PHYSICAL REVIEW B **73**, 125343 (2006)

Segregation of H as a surfactant during the formation of an Ag cluster on H-terminated Si(111): First-principles total-energy calculations

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(Received 27 August 2005; revised manuscript received 11 January 2006; published 28 March 2006)

The initial stages of Ag nanocluster formation on the H-terminated Si(111) surface are investigated using first-principles total-energy calculations. The surface remains structurally unchanged by the adsorption of a single Ag adatom that slides nearly freely with a diffusion barrier of 0.14 eV on the H/Si(111) surface [Phys. Rev. B **71**, 035310 (2005)]. When the Ag adatoms aggregate on this surface, however, the H atoms segregate from the substrate with extremely small energy barriers of ~0.2 eV. The Ag_n clusters ($n \geqslant 2$) with H segregation, where n is a number of Ag atoms in a cluster, are more tightly bound to the Si substrate than the clusters without H segregation since they make strong Ag-Si bonds, suggesting that such clusters can serve as seeds for island growth. The present findings are consistent with the depth-resolved measurement of H and real-space observations of the Ag islands on the H/Si(111) surface.

DOI: 10.1103/PhysRevB.73.125343 PACS number(s): 68.35.−p, 31.15.Ar, 68.43.Jk, 68.43.Fg

I. INTRODUCTION

Hydrogen, introduced as a surfactant on semiconductor surfaces during hetero- and homoepitaxies, alters growth mode[1–4] and morphology[5,6] of the overlayers on the surfaces. It is generally accepted that these phenomena originate from differences in surface kinetics and energetics between clean and surfactant-decorated surfaces. This implies that whether the surfactant is located on the surface (the growth front) or at the interface between the overlayers and the substrate is important in understanding the surfactant-mediated growths. In this case, one of the essential atomic processes concerning the surfactant is the position exchange between the overlayer atoms and the interface surfactant atoms during overlayer growth.[6–9] For deposition of the covalent bonding materials such as Si and Ge on the H-terminated Si surfaces, the previous first-principles calculations showed that the exchange process takes place spontaneously.[6,10–12] However, in the case of metal growth, the detailed roles of H atoms are still unclear. Thus, in this study, we theoretically investigate the roles of H atoms in metal growth, focusing on H segregation for Ag on the H-terminated Si(111) surface, which has been extensively studied in the last decades from both academic and practical points.[1,3,4,13–19]

As for H position in the Ag growth on the H/Si(111) surface, there are two different arguments. The first one states that the H layer remains at the Ag-Si interface even at the later stages of overlayer growth.[1,13,15] The second one states that a significant amount of interface H atoms segregate from the Ag-Si interface.[16,17] From their ion scattering measurements on the Ag growth on the H/Si(111) surface, Sumitomo *et al.*[1] and Nishiyama *et al.*[13] conjectured that most H atoms are present at the Ag-Si interface. Recently, Bording *et al.*, based on a combination of transmission electron microscopy and classical potential simulation, argued that the Ag islands are formed on this surface with weak interfacial interaction without H vacancies.[15] This looks plausible considering the Si-H bond energy of 3.45 eV (relative to a spin-polarized H atom) and the fact that a single Ag adatom migrates just on H/Si(111) without distinct surface reconstruction.[19] Conversely, Fukutani *et al.* performed a nuclear reaction analysis (NRA) for Ag on H/Si(111) suggesting that the H atoms are partially removed from the interface even at the low temperature of 110 K.[17] They assumed that H segregation is a thermally activated process due to the difference in bond strengths of Ag-Si and H-Si. However, our total energy calculation reveals that the Si-H bond is stronger than the Ag-Si bond [bond energy: less than 2.2 eV (Ref. 20)] and that for a complete Ag monolayer on the H/Si(111) surface H segregation toward the Ag layer from the interface increases the total energy, which are in contrast to the model of Fukutani *et al.* (Fig. 5 in Ref. 17).[21] In addition, the microscopic kinetic processes that are essential for complete understanding of the appearance of the H-segregated configuration are not clarified yet.

