

## First-principles investigation of geometric and electronic structures of aluminum adsorbed on silicon surfaces

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The electronic structure of aluminum-adsorbed silicon (111) surfaces has been studied by the self-consistent-field Hartree-Fock cluster method with the aim of obtaining definitive assignments of the adsorption site(s). Calculations have been made for clusters representing adsorption at different high-symmetry sites, namely, substitutional, atop, open, and eclipsed. Besides the studies of adsorption at all these sites on the ideal surfaces, an adsorption study on a relaxed substrate has been made for the eclipsed site. Minimization of the total energies of the clusters with respect to the vertical distance of the adatom from the surface silicon layer leads to Si—Al bond lengths of 2.26, 2.37, 2.55, 2.68, and 2.44 Å for the substitutional, atop, open, eclipsed, and relaxed eclipsed sites, respectively, the corresponding binding energies being 9.50, 3.94, 1.96, 0.59, and 4.21 eV. Assuming that the surface vacancies are not abundant at low temperature ( $< 300^\circ\text{C}$ ), so that substitutional adsorption is insignificant, it is proposed that there is coadsorption at the relaxed eclipsed and atop sites. This assignment is shown to provide successful explanations of low-energy electron diffraction and ultraviolet photoemission data and vibrational frequency data from high-resolution electron-energy-loss spectroscopy measurements. Vibrational amplitudes of the adatoms have been predicted. Also, it is shown that the results for the Si—Al bond distances modified to apply to the Si-Ga system explain the x-ray standing-wave results for Ga-adsorbed Si(111) surfaces.

### I. INTRODUCTION

Metal-semiconductor interfaces are technologically important because Schottky barriers, a major component in solid-state devices, are formed at such interfaces. A large number of experimental and theoretical investigations of semiconductor surfaces with metal overlayers<sup>1–12</sup> have been made to study the geometric and electronic structure of the interfaces. The adsorption of Al on Si(111) surfaces has been studied experimentally using techniques such as low-energy electron diffraction (LEED),<sup>2–4</sup> ultraviolet photoemission spectroscopy (UPS),<sup>5</sup> angle-resolved ultraviolet photoelectron spectroscopy (ARUPS),<sup>6</sup> electron-energy-loss spectroscopy (EELS),<sup>3</sup> and high-resolution electron-energy-loss spectroscopy (HREELS),<sup>4</sup> and theoretically by the self-consistent pseudopotential technique<sup>7–9</sup> and extended Hueckel theory.<sup>10</sup>

In all previous theoretical studies except Ref. 9, the calculations were done with preselected Si—Al bond distances instead of ones determined from energy minimization. Moreover, in none of the previous investigations have enough high-symmetry adsorption sites been considered. Thus, considerations have been given to only the substitutional site in Ref. 7; to substitutional, atop, and open sites in Ref. 8; to substitutional and open sites in Ref. 10; and to open and eclipsed sites in Ref. 9. In all these works except for Ref. 9, the Al atom was placed at different sites on the Si(111) surfaces and the electronic local density of states (LDOS) was calculated for each site. The LDOS's were then compared with the UPS spectra from Al-adsorbed Si(111) surfaces in order

to determine the adsorption site. This is an indirect method for the determination of the structure of the interface and could lead<sup>13,14</sup> to erroneous results. Possible sources for the misdetermination of the adsorption site in this approach are the effects of the oscillator strengths for the photoelectric transition in the UPS spectra with which the LDOS is compared, or the preselection of the host-adatom distance in the calculation, since the nature of the bond, for instance its ionicity, depends on this distance.<sup>15</sup>

In Ref. 9, the Si—Al bond length was determined using the energy-minimization criterion. However, in this investigation only two adsorption sites were studied, namely the open and the eclipsed sites. By LEED experiments, Lander and Morrison<sup>2</sup> have discovered five different phases of Al-adsorbed Si(111) surfaces, depending on the adsorbate coverage and substrate temperature. This indicates the possibility of adsorption at different sites. This multiphase feature has also been observed in the adsorption of other group-III metals, such as Ga (Ref. 12) and In (Ref. 2), on Si(111) surfaces.

In addition to attempting to understand the interesting nature of the Si(111)-Al interface itself, another motivation for the present work was to provide an explanation of the x-ray standing-wave interference spectrometry (XSWIS) results of Ga-adsorbed Si(111) surfaces obtained in our laboratory.<sup>16</sup> Aluminum was used in this computation because the valence shell of Al is isoelectronic with Ga, and therefore the bonding behavior is expected to be similar. Besides, Al has fewer total electrons, and is more amenable to calculations. The XSWIS technique measures the Fourier components of the adsorbate-atom distribution function. When all the adatoms are adsorbed at

a single adsorption site, the extraction of the adsorption site and the corresponding host-adatom distance is relatively simple.<sup>17,18</sup> However, for multisite adsorption, the result of the XSWIS analysis is the combined effect of the different response functions arising from the adsorbed atoms at different sites.<sup>19</sup> This complicates the extraction of the adsorption sites and the corresponding host-adatom bond lengths. In this situation, a knowledge of the probable adsorption site(s), which can be obtained,<sup>15,18</sup> by computing and comparing the binding energy per adatom for various possible sites, and of the corresponding host-adatom bond length is extremely helpful.<sup>19</sup>

The present work is mainly concerned with the determination of the probable adsorption site(s) and the corresponding host-adatom bond length(s). We have studied the optimum configuration of the Al-covered Si(111) surface with the Al atom at the substitutional, atop, open, and eclipsed sites. For adsorption at the substitutional site, the aluminum atoms occupy surface vacancies. In the atop site an Al atom is directly attached to the dangling bond of a surface silicon atom. The open and the eclipsed sites are both threefold, and also above the surface layer, the first being directly over the fourth-layer and the second over the second-layer silicon atoms. The adsorbate-covered surface has been simulated by clusters (Fig. 1) representing adsorption at the aforementioned sites, and the self-consistent-field (SCF) Hartree-Fock linear combination of atomic orbitals (LCAO) method has been used for computing the total energy of each cluster as a function of host-adatom distance. For a particular cluster, the optimized bond length corresponds to the minimum total energy. The total energy of each cluster was then calculated without the adatom and the binding energy was computed from the difference of total energies with and without the adatom.

