Effect of hydrogenation on the adsorption of Ge on Si(001)

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Ab initio calculations, based on pseudopotentials and density functional theory, have been performed to investigate the effect of hydrogenation on the atomic geometries and energetics of half-monolayer and full-monolayer coverages of Ge on the Si(001)-(2×1) surface. For the half-monolayer Ge coverage without hydrogenation, we find that the Ge-nondiffused case (i.e., the mixed Ge–Si dimer structure) is 0.25 eV/dimer energetically more favourable than the Ge-interdiffused case (i.e., intermixed Ge–Si bond structure), while for the hydrogenated surface both structures become almost equally favorable. For the full-monolayer coverage of Ge without surface hydrogenation the formation of a pure Ge–Ge dimer is energetically more favourable by 0.19 ± 0.03 eV/dimer compared with the interdiffusion of Ge into any of the second, third, and fourth substrate layers. The process of surface hydrogenation makes both the nondiffused and interdiffused structures almost equally favorable. In all cases the effect of hydrogenation is to make the surface dimer symmetric and elongated.

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I. INTRODUCTION

The epitaxial growth of Ge upon the Si(001)-(2×1) surface is of profound technological importance. The growth mode for this system is well known to follow a layer-by-layer pattern up to several monolayers before island formation, the so-called Stranski-Krastanov (SK) growth mode.[1–3] At the initial stage of Ge growth on Si(001), mixed Ge–Si dimers are preferentially formed. As Ge coverage increases, the percentage of pure Ge–Ge dimers increases and the surface is covered with pure Ge dimers at coverages more than one monolayer (1 ML). At elevated temperatures, the deposited Ge atoms interdiffuse into the second or deeper layers of the Si substrate[4,5] and the pure Ge–Ge dimers are converted into mixed (i.e., Si–Ge) dimers. Recent scanning tunneling microscopy (STM) studies[6] have confirmed Si and Ge intermixing for Ge deposited on Si(001). Uberuaga *et al.*[5] have, based upon density-functional-theory calculations, forwarded a mechanism for the interdiffusion of Ge down to the fourth substrate layer.

During the chemical vapor deposition (CVD) of germane and silane, hydrogen atoms are always present on the Si(001) surface as a reaction by-product. The hydrogen atoms can work as surfactant species to suppress the growth of three-dimensional islands by reducing the surface diffusivity of Ge atoms.[7] Using the high-energy electron diffraction (RHEED) technique it has been confirmed that, especially at 300°C, a change from the well-known SK mode without the presence of H to a layer-by-layer growth mode with the presence of H takes place.[8] Another experimental work by Rudkevich *et al.*,[9] using Fourier-transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR), observed that there is a reversible place exchange between Ge and Si on Ge-covered Si(001) when the surface is dosed with atomic H at elevated temperatures. These authors have also used first-principles calculations in order to confirm a thermodynamic driving force for this place exchange. Recent scanning tunneling microscopy work on the growth of Ge on the monohydride-

covered Si(001)-(2×1) surface by Kahng *et al.*[10] also found that hydrogen plays the role of surfactant, promoting growth of flat Ge overlayers but with the development of uniform strain in the direction perpendicular to surface. A more recent study,[11] using x-ray photoemission diffraction (XPD) and high-resolution electron-energy-loss spectroscopy (HREELS), has independently confirmed the observations made by Rudkevich *et al.*[9] and has correlated the increase of Si at the surface with the decrease of Ge–H bonds with increasing temperature.

Detailed theoretical studies of the energetics and geometries of full- and half-monolayer Ge deposition on the clean Si(001) surface have been performed by a significant number of research groups.[9,12–15] The general consensus is that the Ge-nondiffused (i.e., the mixed Ge–Si dimer structure on the surface layer) is energetically more favorable than structures with Ge interdiffused into deeper surface layers. To our best knowledge, the only theoretical work regarding the energetics of Ge deposition on hydrogenated Si(001) surface has been carried out by Rudkevich *et al.*[9] However, this work only provides a limited amount of information on the energetics of a place exchange between Ge and Si on the hydrogenated surface with 1 ML deposition of Ge. Clearly, the role of surface hydrogenation on the atomic geometry and energetics of Ge-deposited surfaces must be thoroughly investigated. In this work we employ a first-principles pseudopotential method to examine these issues, with a view to providing a clear understanding of the atomic-level stoichiometry of Si(001) during the initial stages of Ge adsorption with and without the presence of hydrogen on the surface.

