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Theoretical evidence concerning mixed dimer growth on the Si(001)(2 × 1)–Ge surface

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Abstract. The local atomic geometry, chemical bonding and energetics for half- and full-monolayer Ge coverages on the Si(001)(2 × 1) surface have been studied by applying the *ab initio* pseudopotential method. For one monolayer coverage we find that the adatoms form an asymmetric dimer with length equal to the bond length in bulk Ge. At half-monolayer coverage we find that the formation of mixed Si–Ge dimers is comparable to growth of Ge–Ge dimers in islands, confirming recent experimental observations. Our work also shows that Ge diffusion into the substrate will only become important at unusually high growth temperatures, in the region of 1000 K or above.

1. Introduction

The growth of Ge upon the Si(001)(2 × 1) surface is of profound technological importance. Desirable properties of proposed combined Si/Ge devices have led to significant experimental and theoretical efforts to understand the process of Ge adsorption upon this surface. However, the initial stages of Ge growth on Si(001)(2 × 1) are still subject to considerable discussion, with various unresolved claims concerning different local geometry and bonding properties highlighting the substantial disagreement between several experimental and theoretical groups.

High-resolution electron diffraction studies clearly indicate that beyond about six monolayers the growth of Ge on Si(001)(2 × 1) at 400 °C in an MBE chamber does not occur epitaxially, but rather by the process of Stranski–Krastanov islanding [1]. For a monolayer deposition onto the room temperature substrate followed by annealing at 350–600 °C, the low-energy electron diffraction pattern shows a (1 × 2) structure [1] indicating that there is a dimer formation at the top layer, but in the orthogonal direction to the original dimer direction on the clean Si(001) surface. Sasaki *et al* [2] claim that their Auger electron diffraction and x-ray photoelectron diffraction studies indicate significant diffusion as far as the fifth surface layer after annealing at 600 °C. Recent reports on examination of Ge 3d and Si 2p core level shifts observed in high-resolution photoemission experiments by Patthey *et al* [3] suggest that up to 0.8 monolayer coverage the growth mode is characterized by asymmetric mixed Si–Ge dimers as well as some pure Ge–Ge dimers. The work of Patthey *et al* also shows that there is some Ge diffusion into the second and perhaps deeper layers, which is enhanced upon annealing the sample to 600 °C. These results [2, 3] have negative implications for any hopes of growing an abrupt interface between the two materials, since growth temperatures are typically in the range 350–600 °C. On the other hand, Cho *et al* [4] conclude, from theoretical studies of the half-monolayer coverage of Ge, that interdiffusion is not an important process.

The aim of this paper is to clarify these conflicting results by re-examining the findings of Cho *et al* [4] and extending the investigation of interdiffusion to the monolayer coverage of Ge. To this end we have performed *ab initio* pseudopotential density functional calculations on the clean Si(001)(2 × 1) surface, the clean Ge(001)(2 × 1) surface, and on a number of possible configurations of the Ge-covered Si(001)(2 × 1) surface. In particular, we have studied in detail the local atomic geometry, chemical bonding, and energetics for the half- and full-monolayer Ge coverages. For one monolayer coverage we find that the adatoms form an asymmetric dimer with length equal to the bond length in bulk Ge. Our results confirm the experimental observations of Patthey *et al* that mixed dimer formation is the predominant growth mode at submonolayer coverages, and also shed some light on the extent to which Ge interdiffusion may be a significant factor in the early stages of Si/Ge interface growth. It is shown that such interdiffusion will only become important at unusually high growth temperatures in the region of 1000 K.

2. Method

We have used a supercell technique, in which the surface under consideration is modelled by a slab of material eight atomic layers thick, and a vacuum region equivalent to four atomic layers. On one side of the slab (the ‘back-surface’) the dangling bonds were passivated by H atoms arranged in a dihydride structure. On the other side a number of plausible configurations were used as starting points for geometry optimization. The lattice constants used were our theoretically obtained values of 5.42 Å for clean and Ge-covered Si(001)(2 × 1) surfaces and 5.53 Å for the Ge(001)(2 × 1) surface. For each chosen geometrical configuration the Kohn–Sham equation [5, 6] was solved directly, within a basis set of plane waves, using a conjugate gradient technique [7]. Exchange and correlation were taken into account within the local density approximation [5, 6] including the Ceperley–Alder form of correlation [8]. The electron–ion interaction was replaced by the *ab initio*, non-local, norm-conserving pseudopotentials of Bachelet *et al* [9]. Brillouin zone integration was achieved through summation over four special k-points [10] in the irreducible segment of the surface Brillouin zone.

