ELSEVIER

Surface Science 396 (1998) L261–L266

surface science

Surface Science Letters

Diffusion of adsorbate atoms on the reconstructed Si(111) surface

Kyeongjae Cho [1],*, Efthimios Kaxiras

Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

Received 22 September 1997; accepted for publication 30 October 1997

Abstract

We study the adsorption and diffusion of foreign atoms with different valences (K, Mg, Ga, Ge) on the reconstructed Si(111) surface using density functional theory total-energy calculations. We find that the stable adsorption sites for all the adsorbate atoms considered are high-coordination surface sites (T_4-type, H_3-type or B_2-type) rather than the surface dangling bond sites (T_1 or adatom T_4 site) as might have been expected from simple bond-counting arguments. We also examine the surface diffusion paths and find that the adsorbate atoms, depending on their interaction with the surface, experience certain restrictions in their motion which we refer to as "intermittent diffusion". These results help elucidate a number of experimental observations. © 1998 Elsevier Science B.V.

Keywords: Alkaline earth metals; Alkali metals; Density functional calculations; Gallium; Germanium; Silicon; Surface diffusion

---

The behavior of adsorbate atoms on semiconductor surfaces has been studied extensively as the initial stage of metal–semiconductor interface formation [1–7]. When metal adsorbates are added on a semiconductor surface, the surface undergoes a sequence of reconstructions as a function of coverage before the formation of the interface is complete. The microscopic nature of these structural changes depends sensitively on the interaction between the metal adsorbate atom and the semiconductor surface. Usually, studies of this interaction are confined to stable structures which arise when a certain amount of the adsorbate (a fraction of, or up to one monolayer) has been deposited on the surface [8–10]. A different aspect of the adsorbate–surface interaction, and perhaps an even more important one for the evolution of the surface morphology, is the dynamics of the adsorbate atoms, which is at present poorly understood.

In this paper we report the results of an accurate and systematic investigation of the interaction of metal adsorbate atoms with the reconstructed Si(111) surface at very low coverages. We have chosen this surface because it is the most stable surface of Si and because it exhibits a rich variety of reconstructions (from the low-temperature dimer–adatom stacking fault or DAS structure, with a (7×7) cell, to a mixture of (2×2), $(\sqrt{3}\times\sqrt{3})$, and higher-order $((2n+1)\times(2n+1))$ patterns [11], allowing for interesting dynamical behavior of the adsorbate atoms. When metal adsorbate atoms (e.g. K, Mg and Ga) are added on the Si(111) surface beyond a certain coverage (typically around $\Theta=0.1$ monolayer (ML), where 1 ML corresponds to one adsorbate atom per

---

* Corresponding author: Fax: (+1) 650 7231778; e-mail: kjcho@am-sun2.stanford.edu

[1] Current address: Mechanics and Computation Division, Mechanical Engineering Department, Stanford University, Stanford, CA 94305-4040, USA.

PII S0039-6028(97)00848-0

(1 × 1) surface unit cell), the (7 × 7) reconstruction begins to be destroyed. For the most part, experimental and theoretical studies address the coverage regime at which the (7 × 7) reconstruction has been eliminated. In low-coverage studies where the (7 × 7) reconstruction persists, interpretation of the adsorbate-induced structures has been based on simplistic bond-counting arguments, placing the adsorbate atoms at surface dangling-bond sites.

To obtain a comprehensive picture, we have considered representative atoms of different valences, including K, Mg, Ga and Ge (with valences 1–4) and studied their stable, metastable and saddle-point configurations on the Si(111) surface. We have also calculated the corresponding dynamics of native Si adsorbate atoms for comparison to that of foreign atoms. Our two most important findings are: (i) The rest-atom dangling-bond site (T_1 site) is an unstable high-energy position for all the adsorbate atoms considered, showing that simple bond-counting arguments cannot be used in these systems. While the detailed nature of individual adsorbate atom energetics is different for each element, the stable adsorption sites are generally characterized by high coordination, unlike the T_1 site. (ii) The adsorbate atoms spend a significant (and in some cases overwhelming) portion of their time trapped in basins of attraction, from where they escape very infrequently to jump into adjacent basins. This type of motion, which we refer to as intermittent diffusion, is more pronounced for adsorbates which exhibit a tendency for covalent bonding (Si and Ge), although due to the high coordination, all bonding on the surface should be better described as metallic. These findings help elucidate and suggest new interpretations for several experimental observations.