II. METHOD

Our calculations are made using the local density approximation of the density functional theory (DFT) of Hohenberg, Kohn, and Sham. The electron-ion interaction was considered in the form of *ab initio* norm-conserving pseudopotentials listed by Bachelet, Hamann, and Schlüter (BHS).[16] The

electron-electron interaction was considered within the local density approximation (LDA) of the density functional theory, using the correlation scheme of Ceperley and Alder[17] as parametrized by Perdew and Zunger.[18] Self-consistent solutions to the Kohn-Sham equations were obtained by employing a set of four special **k** points in the irreducible segment of the Brillouin zone for the Si(001)-(2×1) surface.[19] Single-particle wave functions were expanded using a plane-wave basis up to a kinetic energy cutoff 8 Ry. This cutoff was found to be adequate for the structural studies and the electronic structure. We did not find any significant changes in structural parameters when the energy cutoff was increased from 8 Ry to 12 Ry. Our earlier works[20,21] have also concluded that structural results are well converged for H_2S- or Si_2H_6-chemisorbed semiconductor surfaces with 8 Ry energy cutoff. Similar observations regarding converged results for H overlayer systems with 8–10 Ry cutoff have also been made by other groups.[22,23]

We considered an artificially constructed periodic geometry along the surface normal. The unit cell included an atomic slab with eight layers of Si substrate plus a vacuum region equivalent to about six substrate layers in thickness. The two back substrates layers were frozen into their bulk positions, and each Si atom at the back surface was saturated with two pseudohydrogen (H_{ps}, the BHS pseudopotential) atoms. All the remaining substrate atoms, the adsorbate atoms, and the saturating H_{ps} atoms were allowed to relax into their minimum energy positions using a conjugate gradient method.[24,25]

III. RESULTS AND DISCUSSIONS

The clean Si(001) surface exhibits c(4×2) and p(2×2) reconstructions at low temperatures and the (2×1)- reconstruction at room temperature. The atomic geometry of the (2×1) reconstructed surface, which is characterized by Si–Si dimer formation as the building block, has been well studied, both theoretically and experimentally. Recent theoretical works suggest that the semiantiphase dimer (2×2) reconstruction is more favorable than the (2×1) phase by approximately 0.24 eV/dimer.[26] For the 1-ML Ge-deposited Si(001) surface, the energy gain offered by the (2×2) reconstruction over the (2×1) reconstruction is 0.44 eV/dimer.[27] For the mixed Ge–Si dimer geometry, corresponding to 0.5 ML Ge deposition, the energy gain in going from the (2×1) reconstruction to the (2×2) and c(4×2) reconstructions is 0.18 and 0.25 eV/dimer, respectively.[27] The need for the consideration of higher-order reconstruction on the Si(001) and Si(001)/Ge surfaces is basically dictated by surface charge transfer, resulting in a tilt of the surface dimers. However, upon hydrogenation the dangling bonds on the Si(001) surface become fully occupied, resulting in symmetric surface dimers. Therefore hydrogenated surfaces, with and without Ge deposition, are not expected to show reconstructions higher than the (2×1). In view of this reasoning we have considered the (2×1) reconstruction to model 0.5 and 1 ML coverages of Ge on Si(001). In order to make a direct comparison we have also considered the (2×1) reconstruction for the nonhydrogenated surface.
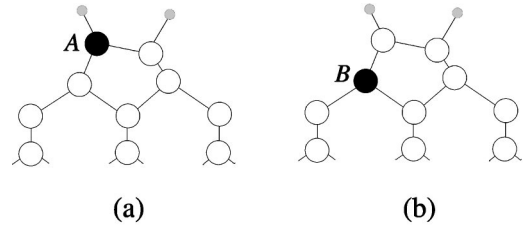

FIG. 1. Schematic side views of the various configurations (a) and (b) at half-monolayer coverage of Ge on Si(001)-(2×1) with and without H that are discussed in this work. Large open and solid circles represent Si and Ge atoms, respectively, while small dashed circles represent H.