Relaxation of the ionic degree of freedom was achieved iteratively within a conjugate gradient scheme [7], utilizing forces calculated from the Kohn–Sham equation at each step of geometry update. Such a scheme (essentially a Hamiltonian approach) is comparable in performance to the Car–Parrinello [11] (Lagrangian) approach. The back two layers of semiconductor atoms were held frozen in their bulk positions, but all other atoms, including the H atoms, were allowed to relax freely.

The plane wave basis set was truncated at the kinetic energy cut-off values of 5, 8 and 10 Ryd for a number of calculations on bulk Si, bulk Ge and the Si(001)(2 × 1) surface, and it was found that the choice of 8 Ryd gave well converged values for the bulk lattice constant and surface atomic geometry. The final calculations were therefore made by truncating the plane wave basis set at a kinetic energy cut-off of 8 Ryd.

3. Results and discussion

3.1. Clean Si(001)(2 × 1) and Ge(2 × 1)(2 × 1) surfaces

In order to understand the Ge-covered Si(001) surface it is instructive to examine first the clean (001)(2 × 1) surfaces of group IV materials. It has long been known that these surfaces reconstruct by the formation of surface dimers [12–14]. In this way one dangling bond per

surface atom is saturated, leading to a gain in energy relative to the (1×1) surface. The fate of the remaining (p_z -like) dangling bond, however, is a point of some interest. On the Ge(001)(2×1) surface there is transfer of charge from one dimer component to the other. Simplistically this can be thought of as resulting in a fully occupied p_z -like dangling bond on one atom and an empty p_z -like dangling bond on the other, although in truth the charge transfer is not quite complete and rehybridization occurs so that the more fully occupied orbital become more s^2p^3 -like, while the other becomes more sp^2 -like. This rehybridization drives a shift of the dimer atoms towards an asymmetric geometry, as the component with the more fully occupied dangling bond is pushed away from the surface, while the other component moves closer. At the other extreme, the components of the dimer on the diamond(001)(2×1) surface are much closer together, and the overlap between their p_z orbitals is thus much greater. This leads to the formation of a fully occupied π -bonding orbital and an empty π^* -antibonding orbital. In this way a double-bond is formed between the dimer components and no asymmetry arises.

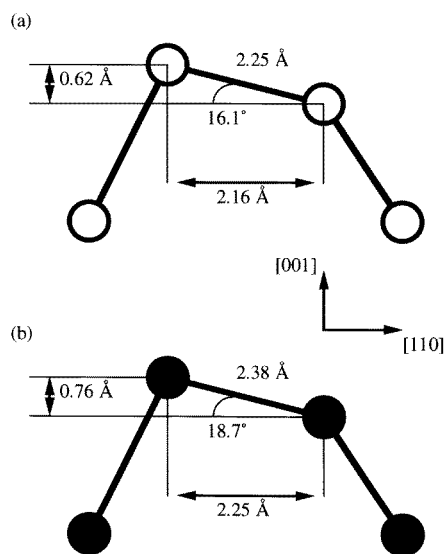


Figure 1. Side view of calculated equilibrium geometries (schematic) for the surface dimers at (a) the clean Si(001)(2×1) surface and (b) the clean Ge(001)(2×1) surface. The $2 \times$ periodicity is considered along the [110] direction.

Precisely where the Si(001)(2×1) surface fits into this picture has been the subject of some controversy in the literature [12]. Both symmetric and asymmetric models have been proposed for this surface, but recently there appears to be some consensus for the asymmetric model [13–18]. Our calculations are in full accord with this recent trend, as we predict a buckling angle of 16.1° for the Si-dimer at the Si(001)(2×1) surface (corresponding to a vertical buckling of 0.62 \AA). This is only a little less than our predicted buckling angle of 18.7° for the Ge-dimer at the Ge(001)(2×1) surface (corresponding to a vertical buckling of 0.76 \AA). Both of these buckling angles agree well with recent theoretical work [4, 13–20].