We begin with a short discussion of the important features of the Si(111) surface reconstruction. The unit cell of the stable (7 × 7) reconstruction contains several important features, referred to as adatoms, rest-atoms, dimers and corner-holes. Of these, the features which also survive in all other reconstructions which appear at higher temperatures (in the so-called (1 × 1) disordered phase) are the adatoms and rest-atoms [11]. These features help stabilize the surface by minimizing the number of dangling bonds, subject to the constraint that the surface stress is also minimized. Since the adatom and the rest-atom introduce stresses of opposite signs [12,13] they tend to form structures where one surrounds the other. A typical arrangement of these features is shown in Fig. 1. This is the local arrangement of adatoms and rest-atoms in each half of the (7 × 7) unit cell, as well as in other reconstructions such as the (2 × 2), c(2 × 8), etc. Accordingly, in our calculations we concentrate on a (4 × 4) supercell with four adatoms and four rest-atoms locally arranged in a (2 × 2) pattern.

The surface is modeled by a four-layer slab configuration with the bottom layer fixed at bulk positions and saturated by hydrogen atoms. Slabs are separated by 12 Å vacuum. The electronic energy functional is obtained from the local density approximation to density functional theory, and minimized using the Car–Parrinello scheme [14] in a parallel implementation [15,16]. Optimized non-local pseudopotentials [17] were used in the Kleinmann–Bylander separable form [18] with a plane wave basis. To establish the accuracy of the calculations we performed extensive tests in a

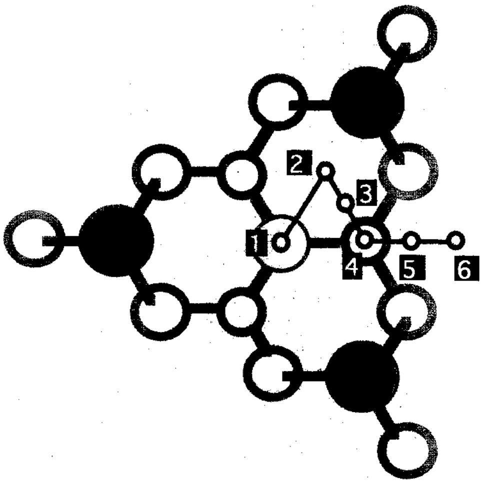

Fig. 1. Schematic top-view representation of a portion of the Si(111) reconstruction containing three Si adatoms (large black circles) and one rest-atom (grey circle) as well as the substrate atoms directly bonded to those (smaller open circles). The sites where the adsorbate atoms are placed are indicated by the numbers 1–6. These sites are used for the energy plots in Fig. 2.

(2 × 2) cell with plane wave cut-offs up to 12 Ry, and reciprocal space samplings with the Monkhorst–Pack (MP) scheme [19] up to a (3,3,1) grid. From these tests we established that relative energy differences suffer from an error bar of 0.05 eV for calculations in the large (4 × 4) unit cell with an 8 Ry plane wave cutoff and the Γ point for reciprocal space sampling. We have also independently confirmed the accuracy of the various pseudopotentials, using representative molecular (for K and Mg) or bulk (for Ga and Ge) structures for comparison to experimental results.

We performed calculations for six different positions of the adsorbate atoms, identified in Fig. 1 as 1–6. We refer to these positions as T_1, H_3-type, B_2-type, T_4-type, B_2'-type and H3′-type. The nomenclature derives from the terms used to characterize positions of the Si adatoms on the Si(111) surface, and the suffix "type" is used to denote positions equivalent to the usual positions if the presence of the nearby Si adatoms is neglected. Notice that the positions 2, 3 and 4 (H_3-type, B_2-type and T_4-type) are repeated symmetrically around the central T_1 position, forming a closed path of which the segment shown in Fig. 1 is one sixth (we refer to this as the "2–3–4 closed path"). In this path, a moving atom would stay within one basin defined by the central rest-atom and the three surrounding Si adatoms. Paths which include the positions 5 and 6 would bring the moving atom into an adjacent basin.