The rest of this paper is arranged in the following way. Section II describes the cluster models for different adsorption sites. The procedures used for obtaining the electronic structures and the properties considered, namely, binding energies, bond lengths, density of states, and vibrational frequencies and amplitudes for the adatom, are presented in Sec. III. Section IV contains the results, including the assignment of the adatom site(s), and discussions, which are followed by the conclusions presented in Sec. V.

## II. CLUSTER MODELS

A surface, due to the absence of neighbors on one side, usually relaxes and reconstructs in order to gain stability. In relaxation the surface atoms undergo an inward or outward displacement with respect to their bulk position, whereas the lateral symmetry changes upon reconstruction. The Si(111) surface relaxes and reconstructs. However, there is evidence that upon chemisorption of certain elements<sup>20</sup> (usually hydrogen and halogens) the  $7 \times 7$  reconstructed Si(111) surface comes back to the ideal  $1 \times 1$  structure. Our cluster calculations<sup>18,21</sup> for halogen chemisorption on Si(111) surfaces with the ideal  $1 \times 1$  structure without relaxation were successful in explaining the host-adatom bond lengths and available UPS spectra. Al-adsorbed Si(111) surfaces have been found<sup>2,4</sup> to have

different phases with  $\sqrt{3} \times \sqrt{3} R30^\circ$ ,  $7 \times 7$ , and  $1 \times 1$  LEED patterns. The four sites we have considered for the Si(111)-Al system would be consistent with the occurrence of these phases. Additionally, for the eclipsed site, which as will be shown is one of the most likely sites, we have included relaxation effects.

Figure 1 shows the cluster models used for adsorption at the (i) substitutional, (ii) atop, (iii) open, and (iv) eclipsed site on ideal Si(111) surfaces, and at the (v) eclipsed site on a relaxed surface. When surface vacancies are available the Al atoms may be adsorbed at those vacancies, that is, at substitutional sites. For the atop-site adsorption an Al atom is directly over a surface Si atom. The open and the eclipsed sites are both threefold and above the surface, the former, as mentioned earlier, being directly over the fourth-layer and the latter over the second-layer Si atoms.

We are interested in determining the binding energy and host-adatom bond length for each adsorption site. In earlier cluster calculations for the Cl-adsorbed Si(111) surfaces,<sup>16,21</sup> we have obtained rapid convergence of these quantities with respect to cluster size. This convergence appeared to be closely related to the strong localization of the interaction of the adatom with its immediate neighbors, a feature also observed in the cluster investigations by Seel and Bagus.<sup>15</sup> In the present work we have tested the convergence with respect to cluster size only for the

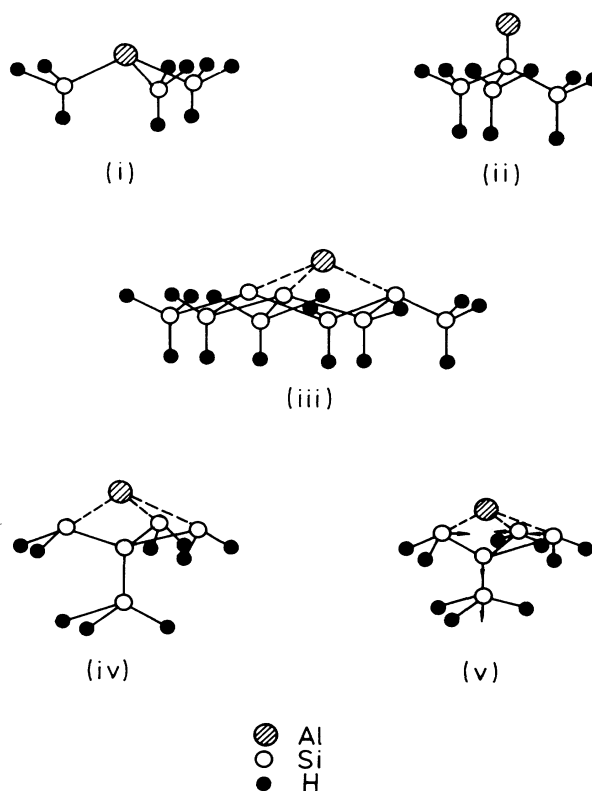


FIG. 1. Clusters representing adsorption of aluminum at different high-symmetry sites on Si(111) surfaces; (i) substitutional, (ii) atop, (iii) open, (iv) eclipsed, and (v) eclipsed with relaxation. In (v), the arrows indicate the directions of displacement.

atop-site adsorption and found a similar localized feature for the Al-Si interaction. It has been assumed that the same feature will hold true for other adsorption sites, and only one cluster, the largest possible (limited by the size of the basis set we can use with our computing facilities), has been considered for each adsorption configuration.

