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Adsorption of group III and group V metals on Si(001): One-dimensional versus two-dimensional growth

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Scanning tunneling microscopy (STM) studies have revealed that when a small fraction of a monolayer of Al, Ga, or In is deposited on Si(001) it forms one-dimensional lines of ad-dimers on the surface. No similar structures have been reported for the case of group V elements. We have studied the adsorption of group III and group V metals on Si(001) by first principles total energy calculations starting with the adsorption of a single atom up to a full surface coverage. Different adsorption sites are found for single group III and V adatoms. When a second atom is adsorbed, in both cases, there is a strong preference of the two atoms to dimerize. However, the orientation and position of the ad-dimer is determined by the binding site of the first atom. The formation of the long lines in the case of group III and not for group V metals is a direct consequence of these differences.

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Fabrication of state of the art electronic devices imposes strict demands in the crystal growth process. In particular, epitaxial growth of one element onto another is necessary to obtain high material uniformity and interface smoothness. This condition requires control at an atomic level. Even though this goal can be achieved through methods such as molecular beam epitaxy and pulsed laser deposition, the elementary processes governing crystal growth are not yet completely understood for most of the systems of interest. This is particularly true for the growth of group III and group V metals on Si(001).

One of the reasons for the interest in the Si(001)/group III and Si(001)/group V interfaces comes from possible technological applications of the epitaxy of III/V semiconductors on Si surfaces. Group III and group V metals form dimer structures at their respective saturation coverages.[1] However, they show completely different growth patterns in the submonolayer regimen. Scanning tunneling microscopy (STM) studies have revealed that when a small fraction of a monolayer of Al, Ga, or In is deposited on Si(001) it forms lines of ad-dimers on the surface.[2–7] These lines can be considered as truly one-dimensional systems and they have been observed also for Pb on Si(001).[8] They are one atom wide and one atom high. No similar structures have been reported for the case of group V metals.[9,10] Among the many unanswered questions about the growth of group III and V metals on Si(001), the first that comes to mind is why one-dimensional growth is preferred for group III and not for group V elements. It is not known either if the lines formed by Al, In, and Ga on Si(001) can grow indefinitely. The current model, based on total energy calculations, does not put a limit in that direction.[7] Also, for many years the ad-dimer has been taken as the basic unit to study the growth of group III and group V elements on Si(001), and there is little information of the adsorption of the first atom on the surface and how the dimer is formed.[11,12] The answer to these questions is critical in the understanding of the heteroepitaxial growth of metals on Si(001), and it is the purpose of this work. We have studied the adsorption of group III (Al, Ga, and In) and group V (As and Sb) metals on the Si(001) surface by first principles total energy calculations starting with the adsorption of a single atom up to full surface coverage. Two different binding sites were found for group III atoms: in the first one, the adatoms are adsorbed on twofold sites between two Si dimers. In the second one, they are adsorbed on threefold sites. On the other hand, only one binding site is found for group V atoms and it is located almost on top of a single Si dimer. As a direct consequence, group V metals form dimers orthogonal and on top of the underlaying Si dimers. Instead, group III elements form dimers parallel and in the trenches between the Si dimers. Minimization of line and row ends[13] is responsible for the initial one-dimensional growth in the case of group III elements. A theoretical maximum length is predicted for the lines. On the other hand, it is found that two-dimensional (2D) growth is preferred for group V elements.

Calculations have been performed within the Car-Parrinello scheme.[14] A combined electronic and ionic steepest descent dynamics has been used to determine optimal surface structures. We have used a repeated slab geometry, each slab consisting of five layers of Si atoms. On top of the first layer we have added the adatoms (Al, Ga, In, As, and Sb). The bottom surface was saturated by hydrogen atoms. Two consecutive slabs were separated by an empty space 9.0 Å wide. The four topmost Si layers of the slab and the adatoms were given full freedom to move, while the fifth layer of Si and the H atoms were held fixed at the ideal positions in order to simulate a bulklike termination. Most of the calculations were performed using a (4×4) supercell with 16 atoms/layer. Due to the large size of our unit cell, only the electronic states at Γ have been included. A similar geometry has been used in the study of As and Sb on Si(001) (Ref. 15) and group III elements on Ge(001) (Ref. 16). The wave functions have been expanded in plane waves with a kinetic energy cutoff $E_{cut}=8$, 10, and 12 Ry. It is found that for adsorption of single atoms an energy cutoff of 10 Ry is needed, but for dimer structures the 8 Ry cutoff is large enough. We have used for Si, Al, Ga, In, As, and Sb norm-conserving pseudopotentials that include *s* and *p* nonlocal terms. They