In all the calculations in this work, we used our theoretical equilibrium lattice constant for bulk Si (5.42 Å). We found earlier that the Si–Si dimer on the clean Si(001)-(2×1) surface is of length 2.25 Å and is tilted by 16.1°, and the Ge–Ge dimer on the clean Ge(001)-(2×1) surface is of length 2.38 Å and is tilted by 18.7°.[20] For the asymmetric dimer geometry the dangling bond at the higher-lying dimer component is fully occupied with the associated electronic state close to the bulk valence band maximum, and the dangling bond at the lower-lying dimer component is empty corresponding to its energy state in the upper half of the bulk band gap. For the symmetric dimer geometry there are two overlapping π-derived dangling bond states: these can be labeled π and π^* according to their orbital symmetries, and both of these are partially occupied, making the surface metallic.

A. Ge (0.5 ML):Si(001)-(2×1)

Figures 1(a) and 1(b) represent schematic side views of the nondiffused and interdiffused half-monolayer coverage of Ge on Si(001)-(2×1) with and without hydrogen. At first, we consider these geometries on the nonhydrogenated Si(001)-(2×1) surface. As discussed in the Introduction, growth of a monolayer of Ge on the Si(001) surface can be either wholly epitaxial or feature some degree of interdiffusion. It is also known that at the early stages of Ge growth (less than 1 ML), mixed Ge–Si dimers are preferentially formed.[4,6] The lowest-energy configuration for the 0.5 ML coverage was achieved when the Ge atom was in the top layer and occupied the up-atom site of the mixed dimer (nondiffused).[12,15] This is also true in our calculations: we find that the total energy of the system increases by 0.25 eV/dimer when the Ge atom is interdiffused into the second layer. Our result for this energy difference is very similar to the result obtained in the works of Cho *et al.*, who obtained 0.23 eV/dimer (Ref. 12) and 0.21 eV/dimer (Ref. 15). We thus conclude that Ge interdiffusion at 0.5 ML coverage and at low temperatures is not favorable. This finding is indeed in agreement with the infrared (IR) spectroscopy work carried out by Kobayashi *et al.*,[4] in which they have found that only after annealing of the 1.2 ML Ge coverage is interdiffusion of Ge possible.

Some structural parameters for the nonhydrogenated deposition are given in Table I. We find that the Ge–Si bond

TABLE I. Calculated structural parameters and relative energies for different configurations of Ge(0.5 ML)/Si(001)$-$(2×1): top-layer Ge at site A and the Ge diffusion site B. The labels A and B are shown in Fig. 1.

System	Dimer bond length (Å)	Buckling angle (°)	Vertical buckling (Å)	ΔE (eV)
Site A	2.32	19.7	0.79	0.0
Site B	2.24	16.3	0.71	0.25

is of length 2.32 Å and is inclined from the surface plane by a tilt angle of 19.7°. The calculated mixed Si–Ge dimer bond length lies between the pure Si–Si and Ge-Ge dimer bond lengths. When the Ge-atom is allowed to diffuse into the second layer of the Si(001) substrate, the Si–Si dimer bond length becomes 2.24 Å, with a tilt angle of 16.3°. These values are nearly equal to those obtained for the clean Si(001) surface and indicate that Ge interdiffusion does not significantly alter the situation.

For studying the 0.5 ML coverage of Ge in the presence of hydrogen on the surface, we started with a symmetric dimer geometry (typically a geometry with a dimer tilt angle of 6°) and placed the H atoms at the dangling bond positions of the dimer atoms. Upon relaxation, the IV-IV dimer becames mainly symmetric with an elongated bond length. As we have seen in the previous paragraph, the interdiffusion is not favorable at this lower coverage of Ge on the clean Si(001) surface. However, we find that the Ge interdiffusion at the hydrogenated surface becomes at least as favorable as the nondiffused geometry. In fact we find the total energy of the interdiffused geometry 14 meV/dimer lower than that of the nondiffused geometry. However, as this energy difference is within the error bar of the DFT and LDA calculations, we cannot state that the interdiffused geometry is more favorable than the nondiffused geometry. The calculated structural parameters are shown in Table II. For the Ge-nondiffused case, the Ge–Si dimer bond length is elongated from 2.32 Å on the clean surface to 2.41 Å on the hydrogenated surface, and the dimer becomes symmetric. For the Ge-diffused hydrogenated case, the Si–Si dimer bond length is elongated from 2.24 Å for the clean surface to 2.39 Å for the hydrogenated surface, and the dimer is again symmetric.

