

Characterization of the Ge(001)/Si-(2×1) surface using lattice dynamics

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We present lattice dynamical calculations for segregated and nonsegregated models of the monolayer Si-covered Ge(001) surface. The calculations were performed using the adiabatic bond-charge model, with structural parameters and electronic charge distributions taken from recent *ab initio* pseudopotential calculations. We find that adsorption of Si results in several characteristic phonon modes above the bulk continuum. These modes constitute a signature that may be used to distinguish between surface and subsurface Si adsorbate layers. [S0163-1829(99)00840-1]

Experimental and theoretical interest in Si growth upon the Ge(001) substrate has been steadily increasing in recent years,¹⁻⁷ driven in part by the potential importance of high-quality Si/Ge interfaces for future optoelectronic devices. One phenomenon of particular importance in this regard is the reported formation of an undesirable subsurface Si layer at temperatures above 400 K. Segregation of substrate Ge to the surface is presumably a consequence of that element's lower cohesive energy, but kinetic and entropic effects preclude confirmation of this surmise from zero-temperature calculations of the internal energy alone.

Within the (2×1) substrate reconstruction, the "segregated" (i.e., Ge-terminated) structure was, in fact, first predicted theoretically by Kelires and Tersoff¹ on the basis of Monte Carlo simulations, and has subsequently been observed experimentally by a number of groups.²⁻⁶ Recent *ab initio* pseudopotential density functional calculations⁷ show that the segregated structure is indeed lower in energy than the "nonsegregated" (i.e., Si-terminated) structure by 0.38 eV per dimer, confirming that its nonoccurrence at low temperatures is not a consequence of *equilibrium* thermodynamics.

The *ab initio* calculations⁷ also revealed that the structural and electronic properties of the segregated and nonsegregated models are very similar. This is not surprising, as Si and Ge are neighbors in Group IV of the periodic table, and differ in covalent radius by only around 4%. In fact, the most striking difference between Si and Ge, and therefore potentially the most useful in characterizing the surface, is the atomic mass difference, but this has no bearing on the static geometrical and electronic properties discussed in the literature thus far. Surface lattice dynamics, on the other hand, can be used as a potential tool for characterizing the Ge(001)/Si system.

In the present paper, we report on lattice dynamical properties of the segregated and non-segregated surfaces, calculated within the adiabatic bond-charge model (BCM). The results highlight striking differences between the Ge(001)/Si(2×1) and Ge(001)/Si/Ge(2×1) systems, which should

easily be measurable experimentally to provide a distinctive signature for the onset of segregation.

The main concept behind the BCM is that the valence-electron charge-density distribution is represented by massless bond charges (BC's), endowed with translational degrees of freedom.⁸ The BC's are allowed to move adiabatically, following the ionic displacements so as to stay in equilibrium with the instantaneous positions of the ions. We have modeled the Ge(001)/Si(2×1) and Ge(001)/Si/Ge(2×1) surfaces in a repeated slab scheme. The supercell consisted of 14 layers of Ge and 2 layers of Si atoms in each case (the slab being double-sided) and a vacuum region equivalent to 8 atomic layers in total. Atoms in the top three layers on each side of the slab were placed at their relaxed positions, while deeper lying atoms were taken at their bulk positions. Bond-charges were, in general, placed midway between nearest-neighbor ions and given charge Z_e . The bond charges representing the dangling bonds of the Si dimer and Ge dimer, however, were instead placed and charged according to the positions and magnitudes of the maxima in the partial electronic charge densities obtained for those states from the *ab initio* pseudopotential calculation.⁷ Figure 1 shows the positions of dangling-bond charges for both surfaces. The application of the BCM has been made as described in Ref. 8. However, the surface BCM parameters have been redefined to achieve equilibrium conditions by invoking translational and rotational invariance throughout the supercell.

