First principles study of Ge/Si exchange mechanisms at the Si(001) surface

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Based on density functional theory calculations, we show that an isolated Ge adatom on Si(001) triggers an exchange mechanism involving three atoms, which leads to the formation of a Si adatom and a mixed SiGe surface dimer. The activation energy calculated from first principles is sufficiently low (0.8 eV) to make such a process viable down to the lowest temperature (330 K) at which intermixing was reported. A second mechanism, with a higher barrier, is also proposed and shown to possibly contribute to the incorporation of Ge into deeper layers as experimentally observed at higher temperatures. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2926683]

Deposition of Ge on Si leads to a wealth of interesting phenomena of great technological relevance. Both flat Ge-rich films and three-dimensional (3D) structures grown in the Stransky–Krastanow regime have been extensively studied and exploited for present and next-generation microelectronics devices.[1,2] In these systems, Ge/Si intermixing has been soon recognized as a key factor, since it affects the formation of sharp interfaces,[3] the release of strain behind the formation, stability, and evolution of 3D Ge islands,[4–10] and the reconstruction of wetting layers.[11,12]

Although Ge would tend to segregate at the surface due to its lower surface energy, entropy would lead to Si/Ge intermixing also in a Ge capping layer on Si. To which extent thermodynamic equilibrium would be reached during heterostructures growth is still a matter of debate. High-resolution photoemission data showed the formation of mixed SiGe dimers by depositing Ge on Si(001) at 623 K,[13] while scanning tunneling microscopy measurements[14] revealed the formation of GeSi mixed dimers down to 330 K. Elementary processes leading to Si/Ge intermixing have been theoretically investigated within density functional theory (DFT) as well.[15–18] An activation energy of 1.6 eV was calculated for a Si/Ge exchange between the first and the second surface layer,[16] while exchanges between adatoms and surface atoms are predicted to have barriers of 1.6 eV [for Ge adatom on Si(001)][15] or 1.5 eV [for Si adatom on Ge(001)].[16] Starting from a stable ad-dimer, intermixing with surface atoms would occur with calculated activation energies of 1.2 eV for a SiGe turning into a SiSi or 1.4 eV for the reverse mechanism.[18] Clearly, activation energies in the range of 1.4–1.6 eV (Ref. 19) are incompatible with intermixing at 330 K as reported in Ref. 14.

In this letter, based on DFT calculations, we shall show that isolated Ge adatoms on Si(001) are able to trigger exchange processes through a three-atom mechanism down to the lowest temperature (330 K) at which intermixing was observed.[14] By combining our results with previously reported ones, we show that theory and experiments seem to be in good agreement for a wide set of observed phenomena.

Spin unrestricted calculations were performed with gradient corrected exchange and correlation (xc) functional,[20] plane waves expansion of Kohn–Sham orbitals up to an energy cutoff of 240 eV, and ultrasoft pseudopotentials,[21] as implemented in the VASP program.[22] Activation energies were estimated by nudged elastic band (NEB) optimizations.[23] The Si(001) surface was modeled in a slab geometry with six layers (16 atoms/layer). Energetics of local minima are converged within 30 meV as checked with slabs of 11 layers thick. Brillouin Zone integration was performed over a $2\times2\times1$ Monkhorst–Pack mesh. All atoms were allowed to relax but frozen to bulk positions for the two bottom layers. The upper surface of the slab was reconstructed in the $c(4\times2)$ geometry, the lower surface was passivated by SiH_2 groups.

In the search for possible mechanisms leading to intermixing, we first reproduced the path proposed in Ref. 15, which involves a Ge adatom (site M_1 in Fig. 1) and the Si atom of a surface dimer. Our calculated barrier is slightly lower than that reported in Ref. 15 with a different xc functional and a less precise localization of the saddle point (E_a=1.4 versus 1.6 eV). As already noticed, this mechanism

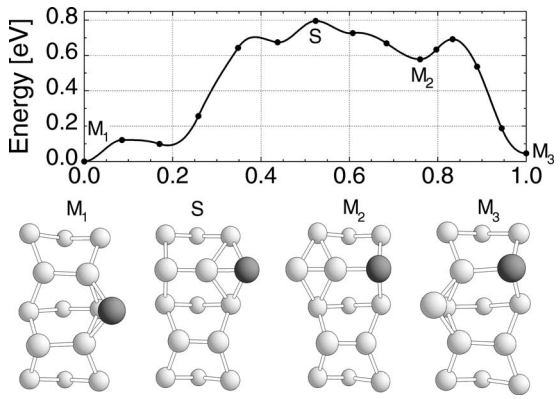

FIG. 1. Energy path for three-adatom exchange inducing the incorporation of a Ge adatom (dark gray sphere) into a surface dimer and the generation of a Si adatom (minimum M_3). The overall activation barrier is ~0.8 eV, which corresponds to the energy difference between the initial minimum (M_1) and the highest saddle point (S).