B. Ge (1 ML):Si(001)-(2×1)

The nature of the Ge-terminated Si(001) surface is quite similar to the Si-terminated Si(001) surface. As discussed in the Introduction, it is known that for 1 ML coverage, at room temperature the Ge atoms form dimers at the surface. However, Ge interdiffusion tends to increase with temperature. Using x-ray photoelectron diffraction and Auger electron dif-

fraction, Sasaki et al.[28] found that at 873 K a substantial amount of Ge atoms interdiffuses to the deeper layers in the Si substrate and the pure Ge–Ge dimers are converted into the Ge–Si mixed dimers. Using the IR reflection spectroscopy, Kobayashi et al.[4] found that after annealing at 1093 K the surface Ge atoms disappear completely and the surface is covered with pure Si–Si dimers.

In this work we have considered that Ge atoms interdiffuse into Si substrate. The same considerations have recently been made in a theoretical work by Cho and Kang,[15] who found that interdiffusion is possible up to the fourth substrate layer. We have repeated their four minimum energy configurations for interdiffusion. In Fig. 2 and in Table III, the labels A, B, C, and D indicate the minimum energy sides for the Ge atom. The geometry labeled A corresponds to a nondiffused configuration, and the geometries labeled B, C, and D correspond to 50% interdiffusion of Ge into the second, third, and fourth substrate layers, respectively. We have also considered the possibility of two Ge atoms per (2×1) cell occupying the second layer while the Si atoms float to the surface (i.e., 100% interdiffusion of Ge into the second substrate layer), as seen in Fig. 2(e). From our total energy calculations, it is noted that the system becomes energetically unfavorable as the content of Ge interdiffusion reaches 100% .

Our calculated relative energies of the configurations A, B, C, and D are 0, 0.16, 0.19, and 0.22 eV per unit 2×1 cell. Estimating an error bar of about 0.03 eV in the context of these similar geometries, we can say that each of the configurations B, C, and D lies at an energy which is about 0.19 ± 0.03 eV higher than configuration A. This estimate is consistent with the work of Cho and Kang who obtain configurations B, C, and D to lie at 0.1 eV relative to A. However, our calculated result of 0.49 eV per 2×1 cell for the relative energy of the structure in which both Ge atoms segregate in the second layer (i.e., for 100% Ge interdiffusion to the second layer) is appreciably higher than the values reported by Cho and Kang (0.33 eV) and by Rudkevich et al. (0.21 eV). Despite these differences, it can be concluded that, when the amount of Ge interdiffusion increases, the structure becomes energetically less favorable. This is also

TABLE II. Calculated structural parameters and relative energies for different configurations of H:Ge(0.5 ML)/Si(001)-(2×1): top-layer Ge at site A and the Ge diffusion site B. The labels A and B are shown in Fig. 1.

