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Unusual Ti adsorption on Si(001) and subsequent activation of Si ejection

B. D. Yu, Yoshiyuki Miyamoto, and Osamu Sugino
Fundamental Research Laboratories, NEC Corporation, Tsukuba 305, Japan

T. Sasaki and T. Ohno
National Research Institute for Metals, 1-2-1 Sengen, Tsukuba 305, Japan

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The epitaxy of Ti on Si(001) exhibits a profound intermixing of Ti and Si atoms giving rise to the formation of titanium silicide. This phenomenon differs considerably from typical epitaxial growth and is not understood. Using first-principles total-energy calculations we examined the reaction of a Ti adatom with a Si(001) surface. We found that the penetration of the Ti adatom into a near-surface interstitial site and the subsequent ejection of its neighboring surface Si atoms onto a terrace is kinematically favored with respect to the ''normal'' hopping diffusion on a Si surface. These reactive processes provide the microscopic mechanism of an initial stage of transition-metal silicidation. [S0163-1829(98)01332-0]

Silicidation is a typical film-growth process with strong reactivity, and it has attracted much attention recently.[1–5] Technologically, controlling the silicidation of transition metals (TM), e.g., titanium, cobalt, and nickel, to form low-resistivity interconnects is an important issue in the future technology of very-large-scale integrated (VLSI) and ultralarge-scale integrated (ULSI) device fabrications. Scientifically, elucidating the reaction kinetics leading to the compound-film formation is of particular interest.[1,2,5] Lee and Bennett[1] reported unexpected competition between the diffusions on surface and through bulk, with a more significant contribution from the latter found for Ni and Co. There is also unpredictable competition between the Si dangling bond, which prefers to reduce its number, and the strong TM-Si chemical bond, which prefers to have its optimal number. In this way, the TM silicidation is behavior totally different from the crystal growth without such reactivity. Such complicated reactive kinetics may be, to some extent, clarified by *ab initio* calculations, because the recent application of the vector-parallel computers has opened a way to investigate a large number of possible reaction processes with the detailed paths being identified state to state.

Toward this end, in this paper, we examine the reaction of a Ti adatom with a Si(001) surface for a model TM-silicon system, Ti/Si(001), by performing first-principles total-energy calculations. We have found that the kinetic process having the lowest activation energy, E_a, is the reactive one, in which the Ti adatom penetrates into a near-surface interstitial site and ejects (desorbs) its neighboring surface Si atoms onto a terrace. The activation energy, about 1.7 eV, is much lower than that for the ''normal'' hopping diffusion on a Si surface, 2.0 eV. These novel reactive behaviors of TM on Si, which have not been found for any other adsorbate systems so far, provide the mechanism of an initial stage of silicidation in epitaxial growth.

All calculations were carried out using the density-functional theory (DFT) together with the local-density approximation for the exchange-correlation functional[6] and norm-conserving, fully separable pseudopotentials.[7,8] The $3d$ states of Ti were treated as valence states and a proper treatment of the nonlinearity of the core-valence exchange-correlation functional[9] was employed. The basis set consists of plane waves up to a kinetic energy of 35 Ry. The calculated lattice constants for the titanium crystal in the hcp structure were $a_0 = 2.94$ Å and $c_0 = 4.64$ Å and the bulk modulus was $B_0 = 1.23$ Mbar, which agreed well with the measured values[10] $a_0^{\mathrm{expt}} = 2.95$ Å, $c_0^{\mathrm{expt}} = 4.68$ Å, and $B^{\mathrm{expt}} = 1.05$Mbar, as have other calculations.[11,12] For Si we obtained $a_0 = 5.38$ Å and $B_0 = 0.95$ Mbar. Again, this agrees well with the experimental data ($a_0^{\mathrm{expt}} = 5.43$ Å, $B_0^{\mathrm{expt}} = 0.99$ Mbar), and with other calculations.[13] Details of the computational technique are described in Refs. 14 and 15.

