

Site-Selective Adsorption of C Atoms on Al(111) Surfaces

J. Furthmüller,¹ G. Kresse,¹ J. Hafner,¹ R. Stumpf,² and M. Scheffler²

¹*Institut für Theoretische Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria*

²*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

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Although carbon is a common contaminant of Al surfaces, neither its favorable adsorption sites nor its bonding and electronic properties are known or understood to date. Here we report on density-functional theory calculations for this system which identify two nearly degenerate adsorption sites: (i) a “fcc-type” sixfold-coordinated site halfway between the first and second Al layers and (ii) a “hcp-type” fourfold-coordinated site slightly below the surface layer. We argue that only the C adatoms at the hcp-type sites have been detected in recent scanning tunneling microscopy experiments, but predict that the fcc-type C adatoms should exist in thermal equilibrium as well.

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Recent investigations of the adsorption of C atoms on an Al(111) surface using scanning tunneling electron microscopy (STM) [1] have shown that, as expected, the adsorption occurs in the threefold hollow sites of the surface. However, the detected C adatoms do not occupy the fcc site (above the Al atoms of the third layer) on the surface which would continue the structure of the substrate, but the STM analysis identifies on-surface adsorption at the hcp site (i.e., above the Al atoms in the second Al layer). The STM images also point to noticeable vertical displacements of the Al atoms surrounding the adsorbate, but the actual vertical height of the C atoms cannot be derived, and it was argued that the apparent vertical displacements of the neighboring Al atoms are not necessarily due to geometric distortions but might arise as well from a modification of the electronic structure of the substrate in the vicinity of the adsorbate: A transfer of electrons from the nearest-neighbor Al atoms to the more electronegative C atom would let the Al site appear depressed in the STM image.

Recently, a number of theoretical studies of chemisorption on Al surfaces using electronic-structure and total-energy calculations for cluster and slab geometries have been published [2–7]. The rare studies of carbon chemisorption on Al suggest [9] that C and O may behave in a similar way, giving rise to strong chemical bonding effects between adsorbate and substrate. On Al(100) both C and O are adsorbed in the fourfold hollow surface site, almost exactly in the surface plane [9]. For Al(111) the conclusion from a number of cluster and slab calculations is that initially O chemisorption will occur in a threefold site (probably the fcc site) at a distance of 0.60 ± 0.10 Å above the surface plane [7]. Experimental investigations using different techniques [8] confirm this picture, but are unable to differentiate between the two threefold hollow sites (fcc and hcp) unambiguously. The work of Brune *et al.* [1] has brought the first convincing evidence for a preferential adsorption on the hcp sites for an important contaminant.

In this paper we present the results of an investigation of the adsorption of C atoms on Al(111) surfaces via *ab initio* total-energy calculations in the local-density approximation (LDA) for the exchange-correlation potential. We show that the binding energy is almost the same in a hcp site slightly below the surface and in a fcc site about halfway between the surface and the first subsurface layer, but the fcc sites can be reached only by overcoming a significant energy barrier, whereas no barrier exists for chemisorption at the hcp sites. In addition, the gradients in the potential energy of a C atom approaching the surface will direct the atom towards the hcp site. Once adsorbed in this position, an even higher barrier hampers migration from the hcp to the fcc site. We also show that the relaxation of the Al sites surrounding the adsorbate and the electron density in the surface correspond to the pattern observed in the STM experiments [1].

In a first series of calculations the total energy of a C atom adsorbed on a four-layer Al(111) slab (with 12 Al atoms per layer) was calculated for the hcp in-surface and the fcc on-surface, in-surface, and subsurface geometries. The calculations were based on fully separable norm-conserving pseudopotentials [10] and used the FHI93CP code performing a calculation of the electronic ground state and of the optimal atomic geometry via a steepest-descent minimization of the total energy with respect to the ionic and electronic degrees of freedom [11]. The carbon atoms are placed only on one side of the slab (which is admittedly very thin), following the approach of Ref. [3] for the treatment of the adsorbate-induced dipole moment. This approach implies that already a four-layer slab gives a reliable estimate of adsorption energy differences. A second series of calculations was based on optimized ultrasoft pseudopotentials [12,13] and used the Vienna *ab initio* molecular-dynamics program (VAMP) [14,15] based on the calculation of the LDA eigenstates via conjugate-gradient techniques and on the optimization of the atomic geometry via molecular dynamics, quasi-Newton quenches, or conjugate-gradient minimizations.