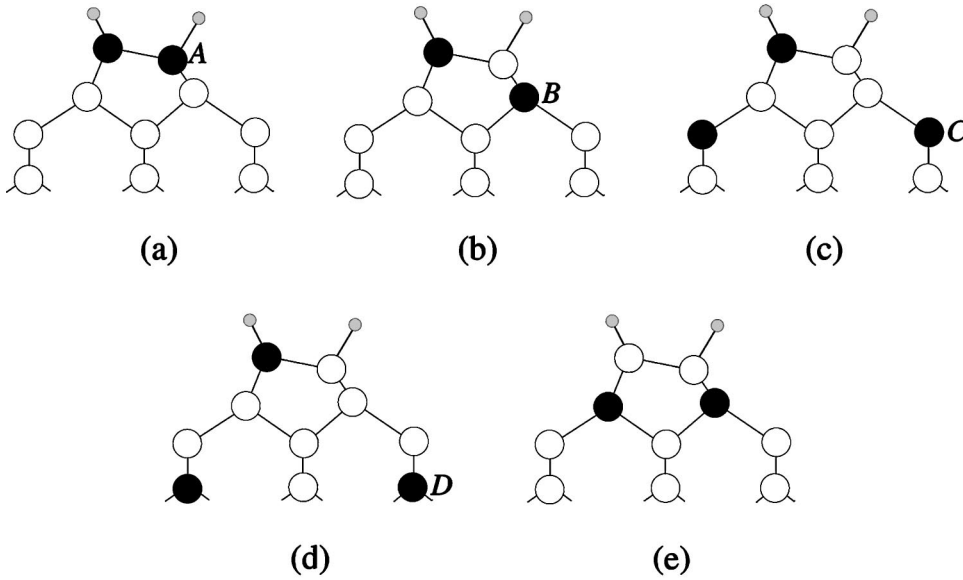| System	Dimer bond length (Å)	Si–H bond length (Å)	Ge–H bond length (Å)	ΔE (eV)
Site A	2.41	1.53	1.56	0.0
Site B	2.39	1.54	–	0.0

FIG. 2. Schematic side views of the various configurations (a)–(e) at full-monolayer coverage of Ge on Si(001)-(2×1) with and without H that are discussed in this work. Large open and solid circles represent Si and Ge atoms, respectively, while small dashed circles represent H.

true for the growth of Si on Ge(001).[29] The energetic favorability of the Ge-on-top structure can be explained by using simple physical arguments based upon different bond strengths between group IV atoms (Si–Si strongest, Si–Ge intermediate, Ge–Ge weakest).[29,30] Such an analysis is presented in Sec. III C.

Two experimental groups have reported the same Ge–Ge dimer bond length for the nonhydrogenated surface. Using the x-ray standing-wave techniques, Fontes *et al.*[31] have concluded that the Ge–Ge dimer is asymmetric with length 2.60 Å . They also determined the tilt angle and the vertical buckling of the Ge–Ge dimer to be 12.4° and 0.55±0.02 Å, respectively. Using transmission ion channeling, Bailes *et al.* proposed an asymmetric dimer with length 2.60 Å.[32] For the Ge atom at the *A* site, we find that Ge dimer tilt angle is 18.40°, the bond length is 2.38 Å, and the vertical buckling is 0.79 Å. In going from site *A* to *D*, indicating Ge-interdiffusion into the deeper layers, the buckling angle increases from 18.4° to 20.09°, while the dimer bond length decreases from 2.38 Å to 2.32 Å, as shown in Table III. The value of 2.32 Å is the average bond length of the Si–Si and Ge–Ge bond lengths. It is clear that there is a vast difference between theoretically calculated and experimentally determined characteristics of the surface dimer on the Ge-covered Si(001) surface. At this stage it is difficult to explain this difference satisfactorily.

In order to study 1 ML adsorption of Ge on the hydrogenated surface we again started with an asymmetric dimer geometry with a tilt angle of 6° and placed the H atoms at the dimer dangling bond positions. Upon relaxation, the IV-IV dimers became mainly symmetric with elongated dimer bond lengths. The largest dimer length, 2.43 Å, was calculated for the Ge–Ge dimer (i.e., when Ge are at *A* sites). The substantial increase in the Ge–Ge dimer length from the nonhydrogenated to the hydrogenated surface is not enough to explain the large dimer lengths obtained in the experimental works carried out by Fontes *et al.* and Bailes *et al.* As we discussed earlier, for the *symmetric* dimer model of clean Si(001) and Ge(001) surfaces there are two overlapping π and π^* bands, both being partially occupied. Upon the adsorption of hydrogen in the monohydride geometry these bonds become fully occupied and the corresponding band energies are lowered down into the bulk valence band. Following the same trend, the saturation of Si and Ge dimer dangling bonds by hydrogen atoms drives the surface states out of the fundamental gap region.[20] The same results were also found for Ge(001) by Rohlfing *et al.*[33]

Furthermore, we have considered the possibility of Ge atoms interdiffusing into the Si(001) substrate up to the fourth deeper layer in the presence of surface hydrogenation. For this system, our total energy calculations reveal no real energy difference between the the four geometries (sites

TABLE III. Calculated structural parameters and relative energies for different configurations of Ge(1 ML)/Si(001)-(2×1): top-layer Ge at site *A*, various Ge interdiffusion at *B*, *C*, and *D* sites, and the segregation model (Seg. model). An estimated error bar in these calculations is approximately ±0.03 eV.