In this paper, we employ a first-principles calculation method to examine the aggregating processes of Ag adatoms and concomitant H segregation in the growth of Ag clusters on the H/Si(111) surface. Unlike a single Ag adatom that slides on the H/Si(111) surface without distinct surface reconstruction,[19] two Ag atoms induce H segregation during the cluster formation and as a result make direct bonds with the Si substrate. This phenomenon persists as more Ag adatoms aggregate to the cluster. One of the striking features of this process is that H segregates from the substrate nearly spontaneously. The activation energies for such segregations are calculated at 0.22 and 0.24 eV for the two- and three-Ag clusters, respectively. These results are consistent with NRA of hydrogen[17] and measurements of surface morphologies for Ag on H/Si(111).[4,18]

II. CALCULATION METHOD

In calculations of atomic and electronic structures, we employ the Vienna *ab initio* simulation package (VASP)[22] which incorporates ultrasoft pseudopotentials[23] and

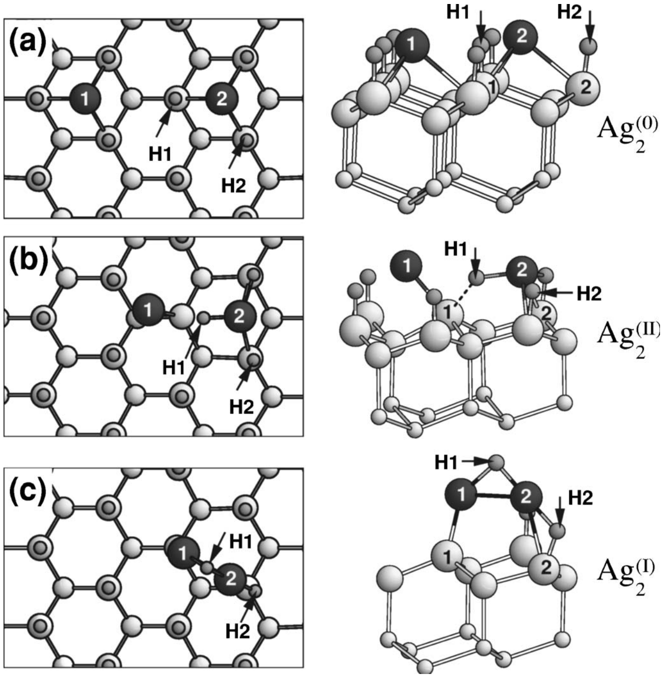

FIG. 1. Atomic structures appearing during formation of a two-Ag cluster on the H/Si(111) surface: (a) The initial structure $Ag_2^{(0)}$ with adatoms at the second-nearest H_3 sites, separated by 6.7 Å, (b) the intermediate metastable structure $Ag_2^{(II)}$, and (c) the final lowest-energy structure $Ag_2^{(I)}$. White, gray, and black spheres represent the Si, H, and Ag atoms, respectively.

generalized-gradient approximation of Perdew and Wang[24] for the exchange-correlation energy. The surface is simulated by a repeated slab model with a 4×4 lateral periodicity in which six Si layers and a 10 Å vacuum layer are included. We use the 15 Ry cutoff energy for the plane-wave basis and a 2×2 k-point mesh for the surface Brillouin zone sampling which produce well-converged results.[19] Other calculational details can be found in Ref. 19. The pathways and activation energies for atomic processes in cluster formation are calculated by the nudged elastic band method.[19,25]

III. RESULTS AND DISCUSSION

We begin with the cluster with two Ag adatoms. We perform extensive searches for more than 20 binding structures of the cluster on the H/Si(111) surface and find that the most stable structure [$Ag_2^{(I)}$, see Fig. 1(c)] is formed on the surface with H segregation. In this structure, the two Ag adatoms make direct bonds with the substrate (bond lengths are 2.42 and 2.82 Å for Ag1-Si1 and Ag2-Si2, respectively) and form a dimer with each other with a bond length of 2.68 Å, slightly larger than the calculated bond length of a free Ag dimer, 2.60 Å, and much smaller than the calculated bond length of bulk Ag, 2.93 Å. The hydrogen atom H1 originally bonded to the substrate Si1 segregates above the Ag dimer and makes a triangle with the dimer with a Ag-H bond length of 1.80 Å. Other hydrogen H2 is still bound to the substrate, but the H2-Si2 bond length increases to 1.62 from 1.50 Å. The binding energy of the $Ag_2^{(I)}$ cluster is calculated at 1.57 eV/Ag. It is larger than those of the Ag dimers without H segregation[26] by about 0.7 eV that can be regarded as the energy gain induced from H segregation.