Figure 1 shows the equilibrium geometries calculated for these surfaces in the present work, while figure 2 clearly illustrates the characteristic charge transfer, from one dimer component to the other, which causes the buckling. The dimer bond length at the Si(001)(2×1) surface is calculated to be 2.25 \AA , while that for the Ge(001)(2×1) surface is 2.38 \AA . The

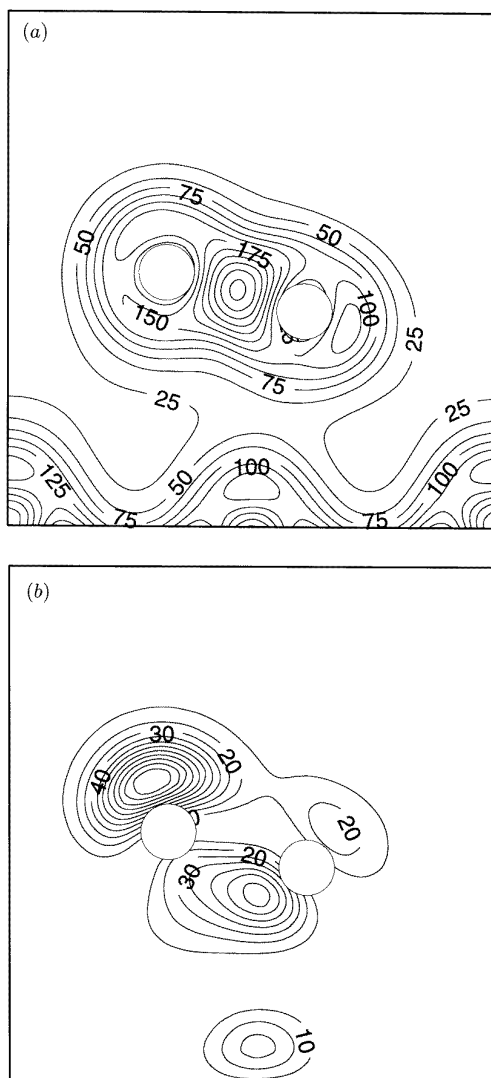


Figure 2. Top layer Si atoms at the clean Si(001)(2 × 1) surface form a strong covalent bond, as evidenced by the total valence electron density plot in (a). The electron density is normalized to the number of electrons in the supercell (i.e. 68 in all the calculations reported here). There are twelve bulk unit cells per supercell. The transfer of charge from the lower atom to the higher atom may be clearly seen in the electron density plots for (b) the highest occupied state and (c) the lowest unoccupied state, at the \bar{K} point (i.e. the corner) of the surface Brillouin zone.

Si dimer bond is approximately 4% shorter than our calculated bulk Si–Si bond length of 2.35 Å, but the Ge dimer bond length is very close to our calculated bulk Ge–Ge bond length of 2.39 Å. Our results for these and the other systems studied are summarized in table 1, along with a collation of previous theoretical [13–20] and experimental results [21–28].