System	Dimer bond length (Å)	Buckling angle (°)	Vertical buckling (Å)	ΔE (eV)
Site *A*	2.38	18.4	0.79	0.00
Site *B*	2.33	19.9	0.76	0.16
Site *C*	2.32	19.9	0.77	0.19
Site *D*	2.32	20.1	0.87	0.22
Seg. model	2.26	17.8	0.72	0.49

TABLE IV. Calculated structural parameters and relative energies for different configurations of H:Ge/Si(001)-(2×1): top-layer Ge at site A, various Ge interdiffusion at B, C, and D sides, and the segregation model (Seg. model).

System	Dimer bond length (Å)	Si–H bond length (Å)	Ge–H bond length (Å)	ΔE (eV)
Site A	2.43	–	1.56	0.0
Site B	2.40	1.53	1.56	0.0
Site C	2.40	1.53	1.56	0.0
Site D	2.40	1.53	1.56	0.0
Seg. model	2.38	1.53	–	0.0

A–D), as shown in Table IV. This clearly suggests that the hydrogenation of the surface promotes Si–Ge intermixing. This behavior, viz., suppression of Ge segregation during SiGe epitaxy in the presence of surface H, has in fact been shown in many experimental studies (see, e.g., Ref. 9 and references therein). We have depicted the electronic total charge density plot along the Ge–Ge and Ge–H bonds for A adsorption site (Ge-nondiffused case) as in Fig. 3(a) and the Ge–Si, Si–H, and Ge–H bonds for C adsorption site (Ge

FIG. 3. Electronic total charge density plots (a) along the line joining the Ge–Ge dimer and the Ge–H bond in H:Ge(1 ML)/Si(001)-(2×1) for site A, (b) along the line joining the Ge–Si dimer, Ge–H bond, and Si–H bond in H:Ge(1 ML)/Si(001)-(2×1) for site C.

interdiffused case) as in Fig. 3(b). From these figures, as the Ge diffuses into the deeper layers, the charge density peak of the mixed Ge–Si dimer becomes higher than that of the Ge–Ge dimer. When the Ge atom difuses from the second layer to the fourth layer, we found no essential difference in the height or position of the charge density peak for the Si–Ge, Si–H, and Ge–H bonds.

In the presence of surface hydrogenation, we have also considered the possibility of two Ge atoms to segregate into the Si substrate. In this case [cf. Fig. 2(e)] we find that the segregated structure tends to be energetically as favorable as the pure Ge–Ge dimer at the surface. This result agrees in essence with the theoretical results obatined by Rudkevich *et al.* within the error bars of calculations, in which they found Ge–H-bond terminated surface to be 0.03 eV/atom higher than that of Si–H-bond-terminated surface. Our findings are also in accord with the FTIR-ATR experimental results obtained by Rudkevich *et al.* This experiment shows that at room temperature there is a large surface peak associated with the Ge–H stretch vibration and only small Si–H stretch peak. At 603 K a large Si–H stretch peak appears according to the previous situation. However, after annealing to 823 K and then quenching to the room temperature the Si–H stretch peak disappears. In Table IV, we have presented some calculated structural parameters for different adsorption sites. In all cases studied here in the presence of hydrogen, occupying the surface dangling bonds, the surface dimer bond lengths are elongated compared with their clean surfaces, while the Si–H and Ge–H bond lengths remain unchanged.
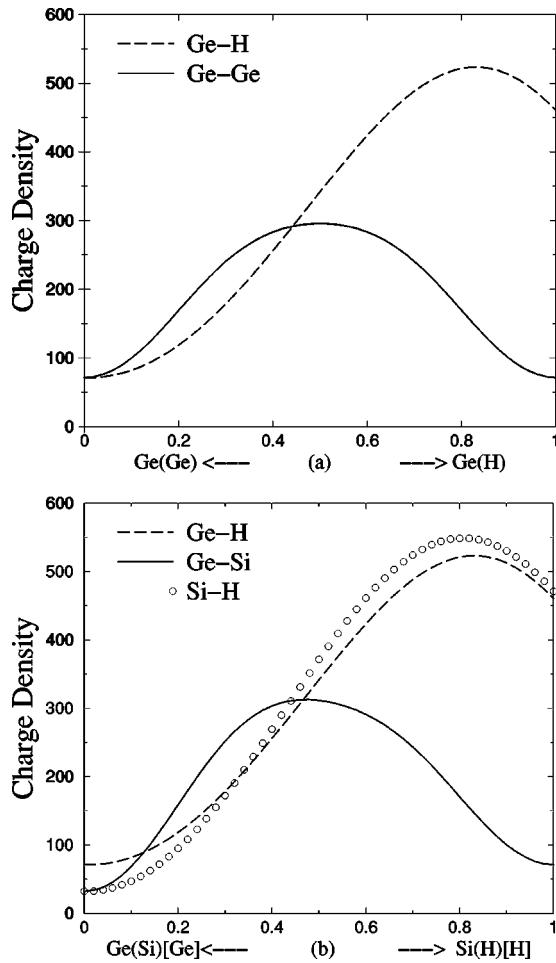
C. Analysis of energy lowering factors