A finite cluster is, in principle, a part of an infinite system, and therefore the boundary of the cluster in the bulk should be terminated in such a way that the termination procedure produces the effect of the rest of the substrate on the cluster. This is referred to in the literature as embedding. For silicon substrates, replacement of the directed covalent Si—Si bonds across the cluster boundary by Si—H bonds has been found to be adequate for this purpose.<sup>15,21</sup> The H atom forces the Si atom at the boundary to have bulk  $sp^3$  hybridization and effectively saturates the bond that would otherwise dangle into the bulk. H atoms also provide the proper atomic coordination for a nonsurface Si atom. The Si-H distance has been taken to be 1.48 Å. Our results were actually quite insensitive to the choice of the Si-H distance. For clusters (i)–(iv) in Fig. 1, the Si-Si distance is 2.35 Å, the bulk Si-Si distance. For the fifth cluster involving relaxation effects, the Si-Si distances are different. These will be discussed later.

### III. PROCEDURE

The self-consistent-field Hartree-Fock procedure with Gaussian basis sets<sup>21–24</sup> has been used for the electronic structure calculations. We used the restricted Hartree-Fock (RHF) method of Roothaan<sup>25</sup> for closed-shell configurations with aluminum present and the unrestricted Hartree-Fock (UHF) method of Pople and Nesbet<sup>26</sup> for open-shell configurations with no aluminum. The basis functions chosen for the calculations are of the STO-3G type,<sup>23</sup> consisting of three primitive Gaussian functions contracted to represent a Slater-type atomic function corresponding to each atomic orbital on each atom in the cluster. The basis functions used are taken from Ref. 23. Molecular calculations using this type of basis functions have been found to provide<sup>27</sup> good results for equilibrium geometries. Also, the computed bond length and the electronic local density of states from our previous cluster calculations for chlorine-adsorbed silicon surfaces<sup>21</sup> employing this type of basis functions were in very good agreement with the observed Si—Cl bond length and UPS spectra. Further, in a recent calculation<sup>28</sup> on the electronic structure of muonium trapped in diamond, a similar choice of basis sets provided good results for the hyperfine field at the muon location.

The size of the cluster in Hartree-Fock calculations is often limited by the size of the basis set. However, cluster calculations using only valence electrons and introducing the effect of the core electrons through the effective-potential approximation<sup>29</sup> have provided comparable results to all-electron calculations.<sup>16,18,21</sup> Thus for the Si(111)-Cl system<sup>16,21</sup> the one-electron energies corresponding to the molecular orbitals (MO's) that have predominantly valence-electron character agree, within 0.2% for the two types of calculations. The Si—Cl bond

length agreed to within 1% in the two cases and the computed binding energies differed only by about 2%.<sup>16</sup> In the present study, the largest cluster involves 25 atoms [Si<sub>9</sub>H<sub>15</sub>Al; Fig. 1 (iii)], for which we could perform only effective-potential calculations. Therefore, in order to make a comparison among the clusters, we have presented in all cases the results of effective-potential calculations.

#### A. Bond lengths and binding energies

The Si—Al bond length has been determined by computing the total energy as a function of the distance of the Al atom from the surface plane and obtaining the minimum. The binding energy  $D_e$  was then calculated from the relationship

$$D_e = (E_b + nE_a - E_c)/n, \quad (1)$$

where  $E_b$  is the energy of the bare cluster (without Al),  $E_a$  is the energy of the isolated adatom,  $E_c$  is the energy of the covered cluster at the optimized host-adatom distance, and  $n$  is the number of adatoms. Since in all the clusters in Fig. 1 there is only one adatom, there are no adatom-adatom interactions present.

The electronic wave functions and the total energies were obtained by SCF-LCAO-MO Hartree-Fock procedure using the GAUSSIAN-80 systems of computer programs<sup>30</sup> adapted to Univac 1100 series of computers.

#### B. Electronic local density of states (LDOS)

In order to make a comparison with the experimental UPS spectra it is necessary to obtain the local-density-of-states curve from the one-electron energy levels associated with the molecular orbitals of the cluster. For a finite cluster one obtains a discrete set of energy levels. But for an infinite system like a surface, one expects continuous bands of energy eigenvalues. Therefore, the discrete energy levels obtained from the cluster need to be broadened to give them an appearance of a band in order to make a comparison with what would be expected from an actual surface system. We have used a Lorentzian broadening procedure<sup>31</sup> to obtain the electronic local density of states using the following expression:

$$D(\epsilon) = \sum_i \frac{\lambda/\pi}{(\epsilon - \epsilon_i)^2 + \lambda^2}, \quad (2)$$

where  $D(\epsilon)$  is the density of states at energy  $\epsilon$ ,  $\epsilon_i$  are the discrete energy levels, and  $\lambda$  is a parameter defining the amount of broadening. The value of  $\lambda$  chosen for the present work is 0.8, the same as that used for the Si(111)-Cl system,<sup>21</sup> where this choice provided the best fit of the computed LDOS to the experimental UPS spectra.<sup>13</sup> The choice of  $\lambda$  does not significantly affect the positions of the peaks. However, it does affect their heights depending on the closeness of the energy levels in the particular energy regions. In order to make a comparison of the peak intensities in the UPS spectrum with theory, one needs to include the appropriate oscillator strengths.

### C. Vibrational frequencies and vibrational amplitudes

The force constant for the vibration of an adatom in a direction normal to the surface can be derived from the total-energy curve. In the harmonic approximation, the vibrational energy  $\hbar\omega$  is given by

$$\hbar\omega = \hbar(k/m_A)^{1/2}, \quad (3)$$

where  $k$  is the curvature of the total-energy curve at the equilibrium distance  $x_0$  and  $m_A$  is the mass of the adatom. The substrate has been assumed to be rigid, a reasonable assumption for a relatively light atom like aluminum.

