

Adsorption of Al on Si(100): A Surface Polymerization Reaction

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We study the adsorption of Al on the Si(100) surface by *ab initio* calculations for a complete range of coverages from an isolated Al adatom up to full surface coverage. Analysis of the energetics of adsorption and the mobility of Al adatoms reveals that the long, one-dimensional strings of Al dimers observed experimentally result from a sequence of reaction steps which can be classified as a surface polymerization. The calculated local density of states (LDOS) of the adsorbed Al row is compared with scanning tunneling microscopy images. The LDOS characteristic of the reaction sites which mediate the polymerization should be observable by scanning tunneling spectroscopy.

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Scanning tunneling microscopy (STM) has made it possible to observe structures at surfaces with atomic resolution. Many studies have revealed that surprisingly complex structures occur in seemingly simple processes such as the adsorption of atoms on semiconductor surfaces [1,2]. To achieve a coherent understanding of the mechanisms of surface reactions is one of the great challenges in surface science today. In the last few years new tools of computational physics have been developed to meet this challenge. Metal surfaces have been studied both by *ab initio* [3] and effective medium techniques [4]. The state of the art in *ab initio* calculations on semiconductor surfaces is the Car-Parrinello approach [5,6]. So far, most calculations have focused on the structures of clean surfaces or surfaces with a fixed coverage of adsorbants. The reaction mechanism which leads to these structures can be elucidated only by studying a whole range of coverages. This paper presents such a complete theoretical study revealing the mechanism of a reaction on a semiconductor surface.

We have chosen the Si(100) surface as the prototype semiconductor surface. Its reconstruction is relatively simple [compared to Si(111), for instance [6]], yet it involves all the complexities of covalent bonding. The adsorption of aluminum is treated as the prototype reaction. STM experiments by Nogami, Baski, and Quate [2] have shown that this seemingly simple process leads to the formation of long one-dimensional strings of Al atoms. These strings become ordered in two-dimensional structures only at high coverages. Aluminum is one of several cases reported where adatoms on the Si(100) surface form long strings one atom wide and up to several tens of atoms long [2,7]. Both the exact structure of these strings as well as a mechanism for their formation cannot be extracted from experiment. In this paper we show how both structure and mechanism can be obtained from *ab initio* calculations. We study the energetics of Al on Si(100) starting with a single adsorbed Al atom and

adding Al until all the Si dangling bonds on the surface are saturated.

We start by putting a single Al atom on the Si(100) substrate. We establish its most stable binding position and, in order to determine its mobility, we assess the energy barriers for diffusion on the surface. Both pieces of information are obtained by mapping out the total energy E as a function of the position (x, y) of the adatom on the surface, following the procedure of Ref. [8]. For each position (x, y) the total energy of the adatom plus substrate is minimized with respect to the electronic charge density, the height z of the adatom and the positions of all atoms in the top five layers of the Si substrate, using the Car-Parrinello technique of simultaneous optimization [5,6]. The local density approximation calculations are carried out using norm-conserving pseudopotentials [9], a plane wave basis set and a periodic supercell. We have used a twelve layer slab to model the Si(100) surface and a $p(\sqrt{8} \times \sqrt{8})R45^\circ$ surface supercell to model the adatom-surface interaction. A plane wave kinetic energy cutoff of 8 Ry is used and a Brillouin zone sampling of 2 \mathbf{k} points. These parameters have been tested for convergence as in Ref. [8], with the result that energy differences presented here have converged within 0.1 eV. The energy surface $E(x, y)$ is given in Fig. 1. The absolute minimum, which gives the equilibrium binding site for the Al adatom, is the position marked as H . The binding configuration of the Al adatom is symmetric with equal distances of 2.54 Å to four Si substrate atoms; the height of the Al adatom is 1.35 Å above these surface atoms. Its calculated binding energy is 3.6 eV [10].

The energy surface $E(x, y)$ is remarkably flat, especially if one compares it to the equivalent surfaces for Si and P adatoms [8,11]. For the Al adatom there exists a channel in the direction parallel to the x axis (perpendicular to the dimer rows of the substrate) which passes between two adjacent dimers in a dimer row. The highest point in this channel, which is marked A in Fig. 1, is only