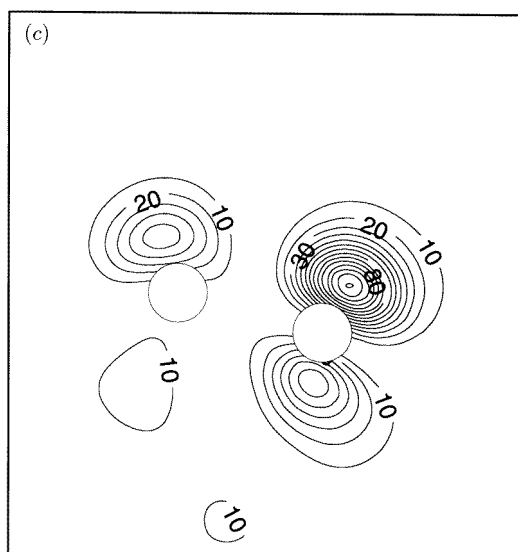


Figure 2. Continued

3.2. One monolayer Ge on Si(001)(2 × 1)

As discussed in the Introduction, growth of a monolayer of Ge on the Si(001)(2 × 1) surface can be either wholly epitaxial or feature some degree of interdiffusion. There are thus a number of possible configurations for the adatoms. Most obviously, the Ge atoms could simply form a dimer at the surface (figure 3(a)). However, if we allow diffusion of Ge atoms into the second layer we can imagine a further four possibilities in which a mixed Si–Ge dimer is formed at the surface (with either the Si or the Ge component taking the ‘up’ position) and the second Ge atom lies in the second layer in either the ‘*cis*’ or the ‘*trans*’ position (figures 3(b) to (e)). We shall call these five configurations ‘non-diffused’, ‘*cis*-diffused/Ge-up’, ‘*cis*-diffused/Si-up’, ‘*trans*-diffused/Ge-up’ and ‘*trans*-diffused/Si-up’. Myriad other possible structures exist if we allow diffusion beyond the second layer, but we will not consider them in this work. Since the stoichiometry of each of these configurations is identical it is perfectly permissible to compare total energies directly.

Our total energy calculations reveal that the lowest energy of these five configurations is for the non-diffused case, suggesting that Ge interdiffusion is not the major growth mode on the Si(001)(2 × 1) surface. All the other listed configurations are metastable, the most stable of these being the *trans*-diffused/Ge-up and *cis*-diffused/Ge-up configurations, both lying 0.19 eV per dimer higher in energy than the non-diffused structure. Thus the favoured position of the Ge atom in the mixed dimer is found to be the ‘up’ position, whether in the *cis* or the *trans* configuration. This finding is consistent with the previous theoretical work by Cho *et al* [4] for the mixed dimer at half-monolayer coverage. Of the two remaining structures it is the *cis*-diffused/Si-up configuration which is the more stable, having an energy 0.26 eV above that of the non-diffused structure, while the least stable of all the structures considered is the *trans*-diffused/Si-up structure, lying 0.34 eV per dimer higher in energy than the non-diffused structure. In reality, the surface may reconstruct to form a (2 × 2) pattern very similar to the structures we have considered, but with slightly more efficient strain relief in the first subsurface layer [29]. This would allow the diffused structures

Table 1. Calculated structural parameters for the top-layer dimer on the clean and covered (001)(2 × 1) surfaces, compared with other theoretical and experimental results.

System	Dimer length (Å)	Buckling angle (°)	Vertical buckling (Å)
Si(001)(2 × 1)			
Present work	2.25	16.1	0.62
Ref. [13]: theory	2.25	19	
Ref. [14]: theory		15	
Ref. [15]: theory	2.30	18.4	0.69
Ref. [16]: theory	2.29	16.8	
Ref. [17]: theory	2.21	6.9	0.26
Ref. [18]: theory	2.26	7.9	0.31
Ref. [21]: expt range	2.20–2.47		
Ref. [22]: expt	2.37	20	
Ref. [23]: expt	2.25	19.0	
Ge(001)(2 × 1)			
Present work	2.38	18.7	0.76
Ref. [4]: theory	2.46	19	
Ref. [13]: theory	2.41	19	
Ref. [19]: theory	2.46	13	
Ref. [24]: expt	2.44	21	
Ref. [25]: expt		20	
Si(001)(2 × 1)Ge (1 ML)			
Present work	2.38	18.5	0.76
Ref. [4]: theory	2.39	16	
Ref. [20]: theory	2.39	17	
Ref. [27]: expt	2.55 ± 0.04	12.4 ± 0.2	0.55 ± 0.02
Ref. [28]: expt	2.51 ± 0.04	0	0
Si(001)(2 × 1)Ge (1/2 ML)			
Present work	2.34	19.3	0.77

discussed above to occur at slightly lower energies, but the essential physics would remain the same. Thus, if anything, our calculations will tend to marginally underplay the effects of diffusion.