To treat the adsorbate we used a repeating slab structure consisting of five Si layers and a Ti adatom with a 7.3-Å vacuum region and a $c(4\times4)$ surface unit cell. We used a theoretical lattice constant $a_0 = 5.38$ Å for the Si slab. The bottom of the slab was terminated with H atoms to passivate the dangling bonds of Si. The **k**-space integration was replaced by a sum over a uniform mesh of 4 **k** points in the surface Brillouin zone (SBZ) of the $c(4\times4)$ cell (displaced from $\overline{\Gamma}$). We relaxed all atoms in the slab except for the bottom-most Si and H atoms. Geometry optimization was terminated when the forces were smaller than 0.05 eV/Å. We also performed test calculations using a more extensive set of parameters, for example, a slab of 6 Si layers, a 40-Ry cutoff energy, and the 9 **k** points in the SBZ. We found that the values in the total energy difference presented here are accurate to ± 0.05 eV, which is fully sufficient for the purpose of our study.

For a clean Si(001) surface, our calculations show that the $p(2\times2)$ structure consisting of alternatively buckled dimers is the configuration that has the lowest energy in the $c(4\times4)$ surface unit cell [see Fig. 1(a)]. This result agrees well with the previous DFT calculations.[16] Upon adsorption of a Ti adatom on Si(001), our total-energy calculations show three adsorption sites: a hollow site on a dimer row (H), and a bridge site (B), and a hollow site (C) in the dimer valley (see Fig. 1). We find that site H is energetically more stable than sites B and C in the dimer valley by 0.25 and 0.52 eV, respectively. This is in good agreement with scanning tunneling microscopy (STM) observation of the Ti

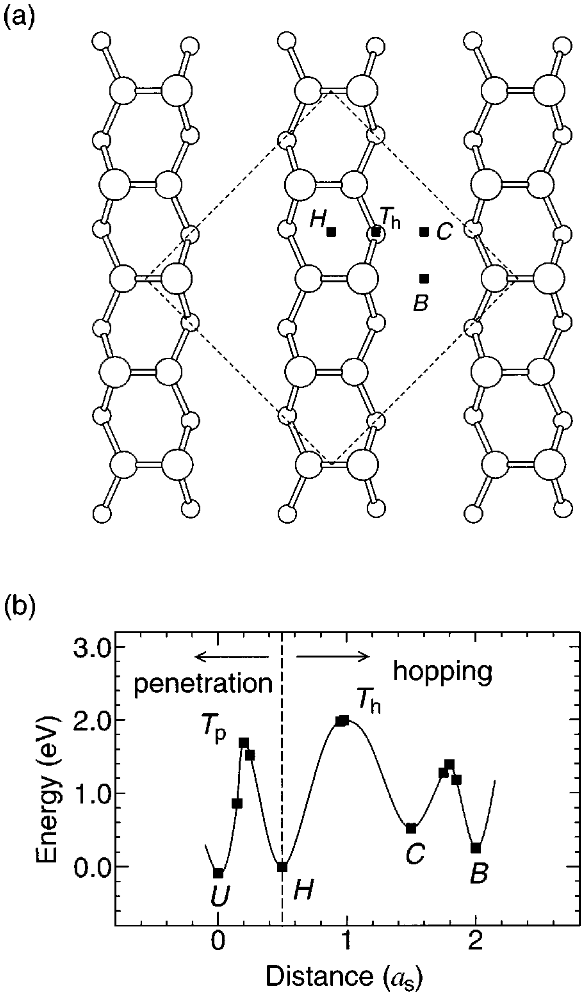

FIG. 1. Total energy of a Ti adatom moving along the reaction pathways for a ‘‘normal’’ hopping process and a penetration process into a near-surface interstitial site. (a) A schematic top view of a clean $p(2\times2)$ Si(001) surface consisting of alternatively buckled dimers. In (b) sites H, B, and C are stable adsorption sites for the Ti adatom on a Si surface, and site U is a stable adsorption site for the Ti adatom at the near-surface interstitial position. Sites T_h and T_p are saddle points for the hopping diffusion of Ti on a Si surface and the penetration process of Ti, respectively. In the calculations, we used the $c(4\times4)$ surface unit cell indicated by the dashed line in (a). The distance is given in units of the surface lattice constant $a_s=3.81$ Å. The corresponding energy for site H is used as a reference. All the coordinates of the diffusing atom as well as all coordinates of the other atoms of the four top substrate atoms have been relaxed for any position along the reaction pathways. The solid squares in (b) are the calculated values and the solid lines are guides to the eye.

adsorption at site H at low temperature (below 440 K).[17] In the optimized geometry for site H [see Fig. 2(a)] the Ti adatom is located 0.55 Å above the neighboring Si atoms, weakening the two adjacent Si-dimer bonds; the Si-dimer bond length increases from 2.31 to 2.62 Å. The Ti adatom has six neighboring Si atoms: The bond length between the Ti adatom and its four surface Si neighbors is 2.42 Å and the bond length between the Ti adatom and its two second-layer Si neighbors is 2.63 Å.