The knowledge of thermal vibrational amplitude of the adatoms is required for a very accurate analysis of the data obtained by the XSWIS measurements. Some surface parameters, e.g., surface melting temperature,<sup>32</sup> are related to the vibrational amplitude. The vibrational amplitude can be obtained from LEED intensity measurements<sup>32</sup> as a function of temperature. It can also be obtained by the XSWIS technique by comparing the results of measurements using different orders of reflections. One such measurement of the vibrational amplitude of bromine on the germanium (111) surface has recently been made.<sup>33</sup> A knowledge of vibrational amplitudes is also of interest in ion-channeling measurements.<sup>34</sup> In view of these results, it is considered worthwhile to evaluate the amplitude of thermal vibration of the adsorbed atoms.

Once the frequency  $\omega$  is known, the amplitude of thermal vibration of the adatom can be obtained in the following manner. For a harmonic oscillator in thermal equilibrium at temperature  $T$ , the mean-square amplitude  $\langle u^2 \rangle$  is given by<sup>35</sup>

$$\langle u^2 \rangle = (\hbar/m_A\omega) \left\{ \frac{1}{2} + 1 / [\exp(\hbar\omega/k_B T) - 1] \right\}, \quad (4)$$

where  $k_B$  is Boltzmann's constant, and  $m_A$  is the mass of the adatom, assuming the substrate to be rigid and neglecting the adatom-adatom interactions. In the real system, however, the surface atoms in the substrate will also vibrate with an amplitude in general given by<sup>36</sup>

$$\langle u_s^2 \rangle = \alpha \langle u_b^2 \rangle, \quad (5)$$

where the subscripts  $s$  and  $b$  stand for surface and bulk, respectively. Since the vibrations of the adatoms and the substrate surface atoms would be incoherent, the effective root-mean-square amplitude,  $\langle u_{\text{eff}}^2 \rangle^{1/2}$ , of the adatom will be given by

$$\langle u_{\text{eff}}^2 \rangle^{1/2} = (\langle u^2 \rangle + \langle u_s^2 \rangle)^{1/2}. \quad (6)$$

For a bare surface, the factor  $\alpha$  in Eq. (5) has been found to vary in the range 1–3.5 (Ref. 37) for various surfaces, most of them lying around 2. While the vibrational amplitude of the surface atoms, when the surface is adsorbate covered, could be different from the corresponding bare-surface value, Eq. (5) with  $\alpha=2$  will be a reasonable approximation for calculating the effective vibrational amplitudes of the adsorbed atoms.

The effective vibrational amplitudes obtained by this procedure for fluorine, chlorine, bromine, and iodine, at the atop site on the silicon (111) surface were 0.12, 0.12,

0.11, and 0.11 Å, respectively.<sup>16,18,38</sup> These values were obtained with  $\langle u_b^2 \rangle = 0.078$  Å; the silicon bulk vibrational amplitude<sup>39</sup> at room temperature. The only experimental value available for a similar system, bromine adsorbed at the atop site on germanium (111) surfaces, gives an upper limit of 0.120 Å.<sup>33</sup> In this connection the germanium bulk vibrational amplitude at room temperature, 0.084 Å,<sup>33</sup> is not too different from the corresponding value for silicon.

## IV. RESULTS AND DISCUSSIONS

### A. Binding energies and the structure of the Si(111)-Al interface

For each of the clusters  $\text{Si}_3\text{H}_9\text{Al}$ ,  $\text{Si}_4\text{H}_9\text{Al}$ ,  $\text{Si}_9\text{H}_{15}\text{Al}$ ,  $\text{Si}_5\text{H}_9\text{Al}$ , and  $\text{Si}_5\text{H}_9\text{Al}$  used to represent the aluminum-adsorbed surface with the Al atoms at the substitutional, atop, open, eclipsed, and relaxed eclipsed sites, respectively, the optimum configuration has been obtained by minimizing the total energy of the cluster as a function of the distance of the Al atom from the surface Si plane. Each cluster contains an even number of electrons, and therefore we used a spin multiplicity of 1 (singlet state) for the ground state. This would correspond to a diamagnetic surface. For the calculation of the total energies of the open-shell clusters representing bare surfaces,  $\text{Si}_3\text{H}_9$ ,  $\text{Si}_4\text{H}_9$ ,  $\text{Si}_9\text{H}_{15}$ ,  $\text{Si}_5\text{H}_9$ , and  $\text{Si}_5\text{H}_9$ , different spin multiplicities have been used. All these clusters and the corresponding covered ones belong to  $C_{3v}$  symmetry. For the clusters  $\text{Si}_3\text{H}_9$ , a multiplicity of 4 has been used. A multiplicity of 2 has been used for  $\text{Si}_4\text{H}_9$ , corresponding to the  $a_1$  configuration. Each of the clusters  $\text{Si}_9\text{H}_{15}$  and  $\text{Si}_5\text{H}_9$  has three dangling bonds of the  $sp_2$  type. The multiplicity for these clusters has been chosen to be four, corresponding to the configuration  $a_1^4 e^2$ . The basis for this latter choice is that, in a comparative study on slightly different clusters but with the same feature of three dangling bonds normal to the surface, Seel and Bagus found the ground state to involve an  $a_1^4 e^2$  configuration, the quartet  $^4A$  state having the lowest energy compared to the other possibilities:  $^2A_2$ ,  $^2E$ , and  $^2A_1$ .<sup>15</sup> The binding energies have been computed using Eq. (1). These are shown in Table I.