Detailed examination of the geometry for the non-diffused case reveals a structure in good agreement with previous theoretical work [4, 20]. The Ge dimer simply assumes an asymmetric form similar to that observed for dimers on both the clean Si and Ge(001)(2 × 1) surfaces. The calculated buckling angle of 18.5° (corresponding to a vertical buckling of 0.76 Å) is rather closer to that found for the Ge dimer on the clean Ge(001)(2 × 1) surface (18.7°) than to that found for the Si dimer on the clean Si(001)(2 × 1) surface (16.1°), indicating that the buckling is largely determined by the composition of the dimer rather than the underlying substrate. We therefore hypothesize that properties of the dimer are relatively substrate independent. This conclusion may further be supported by the observation that the Ge–Ge dimer bond length is 2.38 Å on both the Si and Ge substrates, as compared to the Si dimer bond length of 2.25 Å on the clean Si surface. Additionally, we note that the maximum of the electronic charge density along the Ge–Ge dimer bond on Ge/Si(001) is less than the maximum for the Si–Si dimer bond on Si(001), as revealed by comparison of figures 2 and 4. This is consistent with the longer bond length of the Ge–Ge dimer.

On the experimental side two groups have reported significantly different Ge–Ge dimer lengths. Using the x-ray standing wave (XSW) technique Fontes *et al* [26] have concluded

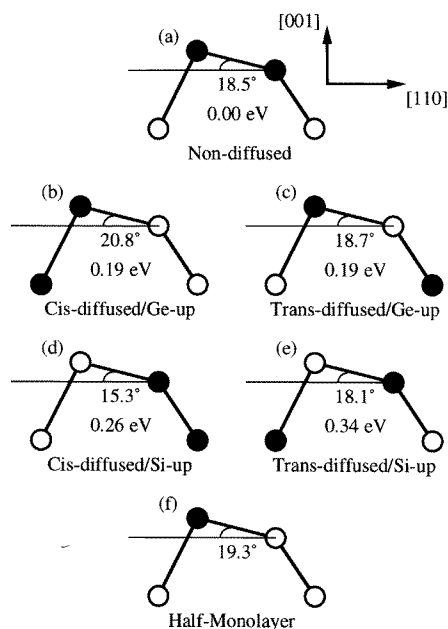


Figure 3. (a)–(e) show schematically side views of the various configurations at monolayer coverage of Ge on Si(001)(2×1) that are discussed in this work. The total energies of these configurations relative to the non-diffused configuration are also shown. (f) shows the lowest energy half-monolayer structure. The $2 \times$ periodicity is considered along the [110] direction. Open and filled circles represent Si and Ge atoms, respectively.

that the Ge–Ge dimer is asymmetric with length 2.60 \AA . Following re-analysis of their raw data this group later reported a value of $2.55 \pm 0.04 \text{ \AA}$ [27]. Fontes *et al* also determined the tilt angle and the vertical buckling of the Ge–Ge dimer to be 12.4° and $0.55 \pm 0.02 \text{ \AA}$, respectively. Using the surface-extended x-ray adsorption fine structure (SEXAFS) technique Oyanagi *et al* [28] proposed an elongated symmetric Ge–Ge dimer of length $2.51 \pm 0.01 \text{ \AA}$. Although the dimer length measurement is essentially the same in both the XSW analysis (revised value by Fontes *et al*) and the SEXAFS analysis (Oyanagi *et al*), the two results are fundamentally different from each other as the former proposes an asymmetric dimer and the latter proposes a symmetric dimer. Our work confirms that the dimer is asymmetric but lends no evidence to support the hypothesis of elongated Ge dimers on the Si substrate.

In structures with a mixed dimer we would expect the asymmetry of the dimer to be influenced by the electronegativities of the components. That is, we would expect charge transfer to occur preferentially from the less electronegative species to the more electronegative species, resulting in the more electronegative component occupying the ‘up’ position. The electronegativities of Si and Ge on the Pauling scale are 1.90 and 2.01 respectively [30]. Thus it is not surprising that both the ‘Ge-up’ configurations are found to be more stable than the ‘Si-up’ configurations. The relatively small difference in the electronegativities, however, ensures that the Si-up structures are only slightly higher in energy than the Ge-up structures. We might additionally expect that the difference in the electronegativities should enhance the asymmetry of the Ge-up structures, as compared to dimers in which both components are the same. Indeed, the buckling angle in the *cis*-