The energy gain due to H segregation in the Ag dimer is unusual, considering that for an Ag monolayer on H/Si(111) the H-segregated configuration, where one interface H atom is put on the Ag monolayer, has a higher energy than the configuration with the complete on-top Ag monolayer.[21] In discussing the energetics of the surface structures, the direct comparison of the bond energies and the number of chemical bonds is not so useful since a bond energy depends on the specific atomic structure[20] and it is a subtle problem to count the number of the chemical bonds in some surface structures. To find the origin of the energy gain, thus, we consider the following virtual processes for forming $Ag_2^{(I)}$ from the Ag dimer on H/Si(111): (1) the Ag dimer is removed from the substrate; (2) a H atom is removed from the substrate; (3) the removed H atom binds to the Ag dimer; and finally (4) the Ag dimer-H complex binds to the substrate. The energy costs during processes (1) and (2) are 0.2 and 3.4 eV, respectively. The energy gains are 1.4 and 3.0 eV for processes (3) and (4), respectively. The large energy gain of process (4) seems to result from the fact that two Ag atoms are involved in surface bonding, but the Ag1-Si1 bond will be clearly stronger than the Ag2-Si2 bond. Hence the energy gains by formation of new bonds (Ag-Si and H-Ag) overcome the energy cost due to breaking of a Si-H bond and the overall energy gain is 0.7 eV as expected. On the other hand, for the Ag monolayer on H/Si(111), the energy gain and cost become comparable because of decrease in the Ag-Si bond energy,[21] which is also inferred from the comparison of the Ag-Si bond lengths (2.55 and 2.42 Å for the Ag monolayer and $Ag_2^{(I)}$, respectively).

Next, we investigate in detail the H segregation process using the nudged elastic band method.[25] We take, as the starting structure, $Ag_2^{(0)}$ in Fig. 1(a) that has each Ag adatom at the H_3 site, the most stable binding site for a single Ag adatom.[19] The distance between the two adatoms is 6.7 Å in $Ag_2^{(0)}$. Since the diffusion barrier is only 0.14 eV for a single adatom, it is highly probable that the two adatoms combine to form a dimer by rapid surface diffusion. The energy variation for Ag dimer formation is presented in Fig. 2. The Ag aggregation proceeds in two steps through a metastable structure of $Ag_2^{(II)}$ [Fig. 1(b)]. In the first step, H1 between the two Ag atoms is pulled toward the Ag2 atom with a simultaneous formation of Ag1-Si1 bond. The required activation energy and the energy gain for this step are calculated at 0.22 and 0.43 eV, respectively. After formation of $Ag_2^{(II)}$, H segregation proceeds nearly spontaneously with an extremely low energy barrier (0.04 eV) and a large exothemicity (energy gain of 1.60 eV) in the second step. The total activation energy for the whole reaction path is only 0.22 eV.

To pursue the origin of the nearly spontaneous H segregation in the clustering of the two Ag adatoms, we examine the charge density variation for the bonding electronic states in the reaction path (see Fig. 3). In the initial structure, the Ag adatoms reside just on the surface without any distinct chemical bonds as shown in Fig. 3(a), in which the electronic charge originates mainly from the 5s states of the Ag ada-

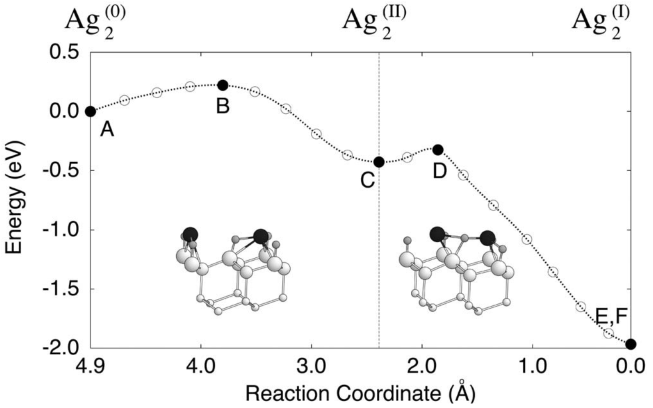

FIG. 2. Energy variation along the reaction path from the initial structure $Ag_2^{(0)}$ to the most stable structure $Ag_2^{(I)}$, passing through the metastable structure $Ag_2^{(II)}$. The reaction coordinate is obtained from the distance from the final structure in the $3N$-dimensional configuration space. The insets display the saddle-point structures for the corresponding steps. Capital letters near the curve correspond to the structures whose charge densities are displayed in Fig. 3.

