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Evidence for two different bonding mechanisms of Al on Si(111)

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By means of the *ab initio* cluster-model approach, we present theoretical evidence for two different mechanisms of bonding of atomic Al to Si(111). On the atop site (T_1) the interaction of atomic Al to Si(111) is characteristic of an ionic bond whereas interaction above the threefold eclipsed site (T_4) leads to the formation of a typical covalent bond. Moreover, both sites have a similar interaction energy if electronic correlation effects are included. While the conclusions regarding the nature of the chemisorption bond in the two sites do not depend either on the cluster-model size, the kind of embedding hydrogen atoms used, or the quality of the wave function (Hartree-Fock or configuration interaction), the chemisorption energy depends strongly on the wave function used. In fact, inclusion of correlation energy is necessary to properly describe the interaction energies.

Deposition of a metal on a Si surface usually produces a thin metallic film of metal-silicide. The metal-semiconductor contact is a very important ingredient of the microelectronics technology due to the formation of Schottky barriers. However, these metallic films may lead to very complicated structures and many phases can be observed depending on the experimental conditions.[1] The question of coadsorption at different sites has also been raised by different authors[2–5] but a definitive answer is not yet available.

From previous theoretical works using periodic[5,6] or cluster models,[3,4] it is quite clear that the more likely sites for Al on Si(111) are the on-top (T_1) and the threefold eclipsed (T_4) ones. Moreover, there is evidence for an adsorbate induced-surface relaxation when considering the T_4 site[7,3,4] whereas the relaxation is fairly small for the atop T_1 site.[3,4]

In order to properly understand the experimental features of such a complex system, a deeper insight into the nature of the chemisorption bond at each of these sites seems mandatory. This is especially true when some experiments are interpreted assuming that covalency is dominating (see Refs. 3–5 and references cited therein), whereas information about the direction of the charge transfer is needed to interpret other experiments such as scanning tunneling microscopy images.[1]

Information about the degree of charge transfer at a given site can be obtained from theory by simply analyzing the dipole-moment curve for displacements of the adsorbate perpendicular to the surface near the equilibrium position (r_e) and by looking at the effects of an external uniform electrical field on r_e.[8,9] Both analyses can be done if a cluster model is used to simulate the surface. However, in order to have definitive answers about the nature of a given adsorbate-surface system, one has to avoid any possible bias arising from the finite size of the cluster model, the embedding scheme used to remove the edge effects, and from the particular kind of the wave function used.

In this work we will obtain *ab initio* Hartree-Fock and configuration-interaction wave functions for cluster models simulating the Si(111) surface and its interaction with atomic Al. From the analysis of the results we will present strong evidence that chemisorption of Al on Si(111) on the atop site (T_1) can be described as an ionic interaction whereas chemisorption on the threefold eclipsed (T_4) is of covalent character with a very small amount of charge transfer from Al to Si(111). These results will be shown to be independent of the particular cluster model employed, the use of different kinds of embedding hydrogen atoms (used to minimize cluster edge effects), and the kind of wave function used to carry out the analysis of the bond.

Chemisorption of the T_1 site has been simulated by the Si_4H_9 an $Si_{10}H_{15}$ cluster models [Fig. 1(a)] while chemisorption on the T_4 site has been simulated through the Si_4H_7 and Si_5H_9 ones [Fig. 1(b)]. Embedding hydrogen atoms are used to saturate the free valences of edge Si atoms. Two different kinds of embedding hydrogen atoms have been used. The first kind of embedding hydrogen atoms is just normal hydrogen atoms as in our previous work[4] and the second kind consists of modified hydrogen atoms (siligens) that mimic the electronegativity of Si.[10,11] Cluster models with modified hydrogen atoms are represented as $Si_n\overline{H}_m$ to distinguish them from those using normal hydrogen atoms (Si_nH_m). *Ab initio* Hartree-Fock self-consistent-field (SCF) calculations have been carried out for the Si_nH_m-Al and $Si_n\overline{H}_m$-Al cluster