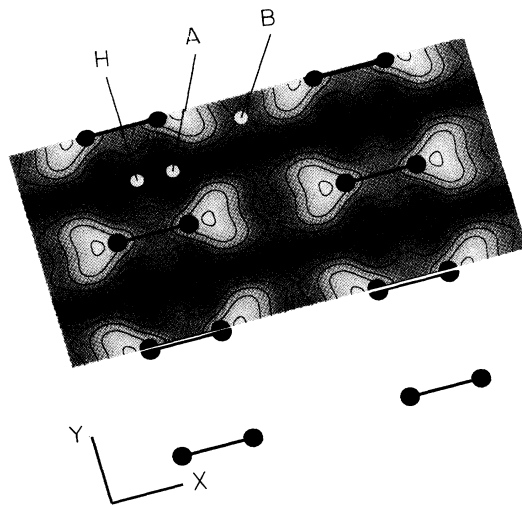


FIG. 1. The total energy surface $E(x, y)$ of an Al adatom on the Si(100) surface. Contours start at 0.1 eV above the absolute minimum H and their spacing is 0.2 eV. Positions of low energy are dark, positions of high energy are light. The points marked A and B are the saddle points for diffusion perpendicular and parallel to the dimer rows.

0.1 eV above the absolute minimum. Within the framework of transition state theory [12], this point determines the barrier for diffusion in the x direction. Diffusion in the y direction involves a minimum energy path along a channel which runs between two dimer rows of the substrate. The barrier, marked B in Fig. 1, has a height of 0.3 eV. The activation energy for diffusion is small for both the principal directions on the Si(100) surface, which means that at room temperature the mobility of Al adatoms is high in all directions. This conclusion is in agreement with experiment, where at room temperature no effects of a limited mobility of Al atoms were observed [2].

We proceed by putting a second Al atom on the surface. The two Al atoms have a very strong preference to form a dimer. We minimized the total energy for a number of possible structures; Fig. 2 summarizes the most important results. The structure given schematically in Fig. 2(a) is lowest in energy. Its effective binding energy, as compared to two separated Al adatoms, is calculated to be 1.1 eV. In terms of forming covalent bonds this structure is the best way of satisfying the valence III of Al, without disrupting the substrate or causing too much strain. Looking again at the energy surface for the single Al adatom (Fig. 1), we see that the optimal structure for the Al dimer has both atoms positioned in the low energy channel discussed above. From this point of view it is not surprising that structures in which the Al ad-dimer is parallel to the Si(100) substrate dimers [cf. Figs. 2(a) and 2(c)] are lower in energy than structures in which the Al dimer is rotated by 90° [Figs. 2(b) and 2(d)]. Positioning the Al dimer between two substrate dimer rows

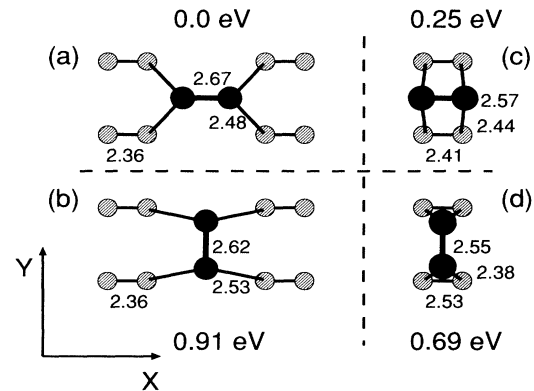


FIG. 2. Schematic drawing of possible structures of an Al ad-dimer on the Si(100) surface. The black circles represent the Al atoms, the shaded circles represent the atoms of the Si(100) substrate. Total energies are given with respect to the minimum, which corresponds with structure (a). The small numbers give the Al-Al, Al-Si, and Si-Si bond lengths in Å. The Si-Si dimer bond length on the clean Si(100) surface is 2.28 Å.

as in Fig. 2(a) is more favorable than on top of a substrate dimer row as in Fig. 2(c) presumably because it leads to better bond angles.

Let us now focus on the electronic states of the ad-dimer plus substrate for the minimum energy structure. The clean Si(100) has two surface states in the bulk band gap, which are both derived from the dangling bonds of the dimers in the top surface layer. The lower (π) state is occupied, the upper (π^*) state is unoccupied and the calculated splitting between the band centers (of gravity) is ~ 0.7 eV. The Al dimer interacts strongly with these states to form local bonds. The energy of these bonding states lies within the Si valence band and for the moment they are not of interest to us. In addition, we find dangling bond states which are located on Si atoms of substrate dimers bonded to Al. These are the remnants of the Si dimer π bonds which are broken by the interaction with the Al dimer. One might expect that these states are located near the Fermi level. The calculated local density of states near the Fermi level, which is given in Fig. 3, clearly shows these dangling bonds. One expects such surface sites to be more reactive than others, since adsorption there does not require breaking a Si-Si π bond. Indeed the preference for this reaction site becomes clear if we put a third Al adatom in the position indicated in Fig. 3. The calculated adsorption energy is 4.0 eV, which is 0.4 eV larger than the adsorption energy of the first adatom [10,13].