Fig. 2 shows the energies of the six positions for the metal adsorbate atoms. The energies at these sites are listed in Table 1, where we also give the absolute adsorption energies, defined as the lowest energy on the surface relative to the a reference energy of the metal atoms in vacuum. For all adsorbate atoms the T_1 site is the highest-energy site, and the lowest-energy sites are the T_4-type (for K and Ga), H_3-type (for Mg) and B_2-type (for Si ang Ge) sites. All the lowest-energy sites are within the basin formed by the three Si adatoms around the rest-atom and are high-coordination sites. We have also considered the possibility that the adsorbates are attached to the dangling bond of the Si adatom site rather than the rest-atom site. The energy for placing a K atom directly above the Si adatom dangling bond is 0.83 eV relative to the lowest-energy site for this adsorbate (the T_4-type site). This is 0.5 eV higher than the next highest energy, the T_1 site (see Table 1), so it is a highly unlikely configuration. Since K is the only monovalent element we considered, and thus the one with the highest probability to form a stable structure with a single bond to a substrate atom, we expect that all the other adsorbates will be even less likely to bond to the Si adatom dangling bond in a stable manner. Thus, the energetic comparisons of Table 1 exclude the possibility that adsorbate atoms will attach to dangling-bond sites (either the rest-atom or the adatom) on the Si surface, thereby invalidating any simple bond-counting arguments for the preferred adsorbate geometry.

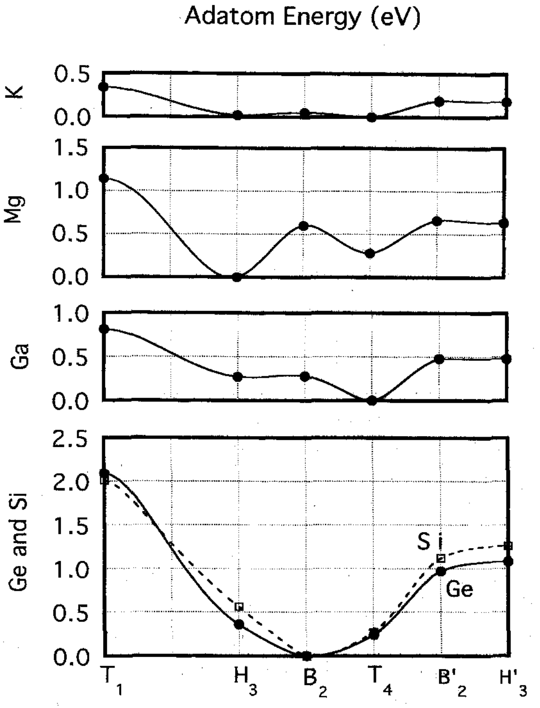

Fig. 2. Plots of the adsorbate atom energies along the six sites defined in Fig. 1 (from left to right the six sites are T_1, H_3-type, B_2-type, T_4-type, B_2'-type and H_3'-type). The energies are relative to the lowest energy sites for each adsorbate atom (see Table 1).

Note that the energy of a K adsorbate atom at different sites on the ideal (1 × 1) surface has been calculated in Ref. [3], where it is shown that it has

Table 1
Relative energies of the various adsorbates on the Si(111) surface in eV per adatom

Site	K	Mg	Ga	Ge	Si
T_1	0.34	1.14	0.81	2.09	2.01
H_3-type	0.02	0.00 (−1.79)	0.27	0.36	0.56
B_2-type	0.05	0.60	0.28	0.00 (−5.16)	0.00 (−3.94)
T_4-type	0.00 (−1.95)	0.28	0.00 (−3.36)	0.24	0.27
B_2'-type	0.19	0.66	0.48	0.97	1.12
H_3'-type	0.18	0.63	0.48	1.08	1.26
ϵ_{cp}	0.05	0.60	0.28	0.36	0.56
ϵ_b	0.19	0.66	0.48	1.08	1.26
$\Delta\epsilon$	0.14	0.06	0.20	0.72	0.70
γ	2×10^2	10	2×10^3	10^{12}	6×10^{11}

The notation for the various positions is that of Fig. 1. The adsorption energy, defined as the energy of the adsorbate atom on the surface relative to the energy of an isolated atom in vacuum, is also given in parentheses at the positions of lowest surface energy. The energy barriers for diffusion along a 2–3–4 closed path and across basins are also given (ϵ_{cp} and ϵ_b, respectively), as well as their difference $\Delta\epsilon=\epsilon_b-\epsilon_{cp}$ and the ratio γ of moves along the closed path versus across basins (see text).