The phonon dispersion curves for the Ge(001)/Si(2×1) and Ge(001)/Si/Ge(2×1) surfaces are plotted in Figs. 2(a) and 2(b), respectively. The calculated surface results are shown by solid lines, while the projected bulk Ge phonon energies are shown by the hatched regions. As can be seen from these figures, adsorption of Si overlayers results in several characteristic new phonon states above the bulk phonon continuum. Figures 3(a) and 3(b) illustrate the phonon density of states for these surfaces. Distinctive peaks due to absorption of Si on the Ge(001)(2×1) surface are labeled S^1 through to S^5 in each case.

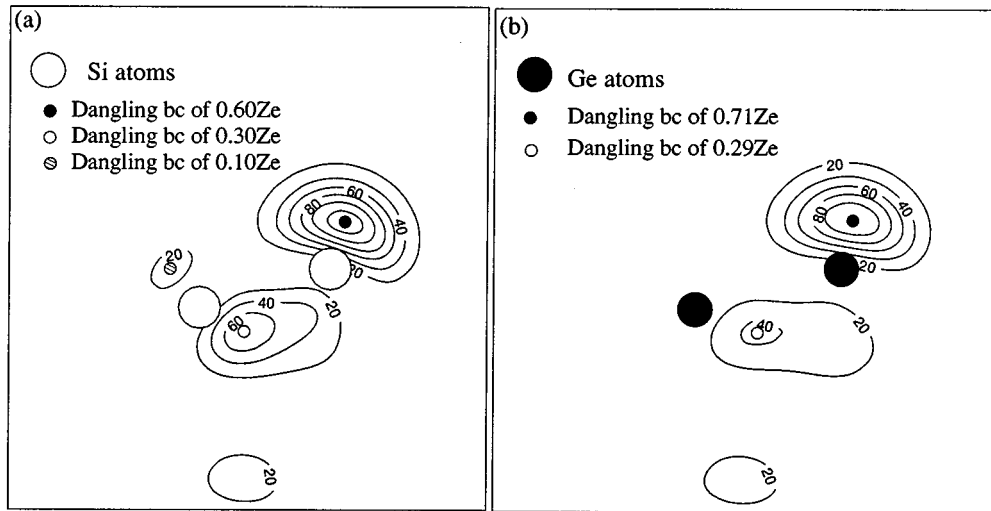


FIG. 1. Electronic charge density for the dangling-bond charges on (a) the Ge(001)/Si(2×1) and (b) the Ge(001)/Si/Ge(2×1).

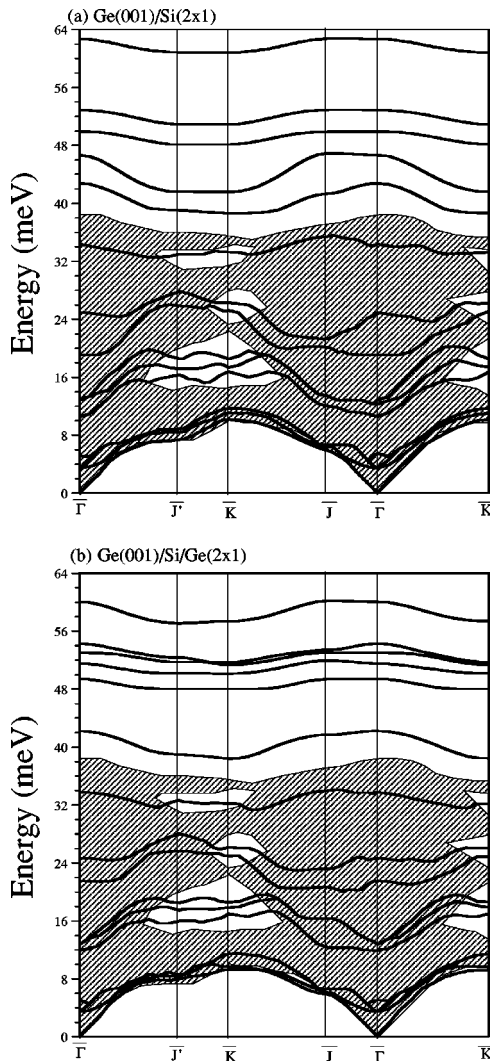


FIG. 2. Phonon dispersion curves of (a) the Ge(001)/Si(2×1) and (b) the Ge(001)/Si/Ge(2×1) surfaces. The calculated results are shown by thick-solid curves while bulk projection is shown by hatched region.