The cutoff radii for the ultrasoft pseudo-wave-functions were $R_{\text{cut}} = 1.9$ a.u. for the s, p , and d states of C, and $R_{\text{cut}} = 2.1, 2.05$ and 2.3 a.u. for the s, p, d states of Al. Two reference energies (two projectors) were used for the s and p states, and one projector was used for the d states. Detailed tests of the ultrasoft pseudopotential for C are reported in Ref. [16]. With these pseudopotentials total-energy convergence could be achieved for a cutoff energy of $E_{\text{cut}} = 270$ eV in the plane-wave expansion; for energy differences a smaller cutoff of 200 eV is sufficient. For this cutoff, the smooth part of the wave functions and charge densities were represented on a $42 \times 36 \times 96$ grid (for the largest cell), the augmentation charges were calculated on a $60 \times 56 \times 144$ grid. These meshes correspond to cutoff energies of 48 and 105 Ry for the charge densities. The calculations were extended from four- to five- and six-layer slabs (with up to 72 Al atoms in the supercell). For the Brillouin-zone integrations a $2 \times 2 \times 1$ grid of special points was used, together with a Gaussian smearing of $\sigma = 0.1$ eV and extrapolation of the energies to $\sigma = 0$. The atomic coordinates of the two lowest layers were fixed, all other coordinates were relaxed via conjugate-gradient minimization of the total energy.

Table I summarizes the binding energy differences calculated for the hcp in-surface and fcc on-surface, in-surface, and subsurface sites using different pseudopotentials, different thicknesses of the Al and vacuum layers, and different cutoff energies. These results demonstrate that the results are essentially independent of the pseudopotential and of the cutoff energy, and also practically converged with respect to the thickness of the Al slab and the separation of the repeated Al slab by vacuum layers. The only important change is that the fcc subsurface site is stabilized by about 0.1 eV with respect to the hcp in-surface site as the thickness of the slab increases from four to six layers. The conclusion is that the fcc subsurface site is energetically more favorable than the hcp in-surface site by 0.1 ± 0.05 eV/atom.

This result is in apparent contradiction with the results of the STM studies. The answer to that is found in the variation of the binding energy of the adatom as a function of the distance from the surface. This calculation has been performed for a six-layer slab, and the results are given in Fig. 1. We find that for the hcp site the energy decreases continuously as the C atom approaches the Al surface; the stable adsorption site lies 0.2 \AA below the unrelaxed surface and 0.05 \AA below the relaxed surface layer. In this site the C atom is coordinated in an almost ideal tetrahedral configuration by four Al atoms (three Al atoms at a distance of 1.9 \AA , one at a distance of 2.0 \AA). For the fcc site, a metastable site with threefold coordination (nearest-neighbor distance $\sim 1.9 \text{ \AA}$) is found about 0.96 \AA above the surface. The threefold fcc in-surface site corresponds to a saddle point with an energy about 0.14 eV higher than the fcc on-surface site and 0.8 eV higher than the hcp in-surface site. In the fcc subsurface site about 1.17 \AA below the surface the C atom resides in a sixfold-coordinated position in the octahedral interstitial site, with a nearest-neighbor distance of about 2.0 \AA . More important than the energy barrier for approaching the energetically most favorable fcc subsurface site is the fact that, at distances $\leq 0.9 \text{ \AA}$ above the surface, the energy decreases continuously along a line leading from the fcc to the hcp surface site (see Fig. 2). Hence the chemical bonding forces direct the approaching C atom to the hcp adsorption site, even if it is initially directed towards the fcc site. For C atoms adsorbed in positions below the surface, there is also a large barrier of more than 0.5 eV hampering the migration from the hcp to the fcc site. If an atom is displaced from the hcp site in the direction of the fcc site, the energy increases steeply, but the energetically most favorable distance to the surface remains the same until the bridge position is reached. Beyond this point the position slightly below the surface is first metastable and then unstable, the atom moves deeper into the Al layer. The corresponding result is found when the C atom is displaced out of the fcc site (see Fig. 2).

TABLE I. Binding energy differences ΔE_b (relative to the hcp site) for adsorption of C atoms in fcc sites on, in, and below the Al(111) surface, calculated for slabs of different thickness, with different pseudopotentials and varying cutoff energies E_{cut} .

Pseudopotential	Layers Al	Layers vacuum	E_{cut} (eV)	fcc sub	ΔE_b fcc in	fcc on
NC ^a	4	4	480	-0.140	0.780	0.590
US ^b	4	3	270	0.009	0.842	0.639
US	4	5	270	0.008	0.843	0.637
US	5	4	270	-0.084	0.739	0.710
US	5	4	200	-0.085	0.733	0.706
US	5	5	270	-0.081	0.739	0.710
US	6	4	270	-0.118	0.801	0.669
US	6	4	200	-0.104	0.800	0.661

^aNorm-conserving pseudopotential.