toms at the Fermi level. Figure 3(b) for the saddle-point structure in the first reaction step indicates that as the distance between both the Ag adatoms decreases Ag1 begins to interact with the substrate atom Si1 with simultaneous weakening of the H1-Si1 bond and formation of the H1-Ag2 bond. Then, in structure $Ag_2^{(II)}$, the Ag1-Si1 bond almost takes the place of the H1-Si1 bond [Fig. 3(c)]. In short, H1 changes its bonding partner from Si to Ag almost at the same time, which possibly facilitates the very low activation energy for the first reaction step. In the second reaction step, H1 is completely segregated from the substrate with the aggregation of the Ag adatoms. Since the H1-Si1 bond is almost broken in the structure of $Ag_2^{(II)}$, H1 is lifted up with just rotation of the H1-Ag2 bond [Fig. 3(d)] and finally, at the end of the second step, the H1 atom is positioned above the Ag dimer. Figure 3(e) depicts the hybridization of H 1s and Ag 4d states as found in H bonding on the Ag(111) surface.[27] Since the d states of Ag are practically filled, the antibinding state [Fig. 3(f)] as well as the bonding state become occupied.[28]

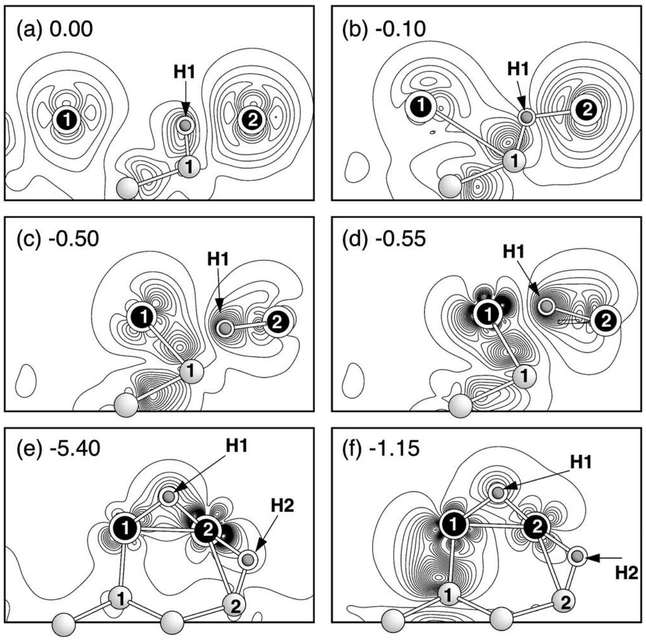

FIG. 3. Charge densities for structures along the aggregation path of the two-Ag cluster indicated in Fig. 2. The charge densities are integrated using states within ±0.1 eV around the characteristic electronic states whose energies in electron volts with respect to the Fermi energy are indicated in each panel. (e) and (f) are the charge densities for the bonding and antibonding states between H 1s and Ag 4d for $Ag_2^{(I)}$. White, gray (small), and black spheres in each panel represent the Si, H, and Ag atoms, respectively.

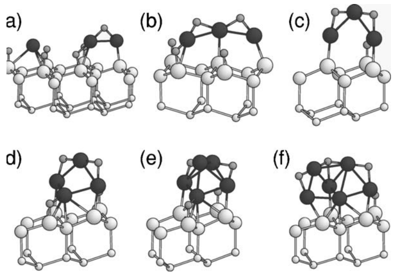

FIG. 4. Metastable and most stable structures for the Ag clusters with 3–6 Ag adatoms on the H/Si(111) surface. (a)–(c) The initial ($Ag_3^{(0)}$), intermediate metastable ($Ag_3^{(II)}$), and most stable ($Ag_3^{(I)}$) structures for the three-Ag cluster. In (a), an additional Ag adatom is placed at the H_3 site, separated by ~5.8 Å from the $Ag_2^{(I)}$ cluster. (d)–(f) The most stable structures for the four-, five-, and six-Ag clusters, respectively. White, gray, and black spheres represent the Si, H, and Ag atoms, respectively.

