important to stress once again the qualitative agreement between present results and the ones of Dev *et al.*[13] However, there are many points that have to be pointed out. First of all, these authors consider relaxation effects only for the T_4 position, and do not consider the relaxation of the isolated clusters. Moreover, their calculations have been carried out by using a minimal basis set and consequently their results are less accurate than the present ones, although they lead to identical conclusions.

Of particular interest is the comparison between the calculated vibrational frequencies and those suggested by the high-resolution electron energy loss (HREELS) experiments of Kelly *et al.*,[59] These authors show that among the three different possibilities, the vibrational peaks appearing at 443.6 and 524.0 cm^{-1} may be assigned to the Al adatoms adsorbed at the atop and T_4 sites, respectively. These values are close to the ones obtained by Dev *et al.*[13] using a minimal basis set, but due to the very small basis set they cannot be considered accurate enough. On the other hand, the present values, although they are about half the values proposed by Kelly *et al.*, show a difference of 63 cm^{-1} between the two possibilities, a value that is close to the experimental one of 81 cm^{-1} and the one reported by Dev *et al.*[13] which is of 53.2 cm^{-1}. At this point it is very difficult to assess if the differences between the present values and those suggested by Kelly *et al.*[59] are due to lateral interactions or to the assumption of a rigid substrate. On the other hand, the assignment of Kelly *et al.* is not definitive, nor are the calculated values due to the above discussion, and from the point of view of the vibrational frequencies the present values add only a weak argument to this assignment.

From the energy point of view it has to be pointed out that although the relaxed T_4 site is the most favored one, the atop possibility differs from the previous one only by about 4 kcal/mol and hence both possibilities have to be regarded as possible. This is in agreement with the discussion of Dev *et al.*[13] according to which Al chemisorption on a cold Si(111) surface takes place in a multisite way.

Finally, it has to be remembered that the present work has been carried out at the Hartree-Fock SCF level and hence lacks the effects of electronic correlation. The general trend is that correlation effects tend to slightly reduce the bond lengths and to increase the binding energy by about 10–15 %.[60] However, it is not clear if they would affect the binding energy of the atop and the T_4 situations to the same extent, although according to qualitative arguments the T_4 site may be slightly more favored since three chemisorption bonds are involved whereas only an Al—Si bond formation occurs in the atop situation. According to these arguments the T_4 position should be preferred in agreement with the present results.

Thus, the present results give further support to the adatom-induced relaxation earlier suggested by Northrup and are also in agreement with the more relevant experimental data, indicating the ability of these kind of approaches to deal with chemisorption and related phenomena.

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