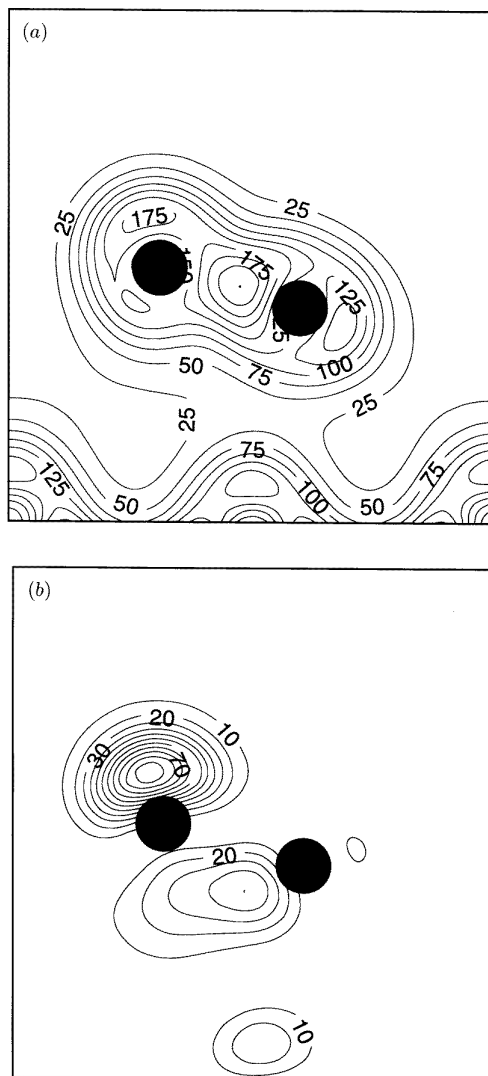


Figure 4. Transfer of charge from the lower dimer component to the higher dimer component is evident in the plots of (a) the total valence electron density, (b) the electron density for the highest occupied state at \bar{K} and (c) the electron density for the lowest unoccupied state at \bar{K} , for the case of a non-diffused Ge dimer adsorbed on the Si(001)(2×1) surface.

diffused/Ge-up dimer is 20.7° , while that for the *trans*-diffused/Ge-up dimer is 18.7° . Both figures are somewhat in excess of the buckling angles reported above for Si–Si (16.1°) and Ge–Ge (18.5°) dimers. Conversely, in the Si-up structures we might expect the asymmetry to be reduced, and hence the dimer buckling angle to be smaller. Once again we find this to be the case, as the buckling angle for the *cis*-diffused/Si-up dimer is 15.3° and that for the *trans*-diffused/Si-up is 18.1° . As one might expect, the bond lengths for the mixed dimers in all the structures considered fall in the range between the Si–Si dimer bond length (2.25 \AA) and the Ge–Ge dimer bond length (2.38 \AA).

Although our calculations were performed at zero temperature and strictly relate to

