Structure and energetics of segregated and nonsegregated Ge(001)/Si(2×1)

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We present the results of *ab initio* pseudopotential density functional calculations for the geometry, energetics and electronic structure of the monolayer Si covered Ge(001)(2×1) surface. A segregated structure, in which Si occupies the second layer while Ge floats to the surface, is found to be energetically favorable by 0.38 eV per dimer compared to the nonsegregated Si-capped structure. In the latter case, the Si dimers are found to be asymmetric, with a bond length of 2.26 Å and a tilt angle of 16.7°, while in the segregated structure, the Ge dimers have a bond length of 2.39 Å and a tilt angle of 17.5°. [S0163-1829(98)00712-7]

Extensive effort has recently been expended on understanding the process of Ge growth upon Si substrates because of the vital technological role expected to be played by high-quality Ge/Si heterostructures in future optoelectronic devices.[1] References 2–10 provide no more than a representative sample of this body of work. Of no less importance is the growth of Si upon Ge substrates, but surprisingly this has been the focus of rather less attention.[11–16]

Experimental work[12–16] has indicated that Si growth on Ge(001) is anything but epitaxial, with evidence of alloy formation, three-dimensional Si islands, and segregation of Ge atoms to the surface (i.e., with Si atoms occupying subsurface sites). Alloy formation and segregation were, in fact, earlier predicted by Kelires and Tersoff, based upon their theoretical Monte Carlo simulations of growth.[11]

Group V adatoms may mediate expitaxial growth and suppress segregation for this system,[17] but an understanding of the surfactant-free growth process is vital before such matters can be discussed. Important open questions which may usefully be tackled by theoretical calculations on the surfactant-free system include the energetic comparison between the Ge-terminated and Si-terminated structures and the precise structural parameters associated with the surface dimers in each case.

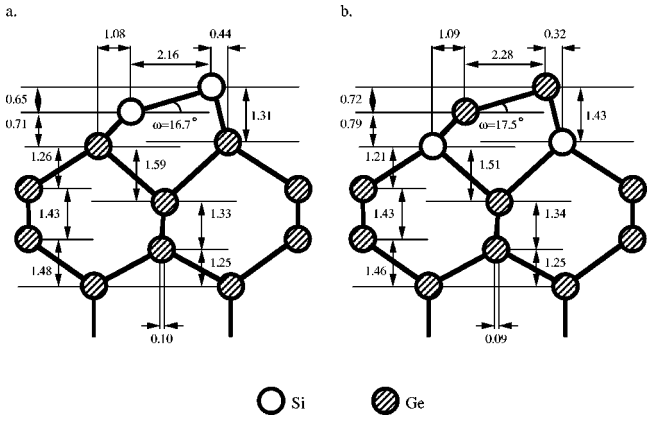

FIG. 1. Schematic side views of Ge(001)/Si(2×1): (a) Si-terminated structure and (b) Ge-terminated structure. All dimensions are in Å.

In order to address these issues, we have performed *ab initio* pseudopotential density functional calculations on Ge- and Si-terminated Ge(001)/Si(2×1) surfaces. The calculations were performed within a (001) (2×1) supercell of length equivalent to 12 atomic layers at our calculated bulk Ge lattice constant of 5.53 Å. The supercell contained a Ge slab of 7 atomic layers and a single monolayer of Si, either capping the Ge slab or diffused into the second layer (see Fig. 1). The opposite side of the slab was passivated with hydrogen in a dyhidride arrangement, and the remainder of the supercell was left as vacuum.

All atoms other than the back two Ge layers were free to relax into their optimum configuration according to an iterative conjugate gradient scheme,[18] with total energies and forces at each iteration evaluated by solution of the Kohn-Sham equation.[19] The pseudopotentials used for the electron-ion interaction were those of Bachelet, Hamann, and Schlüter,[20] and the Ceperley-Alder[21] form of correlation was employed for the electron-electron exchange-correlation potential. Electronic wave functions were expanded in terms of a basis set of plane waves, up to a kinetic energy cutoff of 8 Ryd, and Brillouin zone summation was performed using four special **k** points in the irreducible segment of the zone.

We find the segregated Ge-terminated structure to be lower in energy than the Si-terminated structure by 0.38 eV per dimer. That the segregated structure has the lower energy comes as something of a surprise in view of experimental results, since the works of Hoeven *et al.*,[12] Tsu *et al.*,[15] and Aubel *et al.*[16] strongly suggest that segregation only occurs at temperatures around 400 °C and above. On the other hand, simple physical arguments based upon the different bond strengths between group IV atoms (Si-Si strongest; Si-Ge intermediate; Ge-Ge weakest) would tend to favor Ge termi-

TABLE I. Dimer bond and back bond lengths for the Ge(001)/Si(2×1) Ge- and Si-terminated structures. Units are Å.