lower energy at the high-coordination T_4 and H_3 sites than at the T_1 site (by about 0.3 eV). Moreover, the Si adsorbate atom on the reconstructed surface (which we refer to as a Si extra adatom) is situated in a different chemical environment from the intrinsic Si adatoms of the (7×7) reconstruction (shown as large black circles in Fig. 1). We have performed an extensive set of calculations for the energetics of the intrinsic Si adatom on a patch of (1×1) unreconstructed surface, and find that for this type of adatom the lowest-energy site is T_4, where four covalent Si–Si bonds between the intrinsic adatom and surface atoms can be formed. On the other hand, the Si extra adatom on the reconstructed surface can form only one Si–Si covalent bond with the rest-atom (the grey circle in Fig. 1) when placed at any of the three high-coordination sites (T_4-type, B_2-type or H_3-type). The relative energy of the extra adatom at these three sites is determined by its intricate bonding to the rest of the surface atoms (other than the rest-atom). What emerges from these comparisons is that both on the unreconstructed and on the reconstructed surface, adsorbate atoms in general prefer high-coordination sites. For the intrinsic Si adatom this can be easily rationalized by considering its covalent bonding to the substrate, but for the extra Si adatom it is less trivial to explain this tendency by simply counting covalent bonds.

We turn next to the dynamics of the adsorbate atoms. To extract the general behavior, we define two energy barriers, ϵ_{cp} for motion along the 2–3–4 closed path within a basin and ϵ_b for motion across basins. These are listed in Table 1 for the various adsorbates. We find that in general the difference $\Delta\epsilon=\epsilon_b-\epsilon_{cp}$ is positive, and in some cases it is rather large (especially for Si and Ge). This indicates that the adsorbate atoms will have the chance to diffuse along the 2–3–4 closed path many times before they are able to move across basins. The ratio γ of moves along the closed path versus across basins is given by the expression

$$\gamma=\exp(E\epsilon/kT),$$

which is a measure of the attempts which the adsorbate atom will make to move along the closed path versus the attempts to cross the extra barrier for moving to an adjacent basin. As seen from Table 1, the values of γ at room temperature range from 10 for Mg to $\sim10^2$–10^3 for K and Ga, to $\sim10^{12}$ for Ge and Si. These comparisons indicate that the motion of Ge and Si adsorbate atoms will be strongly restricted within the basins of attraction, and only rarely can these atoms escape to nearby stable sites. This effect is much less pronounced for the metal adsorbate atoms, and is almost insignificant for Mg.

To rationalize this behavior, we note that the adsorbate atoms form bonds to their nearest neighbors, of which the least saturated atom is the substrate rest-atom, having three regular bonds and one dangling bond (the intrinsic Si adatoms have a weak fourth bond to the substrate atoms directly below them). Although, as emphasized above, the bond between the rest-atom and the adsorbate atoms cannot be considered a typical single covalent bond, the presence of the dangling bond on the rest-atom makes this the strongest bond between the adsorbate atom and the surface. When the adsorbate atoms diffuse within the basin formed by three Si adatoms, their bond to the rest-atom need not be broken. Moving outside the basin involves breaking of this bond. This accounts for the fact that $\Delta\epsilon$ is always positive. The significant difference in $\Delta\epsilon$ between metal atoms (less than 0.2 eV) and Ge and Si atoms (more than 0.7 eV) originates in the difference of the corresponding valence electronic structures. Within a simple tight-binding picture, the Ge and Si adsorbate atoms have bonding orbitals which are almost identical in energy to the rest-atom dangling-bond state, whereas the metal atoms have bonding orbitals of higher energy. Consequently, the resulting bonds to the rest-atom dangling bond will be stronger for the Ge and Si adsorbate atoms than for the three metal adsorbate atoms.