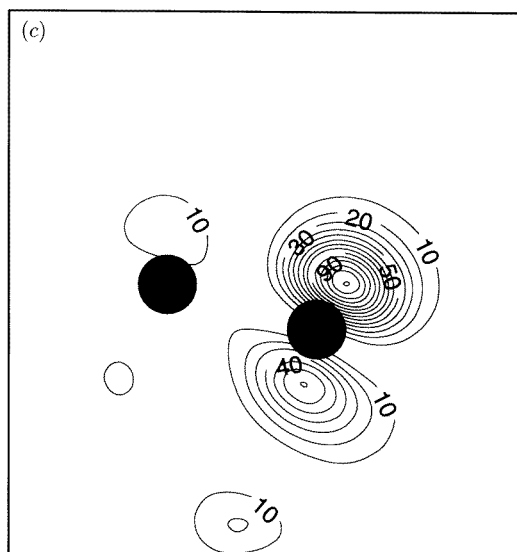


Figure 4. Continued

infinitely repeating arrays of dimers, we can still use the total energy values thus obtained to give a crude estimate of the relative importance of these structures, and an indication of the extent of Ge interdiffusion, at higher temperatures. Let us examine the Boltzmann probability distribution at a temperature T , $p_i = e^{-E_i/k_B T} / \sum_j e^{-E_j/k_B T}$, for a five-state system with energies 0, 0.19, 0.19, 0.26 and 0.34 eV taken from our calculations. Accordingly, at room temperature there will be virtually no diffusion of Ge atoms. We estimate that at a temperature of 1000 K approximately 11% of adsorbed Ge atoms will diffuse into the second layer. It should be emphasized that these figures are lower bounds, indicating that diffusion *may* become an important factor in growth at temperatures perhaps even lower than 1000 K. This would clearly have implications for growth at the upper end of the typical growth temperature range. The surface free energy, $F = E - TS$, calculated from the above probabilities at 1000 K is 0.02 eV per dimer lower than that obtained by considering only the non-diffused structure. In reality, diffusion to layers deeper than the second layer will occur, and so the calculated percentage of atoms which diffuse will only ever be an underestimate. One might think that including diffusion into deeper layers *ad infinitum* would eventually yield a unit probability of diffusion, but kinetic effects, which are beyond the scope of this paper, would in fact prevent this. The five-state Boltzmann approximation used here corresponds to the assumption (probably rather too strict) that kinetic effects absolutely prevent diffusion beyond the second layer.

3.3. Half-monolayer Ge on Si(001)(2 × 1)

In the light of our findings we re-examined the results of Cho *et al* [4] for the case of half-monolayer Ge coverage. They reported that the lowest energy configuration for half-monolayer coverage was achieved when the Ge atom was in the top layer and occupied the 'up-atom' site of the mixed dimer. They also found a metastable structure in which the Ge atom occupied the 'down-atom' site, which lay 0.13 eV higher in energy than the ground state, and noted an increase in the energy of at least 0.23 eV when the Ge atom

was relocated to the second layer. From these figures they concluded that diffusion into the second layer would be negligible. While this is clearly true at low temperatures it ignores the variation of diffusion with increasing temperature. Using our Boltzmann distribution argument again, these energy levels imply that around 10% of Ge atoms would diffuse into the second layer at 1000 K. Once again, this is clearly a minority process, but not an entirely negligible one at this temperature. We conclude that the percentage of Ge atoms which diffuse into the second layer at a given temperature remains more or less constant as coverage is increased from half a monolayer to a full monolayer. The obvious corollary is that the concentration of Ge atoms in the second layer doubles as coverage increases from half a monolayer to one monolayer.

To make a further connection with the work of Cho *et al* [4] we have also investigated the possibility of mixed Si–Ge dimer formation at half-monolayer Ge coverage on the Si(001)(2 × 1) surface (figure 3(f)). Going a step further than the previous work, we find that the total energy of the mixed dimer is 0.02 eV lower than the average of the total energies per dimer of the clean Si(001)(2 × 1) surface and the non-diffused Ge dimer covered Si(001)(2 × 1) surface. However, 0.02 eV is a very small energy difference, and might indeed be reduced still further if (2 × 2) reconstructions were considered. Thus our results merely indicate that growth of Ge on the Si(001)(2 × 1) surface below monolayer coverage is likely to proceed by the formation of both mixed Si–Ge dimers and pure Ge–Ge dimers. This is broadly in line with the conclusions of Patthey *et al* [3].

4. Conclusions

In conclusion, we have studied in detail the local atomic geometry, chemical bonding, and energetics of several possible configurations for monolayer and half-monolayer Ge coverages of the Si(001)(2 × 1) surface. For one monolayer coverage we find that the adatoms form an asymmetric dimer. This dimer is characterized by a vertical buckling of 0.76 Å, a tilt angle of 18.5°, and a length of 2.38 Å, equal to the bond length in bulk Ge crystal. This is in agreement with other theoretical works [4, 20], but does not support the hypothesis of elongated Ge–Ge dimer suggested recently by Fontes *et al* [26,27] and by Oyanagi *et al* [28]. At half-monolayer coverage we find that the formation of mixed Si–Ge dimers is preferable to growth of Ge–Ge dimers in islands. We thus concur with the suggestion of Patthey *et al* [3] that mixed Si–Ge dimer formation is comparable to the formation of pure Ge–Ge dimers at submonolayer coverage. Also, we have provided some evidence, admittedly neglecting kinetic effects, to confirm their observation, and that of Sasaki *et al* [2], that some interdiffusion of Ge into the second layer occurs at coverages between half a monolayer and one monolayer at temperatures around 1000 K. At temperatures towards the lower end of the standard growth temperature range, however, the equilibrium geometry includes virtually no diffused Ge atoms.

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