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cannot contribute to intermixing at 330 K since its reaction rate is as low as $\nu \sim 10^8\ s^{-1}$, as obtained from the Arrhenius relation $\nu = \nu_0 \exp[-E_a/(k_B T)]$, where ν_0 is set to the usual value of 10 THz.

Thus, we switched our attention to three-atom mechanisms, finding the low-energy path depicted in Fig. 1. The overall activation energy E_a is ~0.8 eV, i.e., almost half of the values reported so far in the literature for isolated-adatom exchanges.[15,16] By using the Arrhenius relation for $T=330$ K, one finds an average exchange time of $\nu^{-1}=\tau_{ex} \sim 0.1$ s. Would a Ge adatom remain isolated for a time exceeding τ_{ex} during deposition, then intermixing could take place; otherwise, dimers can form. To further address this issue, we follow the approach presented in Ref. 16. The average number $\langle n \rangle$ of deposited adatoms that a diffusing Ge adatom would meet along a row in time τ_{ex} is given by $\langle n \rangle \sim \Phi \times \tau_{ex} \times \langle l \rangle$, where Φ is the deposition flux in ML/s, and $\langle l \rangle$ is the average length a Ge adatom travels along the row in time τ_{ex} (diffusion perpendicular to the dimer row is much slower and neglected). In turn, $\langle l \rangle$ is obtained from the Einstein relation $\langle l \rangle \approx a[\nu_0 \tau_{ex} \exp(-E_D/k_B T)]^{1/2}$, where E_D and a are the activation energy and jump length for adatom diffusion. The lower the $\langle n \rangle$ is, the higher the probability that an adatom can lead to a Si/Ge exchange before an ad-dimer is formed. By choosing the theoretical value $E_D=0.45$ eV (Ref. 24) and the highest flux experimentally used in Refs. 13 and 14 ($\Phi=0.005$ ML/s), one still finds $\langle n \rangle \lesssim 1$ for $T \gtrsim 320$ K, which suggests that a single adatom mechanism can sustain intermixing down to 330 K. Here, we mention that the experimental data on the segregation of Ge in a thick Si cap on SiGe substrates at 773 K (Ref. 25) were analyzed via a Monte Carlo model, yielding an effective barrier for intermixing of 1.4 eV.[25] However, our result of an activation barrier, which is as low as 0.8 eV, is not inconsistent with the data of Ref. 25. Actually, the total amount of Ge segregated in the uppermost surface layers of the Si thick cap is larger than that of a single monolayer but lower than those of two monolayers (≈1.4 ML).[25] Since mechanisms for Si/Ge exchange involving only adatoms could at most bring a single Ge monolayer in the Si cap, other exchange processes with subsurface layers must be at work. The activation energy of 1.4 eV should, thus, be associated with these latter events. An example of such a process might be the exchange involving the first and second surface layers whose calculated activation energy is 1.6 eV.[16]

All mechanisms discussed above do not allow for deep Ge incorporation. However, at least two experiments identified the presence of Ge below the second layer. Deep intermixing is inferred from photoemission spectra in samples grown at 623 K and annealed at 873 K by Patthey *et al.*[13] or in a 0.8 ML Ge layer grown on Si(001) at $T \geqslant 773$ K by Uberuaga *et al.*[17] The latter experimental work was supplemented by DFT calculation of a path leading to the penetration of a Si atom into Si(001). The results were then extended to Ge/Si(001) from data on the energetics of Ge incorporation in various sites. It turns out that a Ge adatom can deeply penetrate into the substrate, which results in a SiGe dumbbell interstitial down to the fourth layer. The calculated barrier of 2.1 eV is compatible with deep intermixing at and above 773 K.[17] However, the annealing-promoted deep incorporation observed in the other experiment[13] was accompanied by the increase in Si content at the surface,

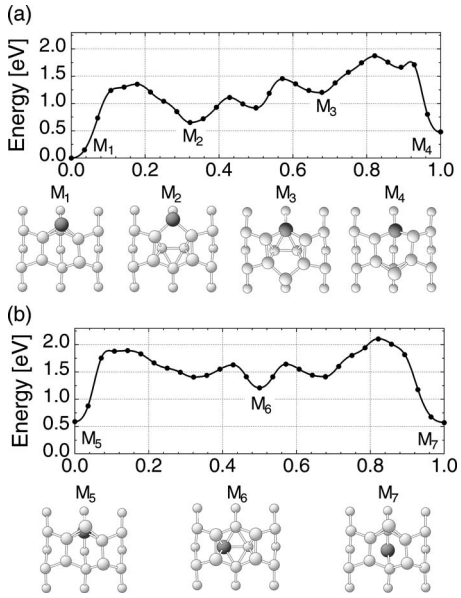

FIG. 2. Reaction path (split into two subpaths) for the incorporation of a Ge adatom into the third layer. (a) Exchange mechanism leading to the incorporation of a Ge adatom into the second layer and formation of a Si adatom (minimum M_4). (b) A Si adatom diffuses upon the Ge atom of the second layer (configuration M_5) and a mechanism analogous to that of panel (a) takes place and brings the Ge atom into the third layer. A Si adatom is recovered as well. The overall activation energy is 2.1 eV.