The results of our theoretical study can be used to shed new light on earlier interpretations of experiments for K, Mg and Ga adsorbate atoms on the Si(111) surface. Hashizume et al. [1,2] obtained STM images of the Si(111)-(7 × 7) surface with 0.005 and 0.01 ML K coverages, which show that some of the Si intrinsic adatom spots are missing. The missing spots were interpreted as the sites where isolated K atoms were adsorbed on top of the Si adatoms. Our calculations show that this interpretation cannot be correct. From the energy curve in Fig. 2 we conclude that an isolated K adsorbate atom will diffuse too fast to be observed at room temperature. It is more likely that the missing spots correspond to clusters of K adsorbate atoms which surround a Si adatom site in a stable configuration. For Mg adsorbate atoms, Vandré et al. [4], using surface EXAFS, found that the nearest-neighbor Mg–Si distances are 2.47 and 2.60 Å at 1/6 and 1/3 ML coverages. These distances were interpreted as corresponding to the two types of bonds which a Mg atom would form if it replaced an intrinsic Si adatom at a T_4 site. However, the XPS experiments of An et al. [5] show different surface symmetries and different Si 2p core-level shifts for 1/6 and 1/3 ML Mg coverages, indicating that the Mg adsorption sites are different. Our calculations show that at 1/6 ML coverage (which is below the limit of one adsorbate atom per basin of attraction) the Mg atoms will be adsorbed at the H_3-type site, where the Mg–Si distances are 2.43 and 2.74 Å, consistent with the experimental values. Therefore, one can re-interpret the EXAFS experiment as indicating a change of reconstruction between 1/6 and 1/3 ML Mg coverages, while the Mg–Si distances are similar for both reconstructions. For adsorption of Ga on Si(111), STM images show domains of $(\sqrt{3} \times \sqrt{3})$ and (7 × 7) reconstructions for coverages less than 1/3 ML. Within our theoretical results, we interpret this as indicating that at this coverage Ga atoms are dominantly placed at the T_4 sites in the $(\sqrt{3} \times \sqrt{3})$ domain, while some of them may reside at the T_4-type sites in the (7 × 7) domain. It will be interesting to determine the ratio of Ga atoms at the two types of sites by more detailed experiments.

Acknowledgements

This work was supported by the Office of Naval Research, Contract #N00014-95-1-0350. The manuscript was prepared in part during a visit by one of us (K.C.) to the Center for Theoretical Physics, Seoul National University, Korea; partial financial support from this institution is gratefully acknowledged. E.K. acknowledges the hospitality of the Institute of Electronic Structure and Lasers, Foundation for Research and Technology Hellas, Heraklion 71110, Crete, Greece, where part of the work was performed.

References

[1] T. Hashizume, K. Motai, Y. Hasegawa, I. Sumita, H. Tanaka, S. Amano, S. Hyodo, T. Sakurai, J. Vac. Sci. Technol. B 9 (1991) 745.

[2] T. Hashizume, Y. Hasegawa, T. Sakurai, Appl. Surf. Sci. 4849 (1991) 119.
[3] F. Huaxiang, Y. Ling, Surf. Sci. 250 (1991) L373.
[4] D. Vandré, L. Incoccia, G. Kaindl, Surf. Sci. 225 (1990) 233.
[5] K.S. An, R.J. Park, J.S. Kim, C.Y. Park, S.B. Lee, T. Abukawa, S. Kono, T. Kinoshita, A. Kakizaki, T. Ishii, J. Appl. Phys. 78 (1995) 1151.
[6] T. Thundat, S.M. Mohapatra, B.N. Dev, W.M. Gibson, T.P. Das, J. Vac. Sci. Technol. A 6 (1988) 681.
[7] J. Zegenhagen, J.R. Patel, P. Freeland, D.M. Chen, J.A. Golovchenko, P. Bedrossian, J.E. Northrup, Phys. Rev. B 39 (1989) 1298.
[8] J.E. Northrup, Phys. Rev. Lett. 53 (1984) 683.
[9] U.K. Köhler, J.E. Demuth, R.J. Hamers, Phys. Rev. Lett. 60 (1988) 2499.
[10] St. Tosch, H. Neddermeyer, Phys. Rev. Lett. 61 (1988) 349.
[11] Y.-N. Yang, E.D. Williams, Phys. Rev. Lett. 72 (1994) 1862.
[12] D. Vanderbilt, Phys. Rev. B 36 (1987) 6209.
[13] R.D. Meade, D. Vanderbilt, Phys. Rev. B 40 (1989) 3905.
[14] R. Car, M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.
[15] M.C. Payne, M.P. Teter, D.C. Allen, T.A. Arias, J.D. Joannopoulos, Rev. Mod. Phys. 64 (1992) 1045.
[16] K.D. Brommer, B.E. Larson, M. Needels, J.D. Joannopoulos, Comput. Phys. 7 (1993) 350.
[17] A.M. Rappe, K. Rabe, E. Kaxiras, J.D. Joannopoulos, Phys. Rev. B 41 (1990) 1227.
[18] L. Kleinman, D.M. Bylander, Phys. Rev. Lett. 48 (1982) 1425.
[19] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.