We now look at the microscopic mechanism for the diffusion of the Ti adatom on a Si(001) surface. The right curve

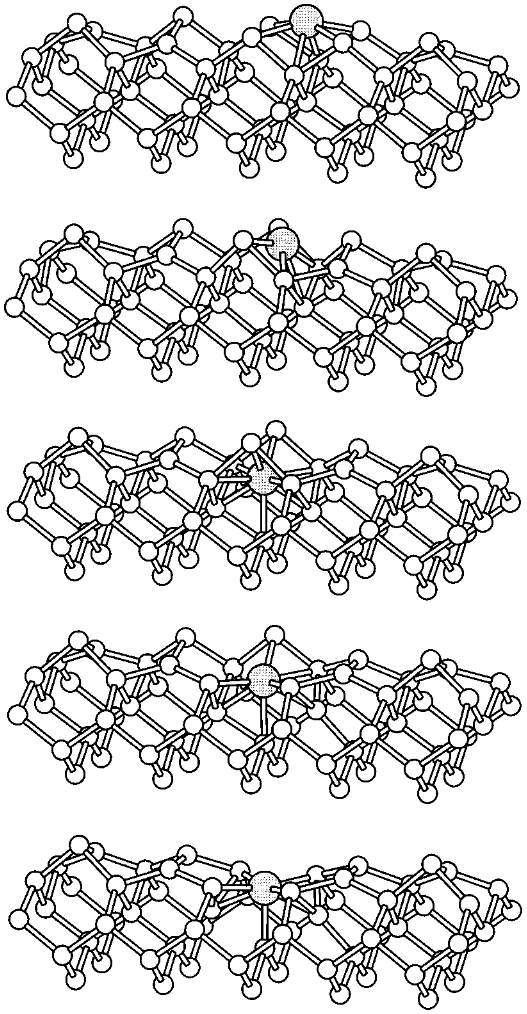

FIG. 2. Bird’s-eye views of a Ti adatom adsorbed at (a) site H, (c) site U, (d) site U', and (e) site DV. The transition state T_p for the penetration process $H\rightarrow U$ is shown in (b). The ejection of its surface Si neighbors onto a terrace proceeds along the reaction pathway $U\rightarrow U'\rightarrow DV$. The shaded and open spheres represent Ti and Si atoms, respectively.

in Fig. 1(b) displays the results for the ‘‘normal’’ hopping process, where the Ti adatom moves across a Si surface by a series of hops between adjacent adsorption sites. The calculated activation energy for the hopping diffusion is 1.99 eV, much higher than the values for the Si diffusion on Si(001) (0.6 and 1.0 eV, respectively, in the directions parallel and perpendicular to the Si dimer rows.[16]) The transition state is identified as being half-way between the two adsorption sites H and C (T_h in Fig. 1). In the optimized geometry, the Ti adatom has three Si neighbors in the range from 2.42 to 2.59 Å, less than at the H site (six Si neighbors).

The left curve in Fig. 1(b) displays the results for the penetration process, where the Ti adatom dives into a silicon interstitial site, site U, just below the surface [see Fig. 2(c)]. We found that the Ti adsorption at near-surface interstitial site U is stable and the total energy at site U is lower than that at site H on a Si surface and that at a T_d interstitial site in the third Si layer, by 0.09 and 0.14 eV, respectively. Figure 2(c) shows the optimized structure of geometry U. The Ti adatom has nine neighboring Si atoms in the range from 2.45 to 2.66 Å. We noticed that the bond of the Si dimer