The strong preference for the third adatom to bind at a specific position adjacent to the Al dimer means that we can set up a chain reaction. After all, a fourth adatom will again form a dimer with the third atom and gain the dimer binding energy of 1.1 eV. This second ad-dimer is an exact copy of the first one (see Fig. 3), which means

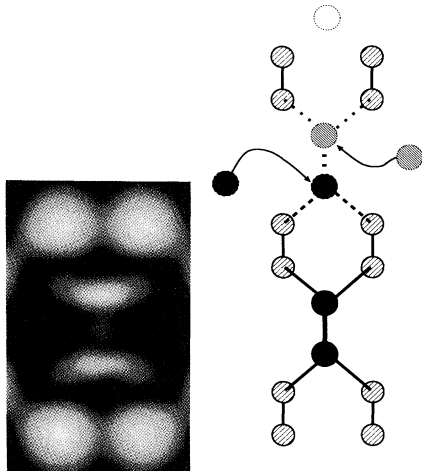


FIG. 3. Reactive sites adjacent to an adsorbed Al dimer. The image gives the local density of states integrated over an interval of 0.15 eV just below the Fermi level. A surface of constant density is shown, where the grey scale represents the height. A third Al atom adsorbs preferentially at this reactive site, a fourth atom forms a dimer again. The end result of the chain reaction is a row of Al ad-dimers as shown in Fig. 4.

that a new reactive site is then formed adjacent to the new Al dimer. As discussed above, the next adatom will bind there preferentially, *et cetera*, which ultimately results in the formation of a long chain of Al ad-dimers. Since the diffusion at room temperature of singly deposited adatoms is very fast, there are no kinetic barriers to this chain formation. This chain reaction is not unlike the addition reactions which are known from organic polymers. After initialization, the reaction can progress via a reactive intermediate species $C\cdot$, a molecule with a partially filled highest occupied state (a radical). The intermediate $C\cdot$ reacts with a monomer C to form a new intermediate $C-C\cdot$, etc. The reaction mechanism we have described for Al on Si(100) belongs to this general class. The difference is that some of the reactive intermediate sites are located on the surface and not on the Al chain itself. By analogy, we therefore call the adsorption of Al on Si(100) a surface polymerization reaction.

The formation of rows of Al dimers was observed in STM by Nogami, Baski, and Quate [2], who also proposed two possible structures. The interpretation was not completely straightforward, however, since the geometric structure could not be extracted directly from the electronic features observed in the STM images. According to our results the structure of an Al dimer row is the one given in Fig. 4 (top). A comparison with experiment can be made by looking at the electronic states. The local density of occupied states (LDOS) in the vicinity of the top of the Si bulk valence band around the Al dimer row is given in Fig. 4 (middle). If one assumes a very simple form of tip-surface interaction for STM, this

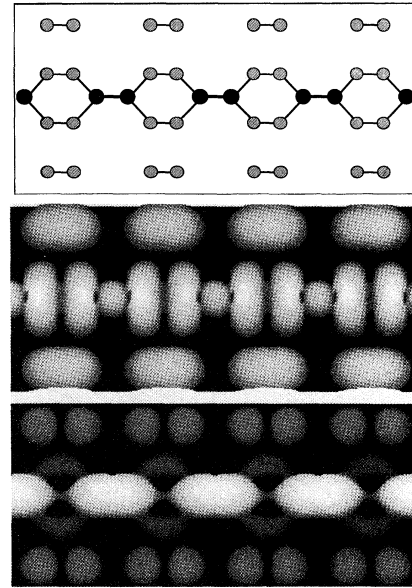


FIG. 4. Electronic structure of an Al dimer row adsorbed on the Si(100) surface; top: geometric structure; middle: local density of states (LDOS) of the occupied states integrated over an interval of 0.5 eV around the top of the valence band, represented as in Fig. 3; bottom: LDOS of the unoccupied states around the bottom of the conduction band.

LDOS corresponds to the STM filled state image [14]; the maxima in the LDOS are where one expects to find the Al-Si substrate bonds. Using a conventional STM image representation, we find a series of white protrusions located on top of the Si dimer rows of the substrate. The local density of states at the bottom of the conduction band, given in Fig. 4 (bottom), corresponds to the empty state image in STM [14]. It consists mainly of the empty dangling bond states of Al and is observed in the form of protrusions between the Si substrate rows. The qualitative agreement with the STM images [2] is satisfactory, especially if one considers that the thermal motion of the surface atoms will round off the sharpest features in the calculated LDOS. For instance the two maxima on top of the Si dimer row in the filled state image may then merge into one.

