Surface hydrogenation as a method to purify and flatten a silicon surface

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We performed first-principles theoretical calculations and found that the hydrogenation of a Si surface causes the segregation of impurity metal atoms from the subsurface onto the surface top. Since the contamination by metallic impurities is a principal cause of surface defects, it is expected that, by the surface hydrogenation, a highly pure and atomically flat Si surface is realized. © 2001 American Institute of Physics. [DOI: 10.1063/1.1377314]

With the rapid progress in the miniaturization of the ultralarge scale integrated Si devices, the achievement of highly pure and atomically flat Si surfaces is an urgent demand in the semiconductor industry. In the preparation of a flat Si(001) surface, which is used in device processes, the removal of the dimer vacancy (DV) defects is highly desirable. A principal cause of the DV defects is the surface contamination by metallic impurities, especially the transition-metal (TM) Ni atoms, existing in the subsurface, though their exact locations are still unidentified.1 Previously, we performed first-principles theoretical calculations to investigate the initial reaction processes of a Ni atom with both the bare Si(001) (Ref. 2) and H-terminated (H/) Si(001)-(2×1) (Ref. 3) surfaces. Then, we clarified the effects of the surface hydrogenation, i.e., the penetration of Ni into the subsurface is blocked, and thus the silicidation is prevented.4 Our results properly explained experimental results obtained by the scanning tunneling microscopy (STM) observations of the initial growth of Ni on both the bare Si(001) and H/Si(001)-(2×1) surfaces.5 In this letter, we present other effects of the surface hydrogenation that we found, i.e., it causes the segregation of Ni from the subsurface onto the surface top. Since a principal cause of the DV defects is the contamination by the Ni atoms, their segregation can lead to the reduction in the density of the DV defects. Therefore, we propose the surface hydrogenation as a method to purify and flatten a Si surface.5

We briefly describe the method of this study. Our first-principles calculations are based on the density functional theory7,8 with the generalized gradient approximation.9 For the atomic potentials, we adopt two types of the pseudopotentials: the norm-conserving type10 for the Si atom and the ultrasoft type11 for the Ni and H atoms. The partial core correction12 is employed for Ni. We use the plane wave basis set up to the cut-off energy of 20.25 Ry. We can reproduce the lattice constant (a) and bulk modulus (B0) for the bulk Si in the accuracies of +0.5% and −5.6%, respectively. For the bulk Ni, the accuracies of a and B0 are +1.2% and +1.3%, respectively. Furthermore, the Si–H bond length of the SiH4 molecule is obtained with the accuracy of +0.3%. The bare Si(001) and H/Si(001)-(2×1) surfaces are modeled by the repeated slab structure consisting of five Si atomic layers, as well as the vacuum region with the same thickness, and the in-plane c(4×4) super cell. The dangling bonds (DBs) of the Si atoms in the bottom Si layer are terminated by the H atoms. In the relaxation, the bottom Si and H layers are fixed. We take one sampling k point at the Γ point in the Brillouin zone. In evaluating the activation energy barrier, the force inversion method13 is utilized.

Now, we present our results. In Fig. 1, we show the penetration paths of Ni into the bare Si(001) subsurface and the segregation paths onto the H/Si(001)-(2×1) surface top with the total energy variations along them, which indicate a series of the penetration, surface hydrogenation, and segregation processes. On the bare Si surface, the most stable site for Ni is found to be the pedestal (P) site on the Si dimer row, where Ni is neighboring to four Si atoms of two dimers.

FIG. 1. The penetration paths of a Ni atom into the bare Si(001) subsurface and the segregation paths onto the H/Si(001)-(2×1) surface top, which are shown in the schematic side views of these surfaces, and the total energy variations along these paths are indicated. The shaded and unshaded circles indicate the Si and H atoms, respectively. The energy value for the P site on the bare Si surface is settled to be zero.