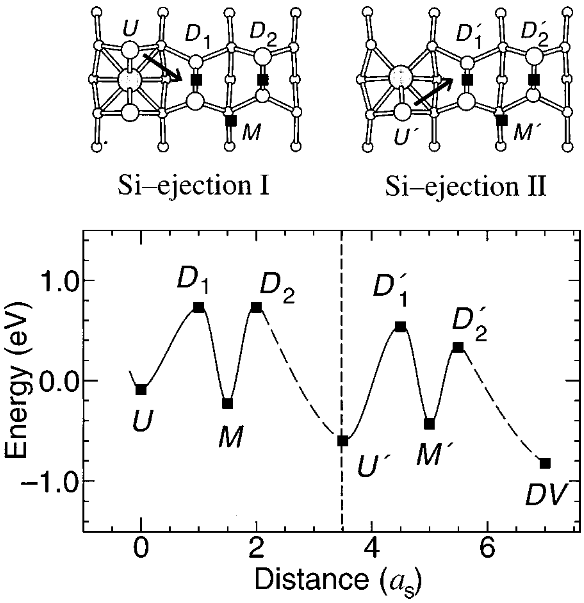

FIG. 3. Total energy of a Si atom moving along the reaction pathways for its ejection onto a terrace: Si ejection I ($U \rightarrow U'$) and Si ejection II ($U' \rightarrow DV$). In the top views of the atomic geometries of sites U and U' (the upper figures), the shaded and open spheres represent Ti and Si atoms, respectively. For the geometries U' and DV, where the supercell contains a different number of Si atoms from the U site, we obtained the total energies using the energy of a Si atom in the bulk as the Si chemical potential.

above the Ti adatom was broken, which indicates that the Si atoms tend to strongly interact with the adsorbed Ti atom rather than the adjacent Si atoms. The calculated activation energy for the process $H \rightarrow U$ was 1.69 eV, 0.30 eV lower than that for the ''normal'' hopping diffusion on a Si surface.

Our calculated results clearly show that the Ti adatom on a Si surface prefers to penetrate into the near-surface interstitial site rather than hop to the adjacent adsorption sites on a Si surface. Inspection of the geometry during the penetration process makes this theoretical finding very plausible [see Figs. 2(a)–2(c)]. During the process, the Ti adatom moves toward one of its two adjacent Si dimers. Since the Si atoms strongly interact with the Ti adatom, the dimer atoms that the Ti adatom approaches are pushed away, keeping in close contact with the moving Ti adatom. At the transition state geometry T_p [see Fig. 2(b)], the Ti adatom has five Si neighbors in the range from 2.45 to 2.75 Å and the other Si dimer again exhibits a buckled dimer structure. Thus, for this penetration process the local coordination of the Ti adatom remains high, lowering the activation energy.

Once the Ti adatom occupies the near-surface interstitial site U below a Si dimer, the ejection of the Si-dimer atoms onto a terrace proceeds very rapidly (see Si ejection I and II in Fig. 3). In the Si-ejection I process, one of the two atoms of the Si dimer goes onto a terrace and is subsequently incorporated into Si islands on the terraces or step edges. As a result, the ejection process leads to the geometry U' [see Fig. 2(d)], and we have computed the total energy of this geometry. To compare the total energies of supercells containing different numbers of Si atoms, we used the energy of a Si atom in the bulk as the Si chemical potential.[19] We found that the reaction $U \rightarrow U'$ is exothermic: geometry U' was energetically more favorable than that of geometry U by 0.51 eV. The calculated activation energy for the process $U \rightarrow U'$ was only 0.82 eV, much smaller than the energy (1.78 eV) that the Ti adatom needs to come back to the geometry of site H. In the transition-state geometry, the Si atom is located near to the top of the Si dimer (D_1 and D_2 in Fig. 3).

The subsequent ejection of another Si atom above the Ti atom onto a terrace (Si ejection II in Fig. 3) also proceeds very rapidly. The ejection of the Si atom and its diffusion to Si islands on the terraces or step edges gives the geometry DV as a final product configuration [see Fig. 2(e)], which agrees with the STM observations made at high growth temperature (above 440 K). Our total-energy calculations show that the process $U' \rightarrow DV$ is also exothermic: the geometry DV is energetically more stable than the geometry U' by 0.22 eV. (The energy difference between the geometries H and DV was previously calculated by Miwa and Fukumoto as well.[18] However, their result, 0.6 eV, is 0.2 eV smaller than our value, 0.82 eV. The difference is due to the use of different parameters in their calculations.[20]) The calculated activation energy for the process $U' \rightarrow DV$ was only 1.23 eV, 0.76 eV lower than that for the hopping diffusion. In the transition-state geometry, the Si atom is again located near to the top of the Si dimer (D'_1 and D'_2 in Fig. 3).