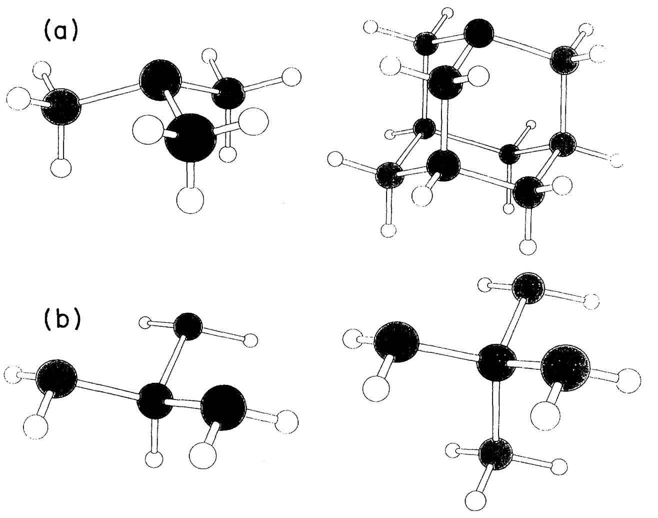

FIG. 1. Schematic representation (a) of the Si_4H_9 and $Si_{10}H_{15}$ cluster models used to simulate the T_1 site of the Si(111) surface and (b) of the Si_4H_7 and Si_5H_9 models simulating the T_4 site.

models using nonempirical pseudopotentials and moderately large basis sets (double-*z* plus polarization on the interacting atoms, double-*z* otherwise and minimal basis set on the embedding hydrogen atoms). For the smaller cluster models (Si_4H_9Al and Si_4H_7Al), the dipole-moment curve has been obtained using variational multideterminantal wave functions including the most important determinants selected through the second-order many-body perturbation theory [configuration interaction by perturbative selective iteration (CIPSI)] algorithm.[12,13] Active orbitals were selected after a corresponding orbital analysis, and the variational configuration-interaction expansion (CI) thus constructed contains around 15 000 determinants.

In Table I we report the equilibrium perpendicular distance above the surface (r_e) and the dipole-moment curve corresponding to a Taylor expansion,

$$\mu(r)=M_0+M_1(r-r_e)+M_2(r-r_e)^2+\cdots \ . \tag{1}$$

For an ionic interaction, we expect $M_1\approx 1$ and $M_2\approx 0$ while for a covalent interaction M_1 should be much smaller and M_2 larger.[8,9] Results in Table I unequivocally show that the nature of bonding on T_1 and T_4 is very different. For the T_1 site, M_1 is near unity and M_2 is very small irrespective of the cluster size, the kind of embedding hydrogen atoms, and the kind of wave function. This strongly indicates that the nature of the interaction of Al on Si(111) on the T_1 site is largely ionic. For the T_4 site, results are just the contrary, with the smaller M_1 and larger M_2 suggesting that the bond is largely covalent with a small (<0.4) charge on chemisorbed Al.

The above analysis is fully confirmed by the *ab initio* Hartree-Fock (SCF) calculations carried out explicitly including the effects of a uniform external field. For an ionic bond we expect large variations on r_e in response to the field while r_e will not be affected for a covalent bond with no (or little) charge transfer. Results for the electric-field effects are reported in Table II for electric fields of ± 0.01 a.u. (5.2×10^7 V cm^{-1}). Electric fields produce large variations on r_e for the T_1 site and rather small variations on r_e for the T_4 site cluster models. In fact, the effects on the T_1 site are at least four times larger than on the T_4 site. Moreover, these effects do not depend on the cluster size nor do they depend on the use of hydrogens or siligens (results for the latter are not reported here). Again, the picture of the bonding of Al on the Si(111) emerging from this analysis is different at each site. Combination of both analyses reveals a dominating ionic interaction on the T_1 site and a mostly covalent interaction on the T_4 site.

A final point concerns the energetics of the chemisorption process. We report in Table III the interaction energy for atomic Al above either the T_1 or T_4 sites computed as

$$D_e=E(\mathrm{AlSi}_n\mathrm{H}_m)-E(\mathrm{Al})-E(\mathrm{Si}_n\mathrm{H}_m) \tag{2}$$

at the SCF level and as

$$D_e=E(\mathrm{AlSi}_n\mathrm{H}_m \text{ at } r_e)-E(\mathrm{Si}_n\mathrm{H}_m \text{ at large } r_e) \tag{3}$$

at the CI level. The ground state of each system is used in Eq. (2) and also in Eq. (3) for the calculation at r_e. The CI calculation at large distance has been performed by starting from the superposition of the SCF ground-state wave functions of both systems. At the CI level, the electronic energy contains the contribution arising from the variational wave function plus the second-order contribu-

TABLE I. Equilibrium distance perpendicular to the surface and dipole-moment curve [see Eq. (1)] for the series of cluster models used in this work. All results are in atomic units.