^bUltrasoft pseudopotential.

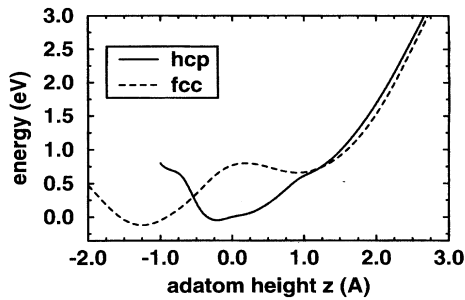


FIG. 1. Energy of a C atom as a function of its height above the Al(111) surface for the hcp and fcc surface sites. The energy zero is the total energy for the hcp equilibrium geometry. The zero of the adatom height is the center of the top Al layer of the unreconstructed surface. The second Al layer is at -2.33 Å.

Hence our results demonstrate that although the fcc subsurface site represents the energetically most favorable adsorption site, a C atom impinging on the Al(111) surface will always be drawn to the slightly less favorable hcp in-surface site due to the strong chemical bonding forces. The C atom will be trapped in this metastable position. However, with an energy difference of only 0.05 to 0.1 eV/atom for adsorption in the hcp and fcc sites, in thermodynamic equilibrium according to the mass-action law both sites should be occupied. This raises the question of why the fcc sites are not seen in the STM experiment. One explanation is that the C atoms in the fcc sites do not sit above the surface, but halfway between the first and second Al layer. Hence it is possible that they are not seen in the STM experiments. Investigation of C adsorption on Al using photoemission and surface-EXAFS (extended x-ray adsorption fine structure) experiments should be performed to complement the STM investigations.

It is also interesting to study the adsorbate-induced relaxation. For the clean Al(111) surface our calculations predict changes in the first three interlayer distances by $\Delta_{12} = 1.38\%$, $\Delta_{23} = -2.14\%$, and $\Delta_{34} = 1.08\%$, in reasonable agreement with recent calculations ($\Delta_{12} = 1.4\%$, Ref. [17]; $\Delta_{12} = 1.0\%$, $\Delta_{23} = -0.07\%$, Ref. [18]; and $\Delta_{12} = 1.18\%$, $\Delta_{23} = -0.40\%$, $\Delta_{34} = 0.22\%$, Ref. [19]) and with experiment [$\Delta_{12} = (1.7 \pm 0.3)\%$, $\Delta_{23} = (0.5 \pm 0.7)\%$, Ref. [20]]. The relaxed configurations of the Al atoms surrounding the C atom are shown in Fig. 3. These results have been obtained with the six-layer slab and the ultrasoft pseudopotential; almost identical results are found with the norm-conserving potentials and the four-layer slab. For the fcc on-surface site, the three nearest-neighbor Al atoms are pulled out of the surface by about 0.17 Å and show an outward relaxation by 0.13 Å. In the fcc in-surface site the position of the C atom and of the three nearest and three next-nearest neighbors is 0.24 and 0.14 Å above the relaxed surface, with an outward relaxation of 0.28 and 0.17 Å, respectively. The fcc subsurface site lies almost exactly halfway between the surface