As we see from the positive signs of the binding energies in Table I, adsorption of aluminum on silicon (111) surfaces is possible at more than one site, which is compatible with Lander and Morrison's observation<sup>2</sup> of different phases depending on the aluminum coverage and the substrate temperature. Let us first focus our attention on the first four cases in Table I. The largest binding energy for Al at the substitutional site indicates that this is the most probable adsorption site. The large binding energy for this site is not unexpected, because it involves three strong covalent bonds with three nearest-neighbor Si atoms with the Si—Al bond length slightly smaller than the sum of the covalent radii [1.17 Å (Si) + 1.18 Å (Al) = 2.35 Å]. However, substitutional sites or surface vacancies are not expected to be abundant at room temperature, because creation of such a vacancy requires breaking of three strong Si—Si bonds. At an elevated temperature, however, this could be a favored situation and would agree with the model of Lander and

TABLE I. Optimized bond lengths and binding energies for different adsorption sites of Al on Si(111) surfaces.

Adsorption site	Bond length Si—Al (Å)	Binding energy $D_e$ (eV/adatom)
Substitutional	2.26	9.50
Atop	2.37	3.94
Open	2.55	1.96
Eclipsed	2.68	0.59
Relaxed eclipsed	2.44	4.21

Morrison,<sup>2</sup> which proposes the substitutional replacement of surface Si atoms by Al atoms. According to their observation, high temperature is required for this process involving long-range migration of Si atoms or vacancies. They observed this phase when a full monolayer of Al was evaporated onto a hot (500–800 °C) Si(111)7×7 surface. However, the first phase they observe corresponding to evaporation of  $\frac{1}{3}$  monolayer of Al on the substrate kept above 500 °C is the  $\alpha$ -Si(111) $\sqrt{3}\times\sqrt{3}$ -Al. In this phase, the surface unit mesh is rotated 30° and its translational periodicities are  $\sqrt{3}$  times enlarged relative to the ideal substrate unit mesh. This surface unit mesh is not likely to arise from the adsorption at the substitutional site or the atop site,<sup>40</sup> which is seen from Table I to have the next largest binding energy among the four adatom sites considered for an ideal surface. In fact, this phase would be consistent with the adsorption at the threefold open or eclipsed site, but from the binding-energy considerations they are less probable adsorption sites. This inconsistency led us to explore the relaxed configuration shown in Fig. 1 (v) for the eclipsed site. The reason for choosing the latter site is that in earlier investigations comparing the open and the eclipsed sites, Northrup<sup>9</sup> found the Al atoms at the eclipsed site with a relaxed configuration to be more stable compared to the open site even though on an unrelaxed surface the binding energy for the eclipsed site was found to be smaller, a feature shared with our work. Also, the computed dispersion of the surface states from the relaxed eclipsed model<sup>9</sup> was found to be in good agreement with the results of angle-resolved photoemission experiments<sup>6</sup> on the  $\alpha$ -Si(111) $\sqrt{3}\times\sqrt{3}$ -Al phase. As seen from Table I, we indeed find a substantial gain in binding energy for the relaxed eclipsed configuration. This binding energy is seen to be larger compared to not only the unrelaxed eclipsed site but also the open and the atop sites. Our computed Si—Al bond lengths for the open and the relaxed eclipsed sites (Table I) are also in good agreement with those of 2.53 and 2.50 Å, respectively, in Ref. 9.

The displacements of the substrate atoms in our relaxed model are not too different from Northrup's.<sup>9</sup> In our model the surface Si atoms are displaced by 0.14 Å towards the axis passing through the second-layer Si atom and the Al atom [Fig. 1(v)]. The second- and third-layer Si atoms move downwards by 0.32 and 0.16 Å, respectively. These displacements allow the Al atom to be closer to the surface Si atoms and still maintain a reasonable distance (2.37 Å) from the second-layer Si atom.

The binding energy (3.99 eV/adatom) with respect to the ideal surface plus a free Al atom is less than the binding energy (4.21 eV/adatom) with respect to the relaxed surface plus a free Al atom. This means that, for a bare surface (that is, without Al), the relaxed surface has a higher energy than the ideal one, which indicates that the relaxation is adatom induced.

Regarding the interface structure, one can assume that a significant number of surface vacancies are not available at room temperature. This is because at room temperature one does not expect any new vacancies to be produced besides the existing holes in the Si(111)7×7 surface, that is, approximately  $\frac{1}{49}$  monolayer. From a consideration of the binding energies in Table I one then expects the Al atoms to be adsorbed at the relaxed eclipsed site. This explains the  $\alpha$ -Si(111) $\sqrt{3}\times\sqrt{3}$ -Al phase corresponding to  $\frac{1}{3}$ -monolayer coverage observed by LEED measurements.<sup>2</sup>

The binding energy for the atop site is slightly smaller than that for the relaxed eclipsed site. This indicates that if the temperature of the substrate is low enough so that desorption or migration does not occur, then Al atoms can be coadsorbed at both these sites. This is in agreement with the observation<sup>2</sup> of a mixture of  $\alpha$ -Si(111)7×7-Al and  $\alpha$ -Si(111) $\sqrt{3}\times\sqrt{3}$ -Al phases when about  $\frac{1}{3}$  of a monolayer of Al was evaporated onto the cold (less than 300 °C) Si(111)7×7 surface. This mixed phase readily changed into a complete  $\alpha$ -Si(111) $\sqrt{3}\times\sqrt{3}$ -Al phase upon heat treatment above 500 °C. This observation could be explained by the migration of the Al atoms at this temperature from the atop site to the lower-lying relaxed eclipsed site causing a full conversion to the  $\sqrt{3}\times\sqrt{3}$  phase. Later we will show that the coadsorption at the atop and the relaxed eclipsed sites provides a good explanation of the observed UPS spectra<sup>5</sup> for a sample prepared at 110 °C substrate temperature.