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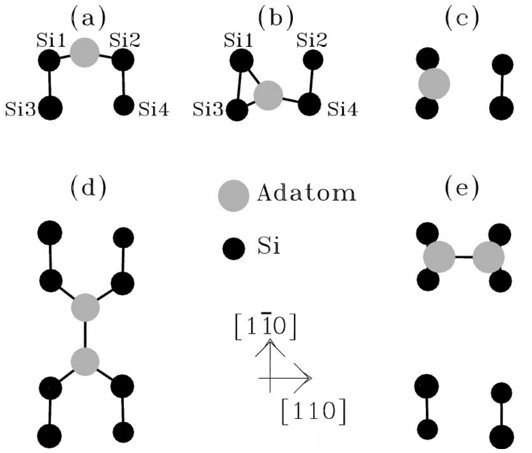

FIG. 1. Schematic drawing of possible binding positions for a single adatom (a)–(c) and a single ad-dimer (d)–(e). Gray circles represent the adatoms, while black circles represent Si atoms. (a) and (b) show the two possible binding sites for a single group III adatom. (c) shows the binding position for a single group V adatom. (d) and (e) show the orientation and position of a group III and V dimers, respectively.

were treated within the Kleinman-Bylander scheme.[17]

We have first studied the adsorption of a single group III adatom on the Si(001)-$c(2\times4)$ surface. The atomic positions were fully relaxed starting from different adatom initial configurations [they included the adsorption sites for Si (Ref. 18), Ge (Ref. 19), and Al (Ref. 7) on Si(001)]. We have identified two binding positions for the adatoms.[20] The first one is located almost on top of a second layer Si atom. In this geometry, known in the literature as the *M* site,[19] the adatom is bonded to two Si atoms in a more or less symmetric configuration [Fig. 1(a) shows the case of Al] and with bond lengths $d_{\text{Al-Si}}\sim2.48$ Å. Si atoms (Si3 and Si4) not bonded to aluminum atoms show a difference of ~1.0 Å in their vertical positions.

In the second minimum, the adatom is on a threefold site above three Si atoms [Fig. 1(b)]. The binding configuration is now asymmetric. There are two different bonding lengths: $d_{\text{Al-Si1}}=d_{\text{Al-Si4}}\sim2.58$ Å, while $d_{\text{Al-Si3}}\sim2.38$ Å is slightly shorter. Substrate atoms Si3 and Si4 are almost at the same height (differences are less than 0.2 Å with Si3 lower), atom Si1 is slightly higher (by ~0.3 Å with respect to Si3), while atom Si2 is considerably lower (~0.5 Å with respect to Si3). In this way, there is a relative vertical buckling of ~0.8 Å between atoms Si1 and Si2. Similar results are found for Ga and for In and details will be presented elsewhere.

For Al and In, the two adsorption sites have the same total energy. For Ga, the twofold site is slightly more favorable by 0.17 eV/adatom. We expect a higher occupancy of the *M* site due to the larger volume of the configuration space associated with it.

A completely different adsorption site is found for group V metals. The adatoms adsorb on twofold sites almost on top of the middle of a Si substrate dimer (*D* site). Figure 1(c) shows the result for As, but a similar arrangement is found for Sb. The binding configuration is symmetric with equal Si-adatom distances: $d_{\text{As-Si}}\sim2.27$ Å, and $d_{\text{Sb-Si}}\sim2.53$ Å. The underlying Si dimer becomes symmetric, and the As (Sb) atom is 2.2 Å (2.1 Å) above the dimer and is shifted 0.5 Å (both for As and Sb) in the plane. Atomic positions of other Si dimers are barely affected by the adatom adsorption.

TABLE I. Calculated bond lengths (in Å) for the (001) surface of Si covered by different coverages of group V elements.