Our total-energy calculations clearly show that the penetrative adsorption of Ti at a near-surface interstitial site triggers the ejection of its surface Si neighbors onto a terrace. We noticed that in the Si ejection processes the Si atom needs to break only one strong Ti-Si bond, less than the number of the broken Ti-Si bonds required for hopping diffusion of the Ti adatom. Thus, the activation energy for Si ejection is much lower than that for the hopping diffusion of Ti.

On the basis of the above calculations, we can conjecture further reactive kinetics. Considering the small activation energy of the Si adatom diffusion, which is 0.6 eV, an ejected Si atom will rapidly migrate on a terrace until it reaches a titanium silicide island or a step edge. In this sense, the ejective adsorption plays a role as the Si adatom source, enhancing the silicidation reaction. A Ti adatom that happens to be initially located at B or C, can migrate along the dimer valley with the activation energy being about 1.1 eV. This would be an important nonreactive process through which Ti mass transport occurs. Further clarification will require very large-scale calculations containing Ti clusters, titanium silicide islands, or steps, which is a promising subject for future work.

In summary, we have presented first-principles total-energy calculations of the kinetic processes for the formation of titanium silicide on Si(001). These total-energy calculations describe and explain the kinetic processes for the formation of titanium silicide on Si where there is a profound intermixing of Ti and Si atoms. The Ti adatoms adsorbed on a Si-dimer row dive into a near-surface interstitial site, and the surface Si atoms adjacent to the Ti adatom are, in turn, ejected onto a terrace. These ejected Si atoms migrate on a terrace very rapidly with the corresponding activation energy for Si diffusion on Si(001). The diffusing Si atoms are then incorporated into titanium-silicide islands on a terrace, leading to the growth of titanium-silicide islands on Si. We found that all these processes are kinematically favorable: the relevant activation energies are smaller than the hopping diffusion barrier. Imaging the near-surface interstitial Ti adsorption with STM would provide direct experimental evidence supporting our understanding of the reactive processes. These reactive processes play a role in promoting the formation of titanium silicide on Si. Our finding that the Ti adatom pumps out surface Si atoms onto a terrace through the penetrative adsorption at a near-surface interstitial site should also be generally applicable to the formation of other TM silicides on Si, for example, TM silicides on a Si(111) substrate where there is no dimerized surface reconstruction.

Part of the computation was performed on the Numerical Materials Simulator of NRIM.

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[1] M. Y. Lee and P. A. Bennett, Phys. Rev. Lett. **75**, 4460 (1995).

[2] P. A. Bennett, D. G. Cahill, and M. Copel, Phys. Rev. Lett. **73**, 452 (1994).

[3] J. S. Huang, H. K. Liou, and K. N. Tu, Phys. Rev. Lett. **76**, 2346 (1996).

[4] T. Meyer and H. von Kanel, Phys. Rev. Lett. **78**, 3133 (1997).

[5] H. Sirringhaus, E. Y. Lee, and H. von Kanel, Phys. Rev. Lett. **74**, 3999 (1995).

[6] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1984).

[7] X. Gonze *et al.*, Phys. Rev. B **44**, 8503 (1991).

[8] M. Fuchs *et al.* (unpublished).

[9] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[10] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (John Wiley, New York, 1986).

[11] P. J. Feibelman, Phys. Rev. B **53**, 13 740 (1996).

[12] J.-H. Cho and K. Terakura, Phys. Rev. B **56**, 9282 (1997).

[13] See M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982), and references therein.

[14] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

[15] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).

[16] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[17] K. Ishiyama, Y. Taga, and A. Ichimiya, Phys. Rev. B **51**, 2380 (1995).

[18] K. Miwa and A. Fukumoto, Phys. Rev. B **52**, 14 748 (1995).

[19] The Si in the bulk is calculated with the same basis as used for the adsorbate system.

[20] In Ref. 18 they used a much lower cutoff energy (20 Ry) and a larger core radius (2.94 bohr) for the $3d$ component of the Ti pseudopotential than we used (35 Ry and 2.25 bohr). For the Si slab we used the theoretical lattice constant $a_0 = 5.38$ Å, while they used the experimental one $a_0 = 5.43$ Å.