Si terminated	Si-Si	Si(up)-Ge	Si(down)-Ge
	2.26	2.40	2.34
Ge terminated	Ge-Ge	Ge(up)-Si	Ge(down)-Si
	2.39	2.44	2.37

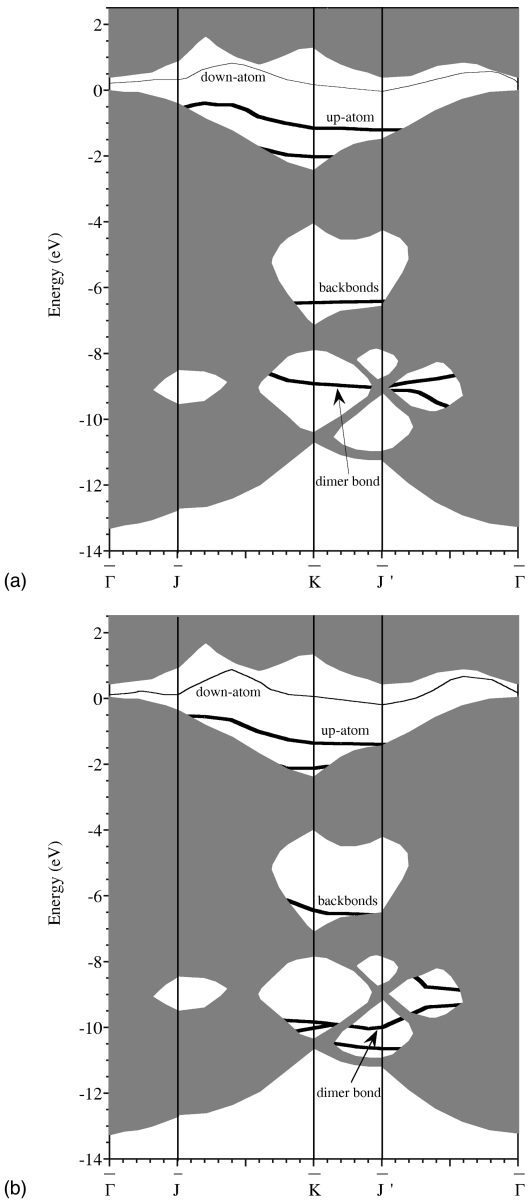

FIG. 2. Electronic band structures of Ge(001)/Si(2×1): (a) Si-terminated structure and (b) Ge-terminated structure.

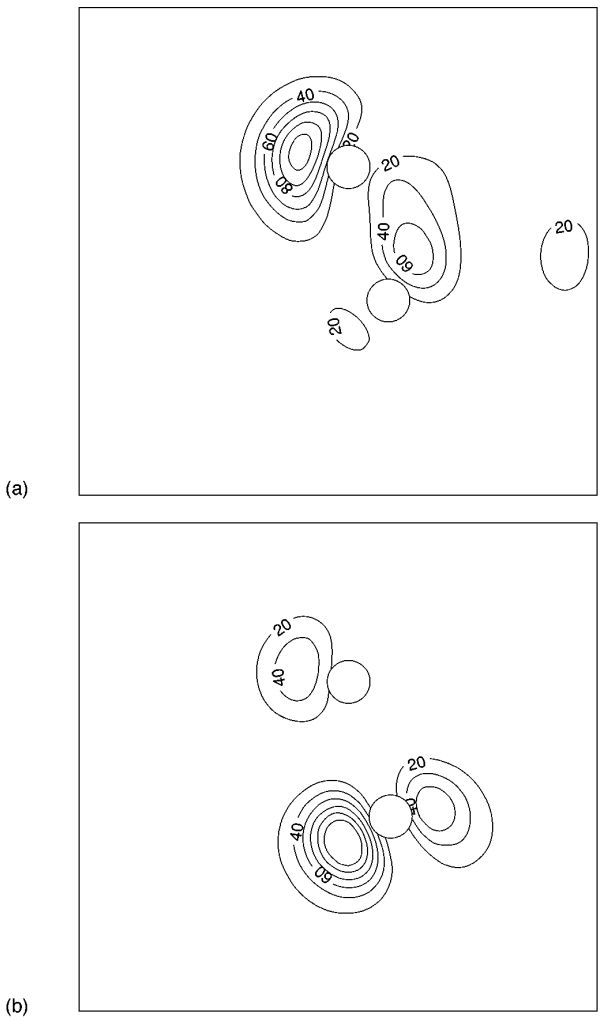

FIG. 3. Charge density plots for (a) the highest occupied surface state and (b) the lowest unoccupied surface state for the Si-terminated structure of Ge(001)/Si(2×1). Units are normalized to 2 electrons per supercell.

nation, in line with our results and those of Kelires and Tersoff.[11]

It is possible, however, that kinetic considerations prevent the surface from achieving the low energy segregated configuration at low temperatures, since the Ge/Si dimer exchange will be subject to an activation energy. At elevated temperatures, the exchange process becomes kinetically allowed, and so the segregated structure becomes realizable. Thus there is not necessarily any contradiction between theory and experiment.