		Adatom-adatom	Adatom-Si	Si-Si
As	Single dimer	2.48	2.41	2.32
As	1D system	2.48	2.41	2.32
As	(2×2)	2.49	2.41	2.32
As	(2×1)	2.52	2.41	Broken
As	(2×1) expt. (Ref. 10)	2.55	2.44	Broken
Sb	Single dimer	2.88	2.61	2.34
Sb	1D system	2.89	2.61	2.34
Sb	(2×2)	2.89	2.61	2.34
Sb	(2×1)	2.95	2.56	Broken
Sb	(2×1) (Ref. 28)	2.88	2.61	Broken

We now consider the adsorption of a second adatom on the surface. In all cases, the two adatoms have a very strong preference to form dimers. However, their position and orientation with respect to the substrate are strongly influenced by the adsorption site of the first adatom. It is easy to see that group V atoms will try to form ad-dimers orthogonal and on top of Si dimers [Fig. 1(e)].[21] In this arrangement, the two atoms that form the dimer are not very far from *D* sites. They are shifted in the ±[110] directions in such a way that they can dimerize. Our calculations show that dimer formation is more favorable than adsorption of two separated adatoms by 2.1 eV and 1.9 eV for Sb and As, respectively. In terms of electron counting arguments, this geometry makes sense: each group V atom binds with two Si atoms and with the other group V atom of the dimer. The remaining two electrons form a lone pair. All Si atoms have their four electrons engaged in bonds. The two Si dimers that support the ad-dimer become symmetric, while other Si dimers remain almost unperturbed. Structural parameters are presented in Table I, together with those of higher coverage. There is little difference between the parameters of a single ad-dimer with those of the 1D system and the (2×2) configuration. Some changes can be observed when the Si dimers are broken and the (2×1) reconstruction is formed.

Although our calculations cannot show that the *M* site is the absolute minimum in the adsorption of group III elements, the fact that at least it is a local minimum with a very favorable energy makes it easy to understand why the ad-dimers are parallel and in the trenches between the Si dimers.[23] In this arrangement, the two atoms that form the dimer are not very far from *M* sites. They are shifted in the $\pm[1\bar{1}0]$ directions in such a way that they can dimerize. Our calculations show that dimer formation is more favorable than adsorption of two separated adatoms by 1.2 eV for Al (Ref. 22) and Ga and 1.0 eV for In. Structural parameters are presented in Table II together with those of higher coverage. Results of the (2×2) structures calculated by Northrup *et al.*

TABLE II. Calculated bond lengths (in Å) for the (001) surface of Si covered by different coverages of group III elements.

		Adatom-adatom	Adatom-Si	Si-Si
Al	Single dimer	2.70	2.48	2.41
Al	1D system	2.65	2.45	2.42
Al	(2×2)	2.67	2.46	2.43
Al	(2×2) (Ref. 23)	2.69	2.47	2.44
Ga	Single dimer	2.58	2.45	2.43
Ga	1D system	2.55	2.43	2.44
Ga	(2×2)	2.57	2.44	2.46
Ga	(2×2) (Ref. 23)	2.63	2.47	2.46
In	Single dimer	2.85	2.59	2.38
In	1D system	2.76	2.55	2.41
In	(2×2)	2.76	2.56	2.41
In	(2×2) (Ref. 23)	2.82	2.60	2.40

are presented too.[23] It can be seen that there is little difference in the structural parameters of a single ad-dimer, the 1D system, and the full coverage configuration.

Different from the case of Ge on Si(001),[24] we found no evidence of metastable structures in which two adatoms stay in almost exact *M* sites without forming a dimer, indicating that indeed, the ad-dimer can be considered as the stable nucleus from which subsequent larger growth structures evolve.

Once a dimer is formed, a third atom will bind at an *M* site adjacent to the dimer. This site is expected to be more reactive than others since adsorption there does not require breaking a Si-Si π bond. A fourth adatom will again form a dimer with the third atom. This process can be repeated again and again, and it will result in the formation of a long chain of ad-dimers. It is what Brocks, Kelly, and Car has called a surface polymerization reaction.[7] Can this process go on forever and have infinite lines of adatoms? To answer this question, we have to consider two different factors: equilibrium thermodynamics and growth kinetics. In the following discussion we will show that under equilibrium conditions the one-dimensional lines should have a maximum length.