As we mentioned before, one of our motivations for the present work was to provide an explanation of the results of XSWIS measurements of gallium adsorbed on silicon (111) surfaces at room temperature.<sup>16</sup> We estimate the Si—Ga bond length for each adsorption site by adding the difference (0.08 Å) of covalent radii of Al and Ga to the computed Si—Al bond length. Then assuming that Ga follows the same binding-energy trend as Al, we consider that there is coadsorption of the gallium atoms at the atop and the relaxed eclipsed configuration. The XSWIS results<sup>16</sup> are explained by assigning equal populations to these two sites. Two adsorption states, with a binding-energy difference of about 0.2 eV (not too different from the binding-energy difference of 0.27 eV that has been obtained in this work for the atop and the relaxed eclipsed sites for Al), were also identified in the thermal desorption studies of gallium adsorbed on Si(111)7×7 surfaces.<sup>12</sup> On a hot substrate, the  $\sqrt{3}\times\sqrt{3}R30^\circ$  LEED pattern was observed corresponding to  $\frac{1}{3}$ -monolayer coverage as in the case of Al.

## B. Electronic local density of states

The electronic local density of states for each model in Fig. 1, obtained using the procedure discussed in Sec. III B, is shown in Fig. 2. The ultraviolet photoemission

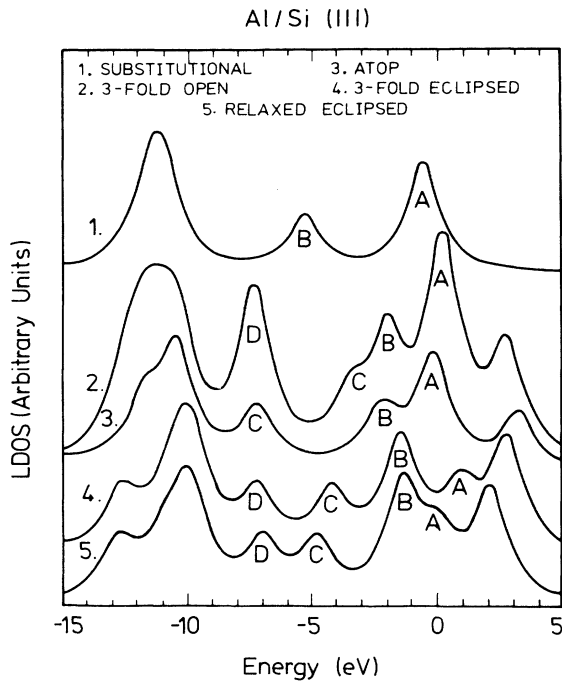


FIG. 2. Local-density-of-states curves for the Si(111)-Al system for different adsorption sites of Al. The zero of energy is at the valence-band maximum.

spectra for Al-adsorbed Si(111)7×7 surfaces are shown in Fig. 3.<sup>5</sup> In order to isolate the metal-related features in the UPS spectra it is convenient to take the difference between the spectra for metal-covered and clean surfaces. Before taking the difference the spectra have to be aligned at some bulk silicon features to remove “derivative” effects present on difference curves due to changes in band bending.<sup>5</sup> Figure 3(b) shows the experimental difference spectra. The peaks shown in Fig. 3(b) are metal-related peaks. These peaks do not correspond to the features in the pure metal photoemission spectra<sup>5</sup> but are related to chemical bonds at the interface. The energies of these peaks and of those in Fig. 2 near the valence-band maximum (VBM) in the theoretical LDOS are listed in Table II. The rest of the peaks occur at very different energies from the experimental peaks in Fig. 3. The similarity of the LDOS near the VBM for the relaxed eclipsed configuration to the low-coverage experimental spectrum [curve 1 in Fig. 3(b)] is clear. These two peaks (*A* and *B* in Fig. 2) in the LDOS are metal related, the peak *A* being Si—Al  $\sigma$  type and *B* being Si—Al  $\pi$  type for the eclipsed site. However, adsorption at the relaxed eclipsed site cannot explain the observed low-energy broad peak at  $-2.0$  eV (from the VBM). From the binding energies in Table I, as discussed earlier, adsorption at the atop site is almost equally probable to the adsorption at the relaxed eclipsed site. Let us examine the LDOS for the atop configuration (curve 3 in Fig. 2). The peak *B* is at  $-2.0$  eV and is Si—Al  $\sigma$  type. Peak *A* is Si  $\pi$  type and thus not metal related. Therefore, coadsorption of Al at the

relaxed eclipsed site and the atop site can explain all three peaks observed in the UPS spectra.