The relative energetic stability of different structures obtained in this work can be explained qualitatively by keeping two factors in mind. First, in general Ge/Si systems prefer a reduction in heterobonds (i.e., bonds between Ge and Si).[34] Second, on the Si(001)-(2×1) surface the Si–H bond is stronger than the Ge–H bond. Thus a relatively more stable structure would prefer to have smaller numbers of Si–Ge and Ge–H bonds. From Table I we note that replacing a Si–Si bond with a Ge–Si bond costs approximately 0.25 eV. From calculations for the bare and hydrogenated Si(001)-(2×1) and Ge(001)-(2×1) surfaces we estimate that the Si–H bond is approximately 0.2 eV stronger than the Ge–H bond.

Considering 0.5 ML coverage of Ge on bare Si(001)-(2×1), we can follow the energy results presented in Tables I

and II by noting that the number of Si–Ge bonds per unit cell is 3 and 4 for models A and B, respectively. On the hydrogenated surface, changing from model A to B results in the number of Si–H bonds increasing from 1 to 2 and the number of Ge–H bonds decreasing from 1 to 0. The increase in the total energy from A to B for the bare surface is compensated by the increase (decrease) in the number of Si–H (Ge–H) bonds. Similarly, for 1 ML coverage of Ge on bare Si(001)-(2×1), the trend in the total energy presented in Table III can be followed by noting that the number of Si–Ge bonds per unit cell is 4, 7, 7, 7, and 8 for models A, B, C, D, and Seg., respectively. On the hydrogenated surface, the number of Si–H (Ge–H) bonds is 0, 1, 1, 1, and 2 (2, 1, 1, 1, and 0) for models A, B, C, D, and Seg., respectively. Keeping in mind a decrease of 0.2 eV/cell in energy with an increase (decrease) of a single Si–H (Ge–H) bond, we can explain the results obtained in Table IV.

IV. SUMMARY

In conclusion, from *ab initio* pseudopotential calculations, within the local density approximation, we have presented a detailed investigation of the atomic geometry and energetic stability of the Ge-nondiffused, Ge-diffused, and Ge-segregated models of 0.5 ML and 1 ML coverage for Ge on bare and hydrogenated Si(001)-(2×1) surfaces. For 0.5 ML coverage of Ge on the bare surface, we find that the Si–Ge mixed dimer at the surface is preferable to the Ge-interdiffused case. However, for the hydrogenated surface both the Ge-nondiffused and -interdiffused geometries are almost equally probable. For 1 ML coverage on the bare surface, interdiffusion of Ge into the first, second, third, and fourth deeper layers of Si(001) is not preferable for the equilibrium geometry. On the hydrogenated surface, Ge-interdiffused geometries, characterized by increased Si–Ge intermixing, have essentially the same energy as the surface Ge–Ge dimer geometry. Reductions in the number of Ge–H and Ge–Si bonds are identified as two contributing factors which determine energetically stable structures during Ge growth on Si(001).

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