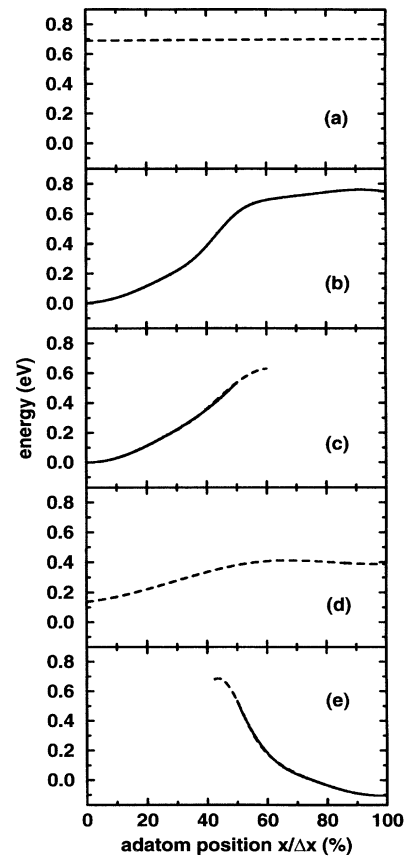


FIG. 2. Energy of a C atom relative to the hcp-site energy minimum along a line (X direction) leading from the hcp to the fcc surface site: $X/\Delta X = 0$ is the hcp site and $X/\Delta X = 100\%$ is the fcc site. Calculations are performed at different heights Z above or below the surface: (a) $Z = 1.15$ Å, (b) $Z = 0.23$ Å, and (c) $Z \sim -0.1$ Å. (The Z coordinate is varied such as to find the minimum energy at fixed x and y , but remains almost constant. Beyond 50% of the distance a stable minimum could be found only for $Z < -1$ Å.) (d) $Z = -0.46$ Å and (e) $Z \sim -1.2$ Å. (The energy was again minimized with respect to the Z coordinate which remains almost unchanged up to 50% of the distance.) Full lines show exactly calculated energies for metastable positions, and broken lines mark tentative interpolations of the energy into an unstable region with Z fixed at the last value. (Compare text.)

and the first subsurface layer. The three nearest-neighbor Al atoms relax upward and downward by 0.08 Å. In the hcp site the C atom is situated 0.05 Å below the relaxed ideal surface plane, the three nearest Al neighbors relax upward by 0.02 Å and outward by 0.28 Å, and the three next-nearest Al neighbors relax downward by 0.02 Å and outward by 0.11 Å. The calculated relaxation pattern reflects the trend towards the formation of a highly symmetric adsorption geometry. The predicted lateral relaxations are at or below the limit of resolution of STM experiments. The calculated vertical relaxations are much smaller than the apparent displacements of -0.3

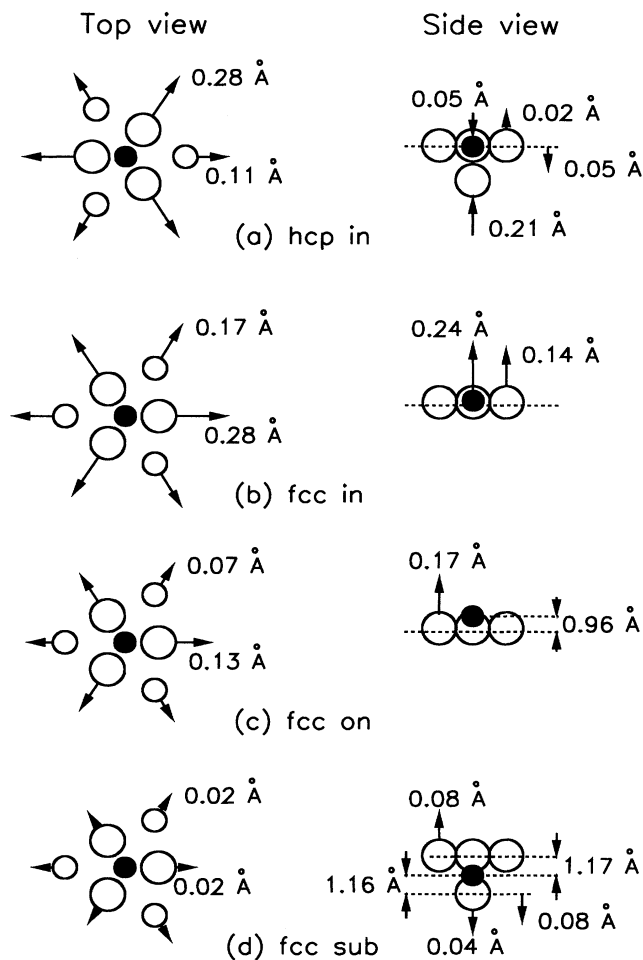


FIG. 3. Top and side views of the relaxations of the Al neighbors around a C atom adsorbed in (a) a fcc on surface, (b) a fcc in surface, (c) a fcc subsurface, and (d) a hcp in-surface site of the Al(111) surface. The C atom is marked by the full black circle, and the first- and second-layer Al atoms are noted, respectively, by the large and small open circles. The dashed line in the side-view pictures indicates the top-layer Al position of the unreconstructed but relaxed substrate.

and $+0.2 \text{ \AA}$ estimated from the variation of the tunneling current. Hence our calculations confirm arguments that the tunneling conditions depend to a large extent on the changes in the electron density in the surface induced by the adsorbate.

In summary, we have shown that the site-selective adsorption of C atoms in the hcp in-surface positions of the Al(111) surface observed in STM experiments may be explained in terms of *ab initio* density-functional calculations. Surprisingly, we find that the observed site does

not correspond to the energetically most favorable adsorption site, but to an energetically slightly less favorable site whose occupation is favored by the adsorption process.

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