For the UPS experiments<sup>5</sup> the substrate temperature was below  $110^\circ\text{C}$  during Al evaporation. Unfortunately, no LEED patterns have been explicitly reported for this

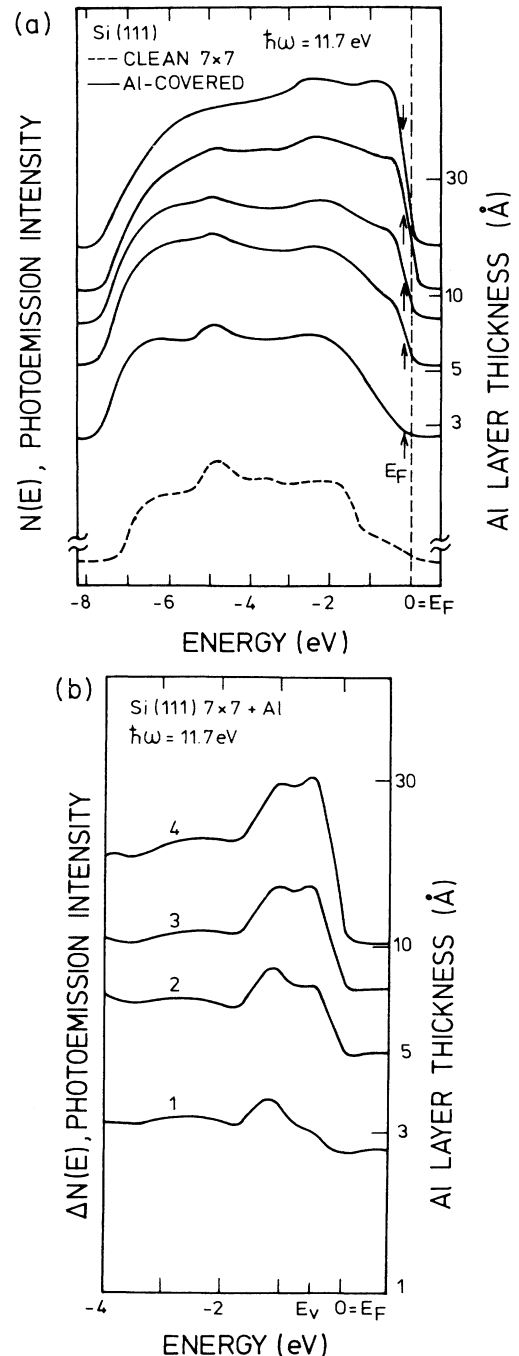


FIG. 3. (a) Ultraviolet photoemission spectra of a clean Si(111)7×7 surface (dashed line) and for increasing Al coverages (solid lines). The arrows indicate the positions of the Fermi level ( $E_F$ ) on the photoelectron energy-distribution curves for the metal-covered surface. (b) Photoemission difference curves between the solid-line curves and the dashed-line curve of (a). Valence-band maximum is  $0.55$  eV below  $E_F$ . (From Ref. 5.)

condition. However, from Lander and Morrison's work,<sup>2</sup> as we have discussed before, the mixed  $7\times 7$  and  $\sqrt{3}\times\sqrt{3}R30^\circ$  LEED patterns observed for Al evaporated onto a cold (less than  $300^\circ\text{C}$ ) substrate are consistent with the coadsorption at the atop and the relaxed eclipsed sites. The adsorption at the atop site can maintain the  $7\times 7$  pattern of the bare surface, and the  $\sqrt{3}\times\sqrt{3}R30^\circ$  pattern would be consistent with the adsorption at the relaxed eclipsed site. There is also evidence in support of the occupation of the atop site in the coadsorption model from the observed drop of the Fermi level ( $E_F$ ) in the UPS spectra from 0.55 eV (above VBM) for a clean  $7\times 7$  surface to 0.35 eV upon Al adsorption. Thus, Zhang and Schluter<sup>8</sup> have found a similar drop in  $E_F$  from their pseudopotential calculations for the atop site only, even though they did not favor this site for Al adsorption.

One disagreement remains for Al adsorbed at the relaxed eclipsed site. The energy difference between the higher energy doublet in the UPS difference curves is 0.6 eV, whereas from theory in the present work it is about 1.1 eV (the difference between *A* and *B*). This difference between theory and experiment could perhaps be attributed to a somewhat different relaxation in the positions of the atoms in the actual system than has been considered for our relaxed eclipsed model.

Peak *B* in the LDOS for the adsorption at the open site is at  $-1.9$  eV and is metal related (Si—Al  $\pi$  type), but peak *A* (Si  $\pi$  type) at 0.5 eV is not. Peak *B* is very similar to that for the atop configuration. However, from binding-energy considerations (see Table I), we find that the occupation of the open site is less probable than the atop site.

Before concluding this discussion about the explanation of the observed UPS spectra, we should mention some other peaks found in our cluster calculation. A strong peak around  $-5$  eV occurred in each LDOS curve from molecular orbitals having predominantly hydrogen  $1s$  character. The contribution to the LDOS from these levels was removed, because it represented an artifact of the cluster calculations arising from hydrogen embedding. Besides the peaks whose characters have already been listed in Table II, there are additional peaks in the theoretical LDOS's. Peak *B* in curve 1 and peak *C* in curve 4 (Fig. 2) are Al  $3s$  type; peak *C* on curves 2, 3, and 5 are associated with Si—Al  $\sigma$ -type orbitals; and the lower-energy peaks on each curve are due to Si

$3s$  states.