H segregation with an extremely small energy barrier is also identified in the three-Ag cluster. Figures 4(a)–4(c) show the initial ($Ag_3^{(0)}$), the intermediate ($Ag_3^{(II)}$), and the final ($Ag_3^{(I)}$) structures in the formation process of the three-Ag cluster. The $Ag_3^{(I)}$ cluster is the most stable structure, in which two H atoms leave the interface and three Ag atoms form an equilateral triangle with an almost vertical arrangement to the surface. The binding energy of the cluster is calculated at 1.62 eV/Ag. The lowest-energy structure with only one segregated H atom (not shown here) has a higher energy than $Ag_3^{(I)}$ by 0.63 eV, which corresponds to the energy gain induced by further H segregation. Similar to the two-Ag cluster case in Fig. 2, the energy curve for the three-Ag cluster formation reveals the two steps: In the first step for $Ag_3^{(0)} \rightarrow Ag_3^{(II)}$, a H atom mainly segregates from the substrate and the resulting energy barrier and gain are calculated at 0.24 and 0.78 eV, respectively; In the second step for $Ag_3^{(II)} \rightarrow Ag_3^{(I)}$, the three Ag atoms rearrange to the lowest-energy structure with the energy barrier and gain of 0.16 and 0.52 eV, respectively. Thus, the overall energy barrier and gain for the $Ag_3^{(I)}$ formation along with H segregation are 0.24 and 1.30 eV, respectively.

As the cluster size increases, it is expected that more H atoms will segregate from the surface. However, additional Ag adatoms do not always induce H segregation, as shown in Figs. 4(d)–4(f). The most stable Ag_4 and Ag_5 clusters are

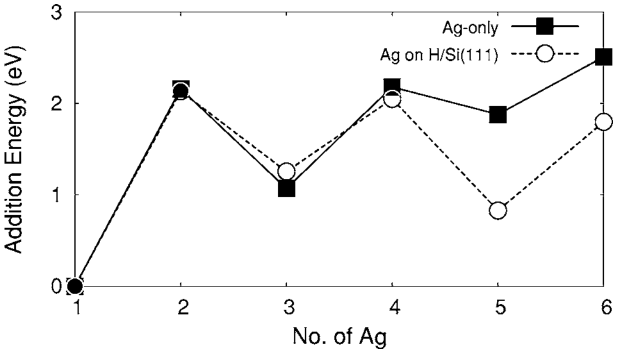

FIG. 5. Addition energies as a function of the cluster size for the lowest-energy structures of the clusters on H/Si(111) (circles) and free ones (squares). The addition energy is calculated as $E_n - E_{n-1}$, where E_n is the binding energy for the cluster of size n. In the case of the clusters on H/Si(111) the binding energy of a Ag atom at the H_3 site, 0.51 eV (Ref. 19), is subtracted. The detailed structures of the free Ag clusters can be found in Refs. 29 and 30.

formed without segregation of additional H, while the Ag_6 cluster lifts up one more H atom. Close comparison of the clusters on H/Si(111) and the free clusters reveals that both kinds of clusters are structurally similar. The most stable Ag_2-Ag_4 clusters on H/Si(111) are similar to the lowest free Ag clusters at each size.[29–31] The most stable Ag_5 and Ag_6 clusters on the surface are comparable to the second lowest-energy structures of the free Ag_5 and Ag_6 clusters, respectively,[30] whose total energies are very close to those of the respective lowest-energy structures. Thus, since the amount of the segregated H atoms will be related to the adsorption area and shape of a cluster, the amount of the segregated H atoms would not be proportional to the cluster size.

The changes of the binding energy due to addition of a Ag atom are shown in Fig. 5 for the clusters on H/Si(111) along with the free Ag clusters.[30] It is interesting that in both cases, the addition energies exhibit an even-odd oscillation with an increase in the number of the Ag atoms, which is related with the electron pairing in the highest-occupied states.[32] Since H segregation induces removal of a H-Si bond and formation of a Ag-Si bond, the cluster is provided with two more electrons (one from H and the other from Si) due to segregation of a single H atom. Thus, in forming a H-segregated cluster, H segregation will not affect electron parity and the oscillation behavior in the addition energy persists for the clusters on H/Si(111). The agreement of the addition energies for both the types of the Ag_n clusters with $n \leq 4$ appears accidental since the energy gains have different origins. For the free Ag_2 cluster, the energy gain of 2.1 eV results only from the Ag-Ag bond while for the $Ag_2^{(I)}$ cluster on H/Si(111) the total energy decreases due to Ag aggregation (1.3 eV) as well as H segregation (0.7 eV).