The state which is associated with the reactive site at the end of the Al dimer row (Fig. 3) is situated near the middle of the band gap. It should be possible to observe this as a peak in scanning tunneling spectroscopy if the tip is positioned on the end of the Al dimer chain. A number of group III and group IV elements (Ga, In, Sn) behave like Al [7]. We expect that an analysis similar to the one presented here is also valid for those cases.

By adding Al atoms, the Al dimer chains have to move more closely together. We may estimate the effective interaction between the Al dimer chains assuming that it is short range. By comparing the energy of one Al chain in a $p(2 \times 4)$ unit cell with that of one Al chain

in a $p(2 \times 2)$ unit cell we find an effective repulsion of 0.1 eV per Al atom between the Al chains [15]. This means that the Al rows have no tendency to form two-dimensional islands; on the contrary, at higher coverages the repulsion results in ordered structures which consist of equally spaced dimer rows with periodicities $p(2 \times n)$ where n goes from 5 to 2 on increasing the Al coverage [2,16].

Eventually a situation is reached where the Si(100) surface dangling bonds are completely saturated by Al ad-dimers. The resulting ordered structure has a $p(2 \times 2)$ symmetry and consists of Al dimer rows like those shown in Fig. 4 [2]. The $p(2 \times 2)$ fully covered surface was studied by Northrup *et al.* [17]. Our findings on the energetics of $p(2 \times 2)$ ordered structures are in agreement with theirs. On the clean Si(100) surface the structure which is most stable consists of "buckled" Si dimers. When the Al overlayer is added, all Si dimers in the substrate become symmetric (i.e., their bond axes lie in the plane of the surface). Apart from this rather subtle change, the reconstruction of the Si(100) remains intact.

In summary, we have shown that the adsorption of Al onto the Si(100) surface can be described by a reaction mechanism which we call a "surface polymerization." We expect that there will be other examples of this type of reaction at semiconductor surfaces, where the topology of the surface and the energetics of covalent surface bonding enable a purely one-dimensional growth.

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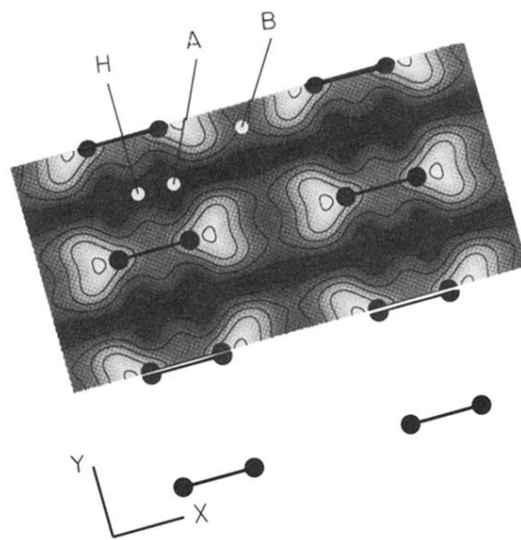


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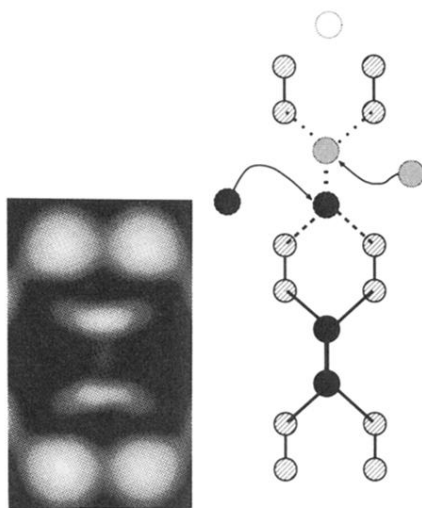


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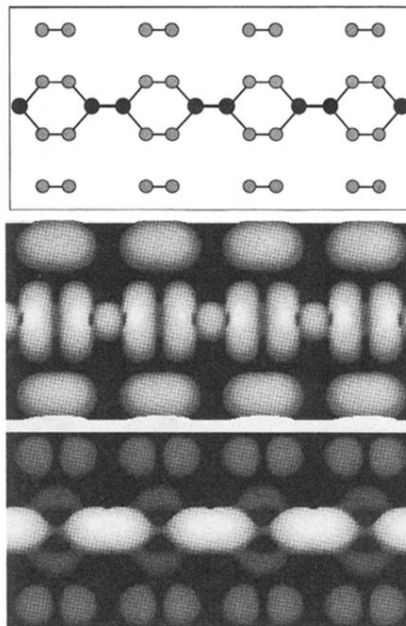


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