Four Si dimers (eight atoms) are involved in the adsorption of a single group III metal ad-dimer. Half of these Si atoms form bonds with the ad-dimer, while the remaining four are left with one free electron each. As a consequence, there will be four dangling bonds per ad-dimer. If a second dimer is adsorbed adjacent to the first one, this number will not be increased. Instead, if it is adsorbed somewhere else, the number of dangling bonds will be doubled. In other words, each end of a line of dimers have an energy cost due to the Si dangling bonds. The formation of long, one-dimensional lines is a way to reduce them.

If line ends are not energetically favorable, it is reasonable to think that there is a similar energy cost to terminate a row of dimers along the [110] direction. Even though there are no Si dangling bonds along this direction, the presence of the ad-dimers alter the buckling sequence of the first layer Si dimers.

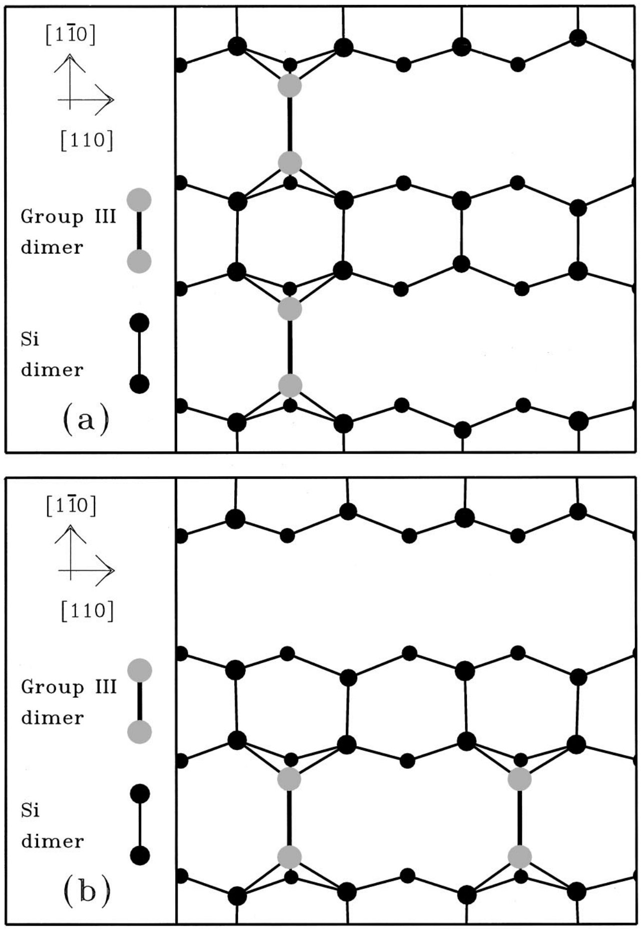

FIG. 2. Top view of the atomic structure of the (001) surface of Ge with 1/4 of a monolayer of a group III element. The figure shows the $p(4\times4)$ unit cell used in the calculation. Gray circles represent the adatoms, while black circles represent Si atoms. Larger circles correspond to atoms closer to the surface. (a) One line of dimers and (b) one row of dimers.

We can estimate the energy of these two different kinds of edges. To this purpose, we calculate the total energy of a system that has neither line ends nor row ends: the infinite (2×2) structure that group III atoms form on Si(001) at 1/2 monolayer (ML) coverage.[25] We compare it with the energy of a configuration that has edges of only one kind: an infinite dimer row to find the energy cost (E_1) of a line end [Fig. 2(b)], and an infinite dimer line to calculate the energy cost (E_2) of a row end [Fig. 2(a)]. In Table III we summarize our

TABLE III. Energy cost of a line end (E_1) and row end (E_2) for Al, Ga, and In. Energies are in eV/end.

	E_1	E_2
Al	0.43	0.11
Ga	0.42	0.10
In	0.41	0.12

results. As expected, the energy cost of a line end is a lot larger than the energy cost of a row end. Therefore, the formation of one-dimensional lines along the $[1\bar{1}0]$ direction is more favorable.