It is clear that segregation of Ge to the surface results in a 3-meV downshift (and 2-meV splitting) of the highest energy peak S^5 , a doubling in height of peak S^4 , and the complete suppression of peak S^2 . Further information that may be of use in characterizing the surface includes the polarization and localization of individual surface phonon modes.

At the zone center for the nonsegregated (i.e., Si-terminated) surface, we observe five surface optical phonon modes above

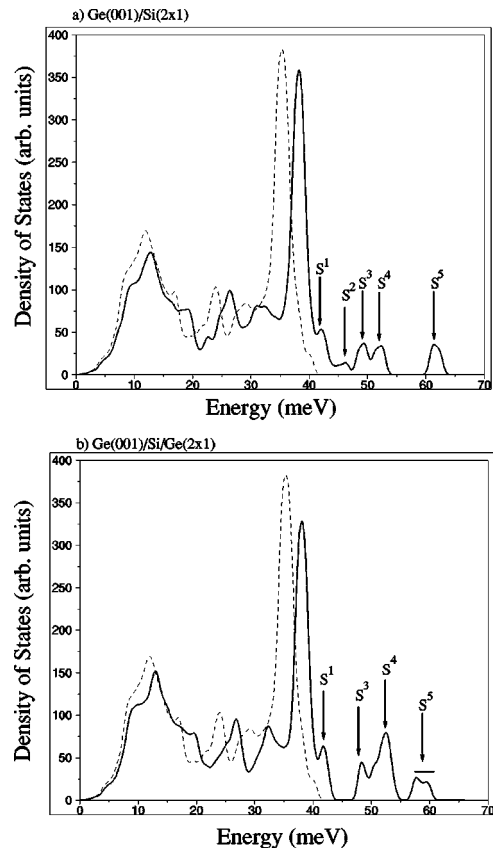


FIG. 3. Phonon density of states of (a) the Ge(001)/Si(2×1) and (b) the Ge(001)/Si/Ge(2×1) surfaces. In each case, the phonon density of states for the clean Ge(001)(2×1) surface is shown, for comparison, by a dashed line.

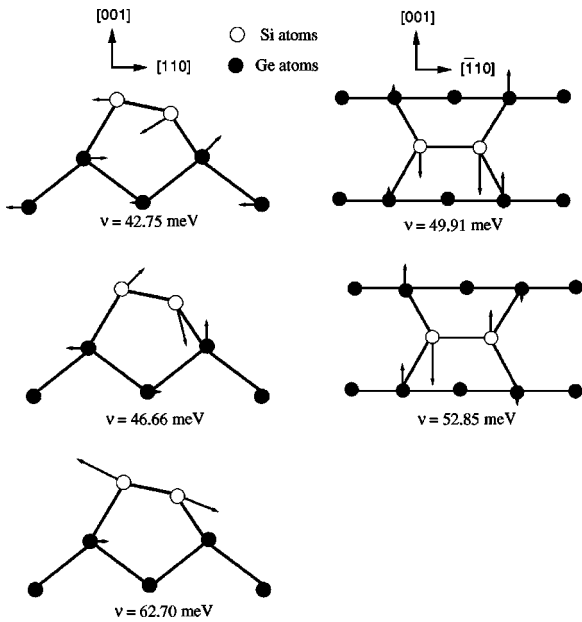


FIG. 4. Atomic displacement patterns of surface optical modes above the bulk continuum at the $\bar{\Gamma}$ point for the Ge(001)/Si(2×1) surface.