Based on the results of the investigation on the formation of the two- and three-Ag clusters on H/Si(111), it is evident that H atoms can easily segregate from the substrate to the surface. It should be noted that H segregation takes place through the concerted processes of bond breaking and formation during the Ag growth. The present results are consistent with the NRA on the Ag clusters on H/Si(111) indicating that H atoms partly leave the Ag/Si interface at 110 K and almost segregate from the interface and finally desorb from the surface at 360 K.[17] The low H intensity at the high temperature in the NRA can also be explained by thermal desorption of H that is reported to occur above 190 K on Ag(111).[33] Since the bonding nature between the segregated H atoms and Ag clusters is similar to that of H on the Ag(111) surface [refer to Figs. 3(e) and 3(f)] and the energy increase due to H desorption as a H_2 molecule is marginal,[34] H can easily escape the Ag clusters, too, resulting in a small amount of H on the surface.

The Ag-Ag bonds in the clusters will play an important role in stabilizing the three-dimensional (3D) clusters on H/Si(111). In the absence of H segregation, the Ag-Ag interaction is dominant because the interaction between a cluster and the H/Si(111) surface is very weak and the 3D form will be favored over the planar form as in the free Ag clusters. When H segregation is present, the 3D cluster is further stabilized since the energy gains due to the Ag-Si and Ag-H bonds overcome the energy cost due to the Si-H bond removal. For the planar structures, the energy gain due to H segregation is reduced (0.48 and 0.39 eV for the Ag_5 and Ag_6 clusters, respectively) and the total energy will even increase for larger islands, as seen in the complete Ag monolayer which can be regarded as the limit form of large planar islands. Also, the Ag-Si bond energy will decrease for the planar structures since the Ag-Si bond near the H vacancy significantly distorts the planar bond network of Ag.

We note that the structures in Figs. 1 and 4 could be seeds for the island growth since the strong Ag-Si bond in these structures can substantially suppress the mobility of the clusters on the surface. It is also expected that such structures can be produced anywhere on the surface due to their low energy barriers for cluster formation, which implies that any surface Si atom can be a nucleation site. Since H segregation, despite its small energy barrier, is a thermal process, the clustering process is more operative at higher temperatures, meaning more nucleation sites (or clusters) on the surface. These characteristics were indeed observed in the recent experiment where room temperature deposition leads to smaller and more irregularly shaped islands compared to the low-temperature grown islands.[18] Similar island density variation can be seen in the transmission electron microscopy study for Ag deposition on the clean and H-terminated surfaces.[4]

IV. CONCLUSION

In conclusion, we have studied the initial stages of the H-mediated Ag growth on the Si(111) surface based on the first-principles total energy calculations. From the extensive searches for the stable structures of the small Ag clusters (2–6 Ag atoms), we have discovered that the H atoms are located above the Ag cluster and thus the Ag atoms make direct bonds with Si in the most stable configurations. The addition energy of the clusters on H/Si(111) exhibits an oscillatory behavior similar to that of the free clusters. In contrast to a single Ag atom, Ag clusters, once formed with H segregation, is expected that rarely move on the surface due to strong Ag-Si bonds. Detailed investigation of the formation processes for the Ag_2 and Ag_3 clusters reveals that H atoms segregate above the Ag clusters with low energy barriers of ~0.2 eV. These results support the experimental observations for H removal from the Ag-Si interface[17] and Ag morphologies on H/Si(111).[4,18]

ACKNOWLEDGMENTS

This work was supported by Korea Research Foundation Grant No. (KRF-2003-015-C00141). Computations have been performed using supercomputers at Korea Institute of Science and Technology Information (KISTI).

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[21] The total energy calculation shows that the H-segregated configuration, which as a result has a significant distortion in the Ag overlayer, has a higher energy than the configuration with the complete Ag monolayer by 0.6 eV. The major energy costs involved in H segregation are breaking of a Si-H bond (3.4 eV) and distortion of the Ag overlayer (0.5 eV). The energy gains come from binding of the H atom to the Ag overlayer and binding of the Ag overlayer to the Si substrate, calculated at 2.0 and 1.5 eV, respectively.

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[34] If the H1 and H2 atoms in $Ag_2^{(I)}$ (the two segregated H atoms in $Ag_3^{(I)}$) are desorbed as a H_2 molecule, the total energy increases by 0.30 (0.42) eV.