The calculations mentioned above correspond to infinite systems: an infinite 2D surface covered by group III ad-dimers in a (2×2) arrangement, an infinite line of ad-dimers, and an infinite row of dimers. To estimate the total energy of the corresponding finite systems, we can use the values of E_1 and E_2. We approximate the total energy of a finite line as

$$E_{1\mathrm{D}}(n)=nE_{(2\times2)}+2E_1+2nE_2+mE_{\mathrm{Si}\,surface}, \qquad (1)$$

where n is the number of ad-dimers, $E_{(2\times2)}$ is the total energy (per dimer) of an infinite arrangement with a (2×2) periodicity and having neither row nor line ends, E_1 and E_2 are the energies of a line end and a row end, respectively, and $mE_{\mathrm{Si}\,surface}$ is the energy (per dimer) of the region not covered by ad-dimers.

In the same way, we write down the total energy of a finite region covered by group III dimers in a (2×2) configuration and square arrangement as

$$E_{2\mathrm{D}}(n)=nE_{(2\times2)}+2\sqrt{n}E_2+2\sqrt{n}E_1+mE_{\mathrm{Si}\,surface}. \qquad (2)$$

We can compare directly Eqs. (1) and (2).

For $E_{1\mathrm{D}}(n)<E_{2\mathrm{D}}(n)$ formation of 1D lines is more favorable. This is the situation for $n<15$ dimers for Al, $n<18$ dimers for Ga, and $n<14$ dimers for In. In calculating these numbers, we have neither taken into account kinetic effects nor the presence of defects in the Si substrate (these two factors can make the lines longer). We want to emphasize here that our calculations show that for a few number of dimers, the formation of one-dimensional lines is thermodynamically more stable than the formation of 2D structures. The fact that longer lines have been observed experimentally indicates that kinetics also plays an important role and it allows the lines to grow slightly longer. Defects and kinetics are probably the reasons why at low coverage, the 1D lines are kept apart and do not collapse in 2D regions of the (2×2) reconstruction. Experimental results show that annealing these surfaces results in the formation of 2D structures.[27]

An effective repulsion of 0.1 eV/atom between dimer lines was proposed for Al.[7] Our calculations show no repulsion between dimer lines. This is consistent with low-coverage STM experiments that in many occasions show pair of lines in their images. Also for Al, In, and Ga, the formation of the (2×2) structure has been observed for coverages as low as 0.16 ML.[6,26,2] If there were such a repulsion, the formation of pair of lines should be highly improbable and the (2×2) reconstruction should start forming very close to the 0.5 ML coverage. It is easy to understand physically why E_1 is positive. On the other hand, it is more difficult to understand why E_2 is positive too. A closer look at the atomic structure formed by the adsorption of group III ad-dimers can give us a hint. The metal ad-dimer not only affects the Si dimers where it sits but also neighboring Si dimers. It, for example, modifies their buckling amplitude. These perturbations have an energy cost, and therefore, having two dimers together along the $[110]$ direction (separated by a distance $2a$) reduces this energy.

We have also studied the growth of group V metals on Si(001) up to a full monolayer. In particular, for As and Sb, we have calculated the total energy of the same infinite configurations that we have considered in the case of group III atoms: an infinite line, and infinite row, and a surface with a (2×2) periodicity and 1/2 ML coverage. It was found that the total energy of an infinite line and an infinite row were the same. This is a clear indication that the energy cost associated to line and row ends are the same. Therefore, the formation of 1D lines is not favorable for group V ad-dimers. Moreover, the most stable configuration corresponds to the (2×1) reconstruction, in which all Si dimers are broken, and the As (Sb) atoms form symmetric dimers. This result is in agreement with experiments that show no formation of lines at low coverages.[10]

In conclusion, we have performed first principles total energy calculations of the initial growth of group III and group V metals, starting from the adsorption of a single adatom up to full monolayer coverage. Our calculations show that group III and group V metals form dimers when adsorbed on Si(001). However, their orientation and position strongly depend on the first adatom binding site. Group III elements form dimers parallel and between the trenches of the Si dimers. Instead, group V atoms form dimers orthogonal and on top of the Si dimers. As a direct consequence, group III atoms form long lines along the $[1\bar{1}0]$ direction. However, under thermodynamic equilibrium, there is a theoretical limit to the size of the lines. For the case of group V adatoms the formation of a (2×1) structure (in which all underlying Si dimers are broken) is more favorable than one-dimensional growth.

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