The true ground state of the system may, however, turn out to be neither of the (2×1) structures considered, but instead a higher-order reconstruction, such as (4×2), because of the greater capacity for subsurface strain relief. Nevertheless, since the basic dimer building blocks of such reconstructions are very similar to those found on our (2×1) surfaces, we do not expect these small higher-order effects to lead to a reversal of our findings. We have also chosen not to investigate the possibilities of submonolayer coverage (both segregated and nonsegregated) and of partial segregation (where some Ge atoms segregate to the surface, but many other surface sites remain occupied by Si adatoms). Our previous work on the Ge-covered Si(001) surface[8] suggests that these cases are likely to be understood simply as interpolations between the segregated and nonsegregated structures considered in this work.

Our calculated structural parameters for the (2×1) surfaces are summarized in Table I and Fig. 1. We note immediately the similarity of the Ge dimer in the segregated structure (bond length 2.39 Å and tilt angle 17.5°) to the Ge dimer on the clean Ge(001)(2×1) surface[8] (bond length 2.38 Å and tilt angle 18.7°). Likewise, the Si dimer on the nonsegregated surface (bond length 2.26 Å and tilt angle 16.7°) is very similar to the Si dimer on the clean Si(001)(2×1) surface[8] (bond length 2.25 Å and tilt angle 16.1°). Experimental work to determine these parameters on the Ge(001)/Si(2×1) surface would be invaluable.

Electronic band structures for the two structures are displayed in Fig. 2. In each case we note both occupied and unoccupied surface states situated within the semiconducting

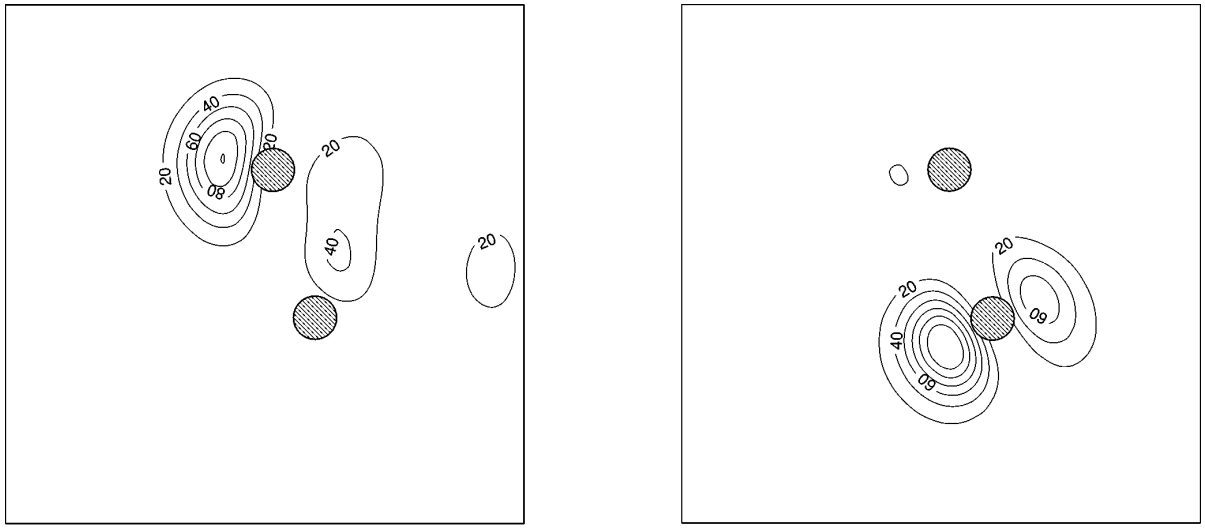

FIG. 4. Charge density plots for (a) the highest occupied surface state and (b) the lowest unoccupied surface state for the Ge-terminated structure of Ge(001)/Si(2×1). Normalization as in Fig. 3.

gap region. Charge density plots (Figs. 3 and 4) reveal that the highest occupied surface state in both structures is localized on the upper dimer atom, while the lowest unoccupied surface state is localized on the lower dimer atom; a situation qualitatively very similar to that observed on clean Si(001)(2×1) and Ge(001)(2×1) surfaces. One additional feature in both structures is the second highest occupied surface state, corresponding to bonding between second and third layer atoms.

Overall, the two structures would appear to be electronically very similar, based upon the location and dispersion of states in the vicinity of the Fermi level. The only slight difference is the greater charge transfer from the down dimer atom to the up dimer atom on the Ge-terminated surface, leading to the greater tilt angle observed for this structure (see Figs. 3 and 4). In both the Ge- and Si-terminated structures, dimer-substrate back bonds appear in the stomach gap, around 6 eV below the bulk valence band maximum. Additionally, a σ-like dimer bond appears at a binding energy of around 9 eV in the case of the Si-Si bond, and around 10 eV in the case of the Ge-Ge bond.

In summary, we have provided detailed structural parameters for, and energetic comparison of, the Ge-terminated and Si-terminated Ge(001)/Si(2×1) structures. We determine the segregated Ge-terminated structure to be more stable than the Si-terminated structure by 0.38 eV per dimer, and suggest that experimental nonobservation of this ordering at room temperature and below is due to kinetic effects. Surface electronic structures and bonding arrangements for both structures may be understood as straightforward generalizations of the equivalent clean Ge(001) and Si(001) surfaces.

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