the bulk continuum at energies 42.75, 46.66, 49.91, 52.85, and 62.70 meV. Atomic displacement patterns of these modes are presented in Fig. 4. The first of these, associated with peak S^1 , involves first- and second-layer atoms vibrating in opposing senses close to the dimer bond direction, and is thus B_2 polarized at this \mathbf{k} point. Similarly B_2 polarized is the slightly higher energy S^2 -related mode at 46.66 meV, which is dominated by opposing motion of the first-layer atoms close to the surface normal direction. The B_1 polarized mode at 49.91 meV may be thought of as a swinging phonon mode, due to the parallel motion of first-layer atoms in the dimer row direction; correspondingly, the phonon mode at 52.85 meV may be called a dimer twisting mode, and is also B_1 polarized. The essential similarity between these two modes accounts for the similar weights of peaks S^3 and S^4 in the density of states. Finally, the highest energy surface optical frequency, at 62.70 meV, is a dimer stretching mode and has B_2 polarization. We find the displacement pattern of this highest energy mode to be largely wave vector independent.

On the segregated (i.e., Ge-terminated) surface, we observe six phonon modes above the bulk continuum, at 42.21, 49.39, 51.54, 53.02, 54.28, and 60.04 meV. Atomic displacement patterns for these are shown in Fig. 5, and it can immediately be seen from this diagram that these phonon modes are mainly localized on the second layer atoms due to large mass difference between Ge and Si atoms. In each case, just one type of Si atom (bonded either to the “up” or “down” dimer atom) is dominant. The S^1 -related phonon mode at 42.41 meV, for example, involves a particularly large surface normal vibrational contribution from the Si bonded to the “up” dimer atom, and is therefore B_2 polarized.

As noted above, there are no modes on this surface in the energy range associated with S^2 , but there is a B_1 polarized S^3 -related mode at 49.39 meV due to the Si bonded to the “down” dimer atom vibrating strongly in the dimer row

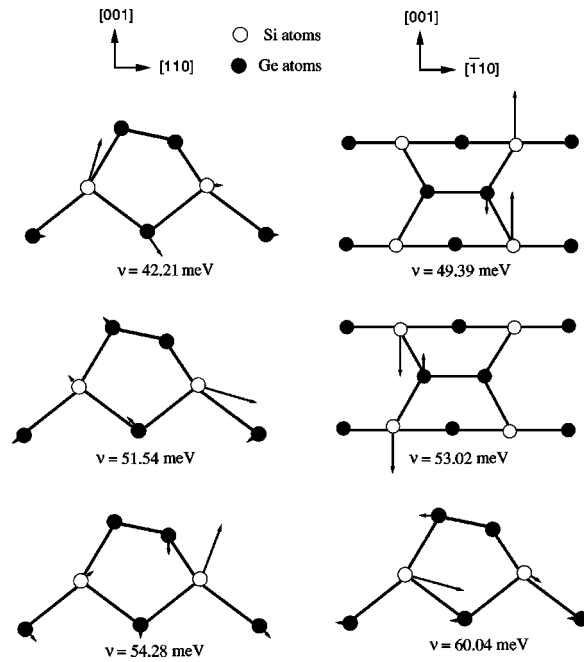


FIG. 5. Atomic displacement patterns of surface optical modes above the bulk continuum at the $\bar{\Gamma}$ point for the Ge(001)/Si/Ge(2×1) surface.

direction, with just a little opposing motion from the “down” dimer atom itself. We then observe a cluster of three modes that jointly account for the increased weight of peak S^4 relative to the non-segregated structure. The mode at 53.02 meV is, in some sense, complementary to peak S^3 , and this may turn out to be important: although it may be impossible to resolve the individual contributions to the S^4 peak in the density of states by examining Fig. 3(b), we note that two of the three modes are B_2 polarized at the zone center (at 51.54 and 54.28 meV), while that at 53.02 meV is B_1 . Once again, we find that the highest energy surface phonon mode (peak S^5) has an essentially wave vector-independent displacement pattern; this time dominated by motion of the “up”-bonded Si atom in the dimer bond direction.