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On the other hand, in the subsurface, the tetrahedral (T) site just below the dimer center (U) and the hexagonal site under the higher Si atom of the buckled dimer (UH) are 0.19 and 0.40 eV more stable compared with the P site, respectively.14 From the P site, Ni penetrates into these sites along the paths \( P-U \) and \( P-BH-UH \), respectively. The \( BH \) site is the off-centered bridge site in the valley between the dimer rows, and locates near the higher dimer Si atom. It needs the activation energies \( E_A \) of 0.97 and 0.71 eV for Ni to penetrate into the \( U \) and \( UH \) sites, respectively. Once Ni penetrates into these sites, \( E_A \) of 1.16 and 1.11 eV are required to be segregated onto the \( P \) and \( BH \) sites, respectively. Thus, we see that Ni adsorbed on the bare Si(001) surface is stabilized by penetrating into these subsurface sites. Then, we connect the \( U \) and \( UH \) sites with the \( U \) and \( UB \) sites in the H/Si subsurface, respectively, assuming the process of the surface hydrogenation. The \( U \) and \( UB \) sites are the \( T \) site in the second and third Si layer, respectively.15 From the \( U \) and \( UB \) sites, it needs \( E_A \) of only 0.16 and 0.13 eV for Ni to segregate onto the \( P \) and off-centered bridge (\( B0 \)) sites, respectively. The \( P \) site is slightly lower than the adjacent dimer Si. The \( B0 \) site is most stable on this surface, all of which are equivalent because of the cancellation of the dimer buckling by the H termination. The \( P \) and \( B0 \) sites are 0.22 and 0.28 eV more stable than the \( U \) and \( UB \) sites, respectively. Then, it is summarized that the surface hydrogenation reduces \( E_A \) required for the segregation of Ni, and makes the subsurface sites less stable than the surface sites. Therefore, it is expected that Ni in the bare Si(001) subsurface is segregated onto the surface top by the surface hydrogenation, even in the room temperature range.

Here, we discuss the effects expected from the segregation of Ni. On the bare Si(001) surface, the DV defects are principally induced by the impurity Ni atoms.1 As the Si surface is hydrogenated, they segregate onto the surface top, so that the density of the DV defects is expected to be reduced. Thus, by the surface hydrogenation, a highly pure and atomically flat Si surface is to be realized. Therefore, we propose the surface hydrogenation as a method to purify and flatten a Si surface,5 whose effects are schematically shown in Fig. 2. In order to actualize this method, it needs two more manipulations, which are the removal of the segregated Ni atoms and the restoration of the DV defects. The former can be attained by techniques such as the gettering.16 On the other hand, the latter requires the supplementation of the surplus Si atoms. For this sake, one should control the surface temperature to make these Si atoms migrate on the surface. However, the surface temperature must be kept below 600 °C, because the H atoms terminating DBs of the surface Si atoms desorb at this temperature.5

Next, we discuss the effectiveness of this method. First, let us look into other plane orientations of Si surfaces. We previously showed that the stability of Ni in the bare Si(001) subsurface is due to the existence of DBs of the surface Si atoms.4 Thus, the key mechanism for the segregation of Ni is the passivation of DBs by the H termination. On various orientations of bare Si surfaces, the surface Si atoms reconstruct to cancel their unstable DBs, though the cancellations are imperfect. Hence, the same effects are expected for other Si surfaces, too. Second, we also found for another 3d TM Ti that the surface hydrogenation makes the subsurface sites unstable as well as Ni,4 so that its segregation by the surface hydrogenation is similarly expected. Furthermore, on the analogy from our results, it is most likely that it also works for other TM impurities.

It is known that the H annealing is an effective surface processing technique to improve the metallic contamination and the surface defects of the Si wafers.16 Here, we make the differences clear between the surface hydrogenation and the H annealing. First, the H annealing literally requires a high temperature around 1000 °C. On the other hand, the surface hydrogenation needs to be done at a much lower temperature, because the surface H atoms desorb at about 600 °C.5 Second, they are much different in the scale of the target defects. The H annealing improves the surface defects with the scale of 10⁻⁷ m. On the other hand, the surface hydrogenation can restore the defects with the atomic scale, i.e., 10⁻¹⁰ m.

In recent experiments, Matsuura et al. observed for Ni17 and also for the 5d TM W18 that, on the Si(001) surface, the surface hydrogenation segregates them onto the surface top and reduces the density of the DV defects, using STM. Segregated Ni and W atoms form silicide islands on the H/Si(001)-(2×1) surface.

In summary, by first-principles calculations, we found that the hydrogenation of a Si surface causes the segregation of metallic impurities from the subsurface onto the surface top, which are a principal cause of the DV defects. Then, we proposed the surface hydrogenation as a method to realize a highly pure and atomically flat Si surface.

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6 S. Higai and T. Ohno, Japan Patent No. 50265 (pending).
14 We exclude the site on the opposite side of the $U_H$ site, i.e., the site to be given as $U_L$, because it is 0.19 eV less stable than the $P$ site.
15 Since the $U_H$ site is the $T$ site, it does not coincide with the $U_H$ site. However, there is no stable site between the $U$ and $U_H$ sites in the H/Si subsurface, so that it is supposed that Ni in the $U_H$ site invariably moves to the $U$ or $U_H$ site by the surface hydrogenation.