Site	Cluster model	Wave function	r_e	M_0	M_1	M_2
T_1	Si_4H_9	SCF	4.952	0.583	1.068	-0.039
	$Si_4\bar{H}_9$	SCF	4.985	1.435	1.261	$+0.024$
	Si_4H_9	CI	4.991	0.632	0.999	$+0.027$
	$Si_{10}H_{15}$	SCF	4.988	1.014	1.322	$+0.055$
T_4	Si_4H_7	SCF	3.120	0.995	0.495	-0.128
	$Si_4\bar{H}_7$	SCF	3.032	1.295	0.539	-0.051
	Si_4H_7	CI	3.310	0.713	0.424	-0.050
	Si_5H_9	SCF	3.136	1.647	0.410	-0.124

TABLE II. Effect of a uniform external electric field on r_e for a series of cluster models. All results are in atomic units and are at the *ab initio* Hartree-Fock level.

Site	Cluster model	Field	r_e (Δr_e)
T_1	Si_4H_9	+0.01	5.233 (+0.281)
		0.0	4.952
		−0.01	4.812 (−0.140)
	$Si_{10}H_{15}$	+0.01	5.353 (+0.365)
		0.0	4.988
		−0.01	4.798 (−0.190)
T_4	Si_4H_7	+0.01	3.191 (+0.071)
		0.0	3.120
		−0.01	3.081 (−0.039)
	Si_5H_9	+0.01	3.115 (+0.070)
		0.0	3.136
		−0.01	3.116 (−0.020)

TABLE III. Interaction energy (in kcal/mol) for atomic Al on the cluster models simulating the T_1 and T_4 sites of the Si(111) surface.

Site	Cluster Model	D_e (SCF)	D_e (CI)
T_1	Si_4H_9Al	39.6	45.6
	$Si_{10}H_{15}Al$	40.6	
T_4	Si_4H_7Al	15.7	47.9
	Si_5H_9Al	19.2	

tion of all those determinants generated by single and double excitations from the reference space which are not included in the variational wave function (see Refs. 12 and 13).

From Table III it is clear that at the SCF level the T_1 interaction is the most favored, contrary to the experimental observation that the T_4 phase is the most common one.[1] Moreover, the SCF energies are not largely dependent on the cluster size. However, when electronic correlation effects are included, the T_4 site appears to be the most stable. This is in agreement with the formation of a T_4 phase but the T_1 interaction cannot be ruled out. However, it is worth pointing out that the T_4 interaction leads to an adsorbate-induced relaxation which again favors the T_4 interaction more than the T_1 one.[4]

In this work we have shown that atomic aluminum can bond to Si(111) in two different ways. If chemisorption occurs at the atop T_1 site a bond with a large ionic character is formed and very large adsorbate-adsorbate interactions are expected, whereas if chemisorption occurs at the T_4 site (as in the $\sqrt{3}\times\sqrt{3}/R30^\circ$ phase) a covalent bond is formed with a very small amount of charge transfer from Al to Si (if any). From the energetic point of view both interactions are likely to occur (at least at low coverages).

Our conclusions are based on the *ab initio* cluster method applied to a series of cluster models of increasing size and using different kinds of embedding hydrogen atoms. The analysis of the nature of the bond has been carried out using *ab initio* Hartree-Fock and configuration-interaction wave functions including the leading instantaneous electron-electron correlation effects. Thus, as far as the nature of the bond is concerned, the conclusions of this work do not depend either on the cluster size, the kind of embedding hydrogen atoms used to saturate the free valences of nonsurface Si cluster atoms, or the quality of the wave function. However, a proper description of the energetics of the process requires the inclusion of the electronic correlation effects. We hope that the description of the nature of the chemisorption bond achieved by these techniques will help form a better understanding of these complex metal-semiconductor systems.

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