which suggests a concurrent migration of Si from bulklike layers. In the search for deep-exchange mechanisms, we, thus, looked at processes, which could provide at the same time, deep incorporation of Ge and appearance of Si adatoms. The NEB path displayed in Fig. 2 provides an example of such a process. The Ge adatom takes the position of the neighboring Si atom in the second layer, which, in turn, forms an interstitial dumbbell pair (M_2,M_3). The Si–Si dumbbell can evolve by pushing up a Si atom on the opposite side of the row (M_4). A Si adatom, diffusing with activation barrier of 0.5–0.6 eV, can eventually reach the position on top of the Ge atom (configuration M_5). From this site, the Si adatom can promote a deeper incorporation of Ge via the mechanism shown in Fig. 2(b), which is the very same mechanism described above [Fig. 2(a)] but for the interchanged roles of Si and Ge. By surmounting an overall activation energy of ~2.1 eV, the Ge atom is incorporated in the third layer and a Si adatom is formed. Our mechanism can be seen as a variation of the path proposed by Uberuaga *et al.*,[17] where instead of keeping the interstitial configuration to the end, the system releases a Si adatom. The two processes also have an identical (by accident) overall activation energy. Since the mechanism displayed in Fig. 2 involves an isolated adatom, the same issues on the availability of adatoms which are previously discussed, must be addressed here. Due to the much higher value of E_a, the lowest temperature at which the process is viable (i.e., $\langle n \rangle \lesssim 1$) is as high as 960 K. The effectiveness of our mechanism and that of Uberuaga *et al.* could, thus, be limited by a too low concentration of isolated adatoms at the experimental temperature of 773 K. Moreover, deep intermixing is observed upon annealing of a film already equilibrated at lower temperatures where only dimers are expected.[13] Therefore, processes leading to deep intermixing involving ad-dimers must be at work.

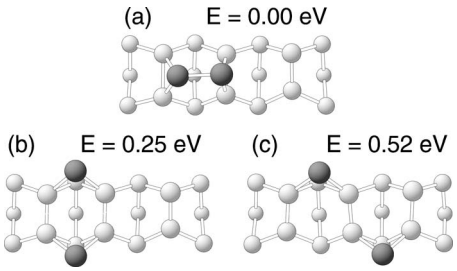

FIG. 3. (a) Epitaxial configuration for a Ge dimer on Si(001). [(b) and (c)] Configurations for an open Ge dimer.

Here, we offer an argument supporting the idea that the path of Fig. 2 could be involved in a mechanism for deep intermixing starting from an ad-dimer. Figure 3 displays three configurations for two adsorbed Ge atoms: the epitaxial dimer [panel (a)], the broken dimer [panel (b)], and two Ge adatoms obtained by a single hop from the broken dimer [panel (c)]. One adatom can follow the path of Fig. 2 starting from both configurations (b) and (c). The presence of the other adatom might change somehow the energetics of the path with respect to Fig. 2, but it is conceivable to believe such effect to be small when we choose the configuration of panel (c). The whole process would then start from (a), evolve toward (c) by surmounting low barriers (dimer rotation and opening from nonepitaxial configurations are fast already at low temperatures[18,26]) and finally lead to deep intermixing via the mechanism of Fig. 2. Would the presence of the second atom in (c) perturb only slightly the path of Fig. 2, the effective barrier for the whole mechanism should be ~2.6 eV [i.e., the isolated-adatom 2.1 eV plus the difference in energy between (a) and (c), cf. Fig. 2], which is still compatible with deep intermixing during prolonged annealing[13] (reaction rate of 10^{-2} s^{-1} at 873 K).

In summary, we have shown that a three-atom concerted exchange mechanism, which involves an isolated Ge adatom and a surface Si dimer, leads to Ge/Si intermixing on Si(001) down to almost room temperature. In a growing surface, this process is viable when the deposition rate is low enough to favor the presence of isolated adatoms surviving longer than the exchange lifetime. We have shown that these conditions are met in the experimental works on intermixing at low temperatures. In addition, we have also proposed a path leading to deeper incorporation of Ge into Si(001) with the simultaneous formation of Si adatoms, which would explain experiments on deep intermixing at high temperatures. Our results provide a justification, at least at high enough temperatures, for the key assumption of equilibrium between surface and subsurface layers proposed in recent models[4,5] of SiGe heteroepitaxy. We notice, however, that the kinetics of SiGe intermixing at any 3D island facet, which is different from (001), is still unknown and demands for an extension of the present work.

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