### C. Vibrational frequency and vibrational amplitude

The vibrational frequency and vibrational amplitude have been calculated using Eqs. (3), (4), and (6). These values are shown for all five models in Table III. In recent high-resolution electron-energy-loss spectroscopy (HREELS) measurements on aluminum-adsorbed Si(111) surfaces<sup>4</sup> two different frequencies, 55 and 65 meV, were observed. A vibrational peak at 55 meV was previously observed for cleaved Si(111) $2\times 1$  surfaces.<sup>41</sup> However, in the work in Ref. 4 no such peak was observed for the Si(111) $7\times 7$  surfaces without aluminum. The fact that for the bare Si(111) $7\times 7$  surface no 55-meV peak was observed in contrast with the Si(111) $2\times 1$  cleaved surface, may be a result of the different atomic arrangements for these surfaces, which could lead to different dynamics. Therefore, the peak at 55 meV observed for the Si(111) $7\times 7$ -Al or Si(111) $1\times 1$ -Al surfaces in Ref. 4 is due to adsorbed aluminum. The LEED pattern and the observed vibrational frequency of 55 meV are consistent (Table III) with the atop-site adsorption for which a vibrational frequency of 46.8 meV is predicted. The vibrational frequency for the unrelaxed eclipsed-site adsorption is very similar to the atop adsorption. However, the smaller binding energy (Table I) and the inconsistent LEED pattern that would arise ( $\sqrt{3}\times\sqrt{3}R30^\circ$  in this case) forbid the assignment of the 55-meV peak to the unrelaxed eclipsed-site adsorption. The higher-energy peak at 65 meV observed for the Al-adsorbed surface, annealed at a higher temperature<sup>4</sup> with the resulting  $\sqrt{3}\times\sqrt{3}R30^\circ$  LEED pattern, agrees very well with the adsorption of Al at the eclipsed site with relaxation, both in terms of symmetry and vibrational frequency.

We notice that even though the trend is right for the above site assignments, the computed frequencies are somewhat smaller than the observed frequencies. In order to understand the source of discrepancy we have performed a calculation for the ground state of the diatomic Si-S molecule, for which the experimental vibrational frequency is available. The mass of sulfur is also close to that of aluminum. It is well known that the SCF force constants in molecular systems are typically too large by about 15%, and sometimes by as large as 30%.<sup>42</sup> For the Si-S molecule our computed frequency is 124.0 meV compared with the experimental value of 92.8 meV<sup>43</sup>; that is,

TABLE II. Comparison of the experimental UPS peak positions and those of the calculated peaks *A* and *B* in Fig. 2 for different Al sites. All peak energies are given in eV measured from the valence-band maximum. The nature of the electronic orbitals associated with the *A* and *B* peaks is included.

Experimental peaks	Adsorption site				
	Substitutional	Atop	Open	Eclipsed	Relaxed eclipsed
0.0	0.0 ( <i>A</i> ) Si—Al $\sigma_z$	0.0 ( <i>A</i> ) Si $\pi$	0.5 ( <i>A</i> ) Si $\pi$	0.7 ( <i>A</i> ) Si—Al $\sigma_z$	0.0 ( <i>A</i> ) Si—Al $\sigma_z$
-0.6				-1.2 ( <i>B</i> ) Si—Al $\pi$	-1.1 ( <i>B</i> ) Si—Al $\pi$
-2.0		-2.0 ( <i>B</i> ) Si—Al $\sigma_z$	-1.9 ( <i>B</i> ) Si—Al $\pi$		

TABLE III. Vibrational frequencies and vibrational amplitudes for different adsorption sites.

Adsorption site	Computed frequency (meV)	Experimental frequency (meV)	Amplitude $\langle u^2 \rangle^{1/2}$ (Å)	Effective amplitude $\langle u_{\text{eff}}^2 \rangle^{1/2}$ (Å)
Substitutional	34.8		0.061	0.126
Atop	46.8	55	0.048	0.120
Open	37.7		0.057	0.124
Eclipsed	46.5		0.048	0.120
Relaxed eclipsed	53.4	65	0.043	0.118

about 34% larger when the effective mass  $m = m_S m_{\text{Si}} / (m_S + m_{\text{Si}})$  is used in Eq. (3). However, using the same force constant ( $k$ ) and  $m = m_S$ , corresponding to the rigid substrate approximation, we obtain a value of 84.8 meV; about 9% smaller than the experimental value and about 32% smaller than the Hartree-Fock value with the proper effective mass. Therefore, we believe that the smallness of the computed frequencies compared to the experimental values for the Si(111)-Al system, could arise partly out of the rigid-substrate approximation.

The vibrational amplitudes are seen from Table III to be very similar for all the sites considered and therefore do not allow any discrimination between these sites. Also, no experimental measurements of the vibrational amplitudes are currently available to compare with our predictions for the relaxed eclipsed and atop positions found in this work by including energy and analysis of LEED, UPS, and vibrational frequency data.

## V. CONCLUSIONS

The chemisorption sites of aluminum on silicon (111) surfaces appear to have been explained by the present analysis. It has been concluded that multisite adsorption takes place on a cold surface, whereas on a hot substrate a single site can be preferentially populated. Recently, x-ray standing-wave measurements under controlled experimental conditions such as ultra high vacuum, controlled temperature, and controlled adatom coverage have been made for the positional determination of germanium ada-

toms on Si(111)7×7 surfaces by filling the possible adsorption sites successively.<sup>44</sup> Similar analysis for the adsorption of aluminum can be easily performed. It may be worthwhile to make thermal desorption measurements to obtain binding energies for different adsorption sites.

The results of adsorption of gallium on both hot and cold silicon (111) surfaces appear to have been explained by the assumption that the gallium atoms occupy the same sites as the aluminum atoms, namely the atop site and the eclipsed site with associated relaxation. However, theoretical calculations with gallium atoms should be made in order to substantiate this assumption by examining the binding energies for different sites and by comparison with various types of experimental data, as has been done in the present work for aluminum.

In the present work we have used relaxation of the substrate only for one adsorption site. Theoretical work involving relaxation for the other adsorption sites as well as the influence of many-body correlations to the Hartree-Fock analysis carried out here, especially on the binding energies for different sites, should be explored. These calculations would be rather time consuming. However, they would provide more stringent tests of our conclusions.

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