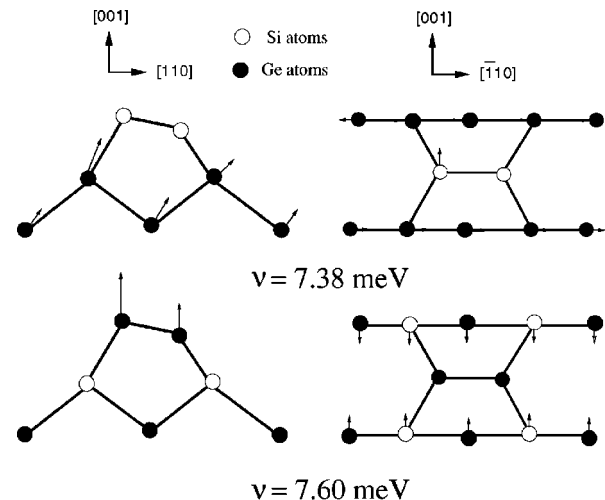


FIG. 6. Atomic displacement patterns of the Rayleigh wave phonon mode on Ge(001)/Si(2×1) and Ge(001)/Si/Ge(2×1) surfaces.

In contrast to the high-lying optical modes, the energies of surface acoustic modes on both surfaces are hardly changed at all from those of the clean Ge(001)(2×1), by virtue of the fact that they are dominated by vibrations of the Ge atoms. At \bar{J}' , for example, the Rayleigh wave (RW) frequencies are found at 7.60 and 7.38 meV for the segregated and non-segregated surfaces respectively. This phonon mode has been reported at 7.60 meV for the clean Ge(001)(2×1) surface.⁹

Despite this energetic similarity, however, the atomic displacement pattern of the RW phonon mode on the segregated surface is radically different from that on the non-segregated surface (Fig. 6). With Ge-termination, the displacement pat-

tern at \bar{J}' features large amplitude vibrations of the dimer atoms, as observed previously on the clean Ge(001)(2×1) surface⁹. On the other hand, the RW mode on the Si-terminated surface features very little dimer contribution at all. Similar differences in vibrational localization are evident at the \bar{K} and \bar{J} points.

In summary, in this paper we have investigated surface phonons on segregated and non-segregated Ge(001)/Si-(2×1) surfaces using the adiabatic bond-charge model. In both cases, we have shown that adsorption of Si leads to characteristic peaks in the phonon density of states. We suggest that evolution of these peaks may be a useful indicator for experimental characterization of the onset of segregation.

¹P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989).

²A. J. Hoeven, J. Aarts, and P. K. Larsen, J. Vac. Sci. Technol. A **7**, 5 (1989).

³D. S. Lin, T. Miller, and T. C. Chiang, Phys. Rev. B **45**, 11 415 (1992).

⁴D. D. Koleske and S. M. Gates, J. Appl. Phys. **76**, 1615 (1994); Appl. Phys. Lett. **64**, 884 (1994).

⁵R. Tsu, H. Z. Xiao, Y. W. Kim, H. K. Birnbaum, J. E. Greene, D. S. Lin, T. C. Chiang, and M. A. Hasan, J. Appl. Phys. **75**,

240 (1994).

⁶D. Aubel, L. Kubler, J. L. Bischoff, L. Simon, and D. Bolmont, Appl. Surf. Sci. **99**, 169 (1996); D. Aubel, L. Kubler, J. L. Bischoff, and D. Bolmont, Surf. Sci. **352**, 634 (1996).

⁷S. J. Jenkins and G. P. Srivastava, Phys. Rev. B **57**, 8794 (1998).

⁸W. Weber, Phys. Rev. Lett. **33**, 371 (1974); Phys. Rev. B **15**, 4789 (1977).

⁹H. M. Tütüncü, S. J. Jenkins, and G. P. Srivastava, Phys. Rev. B **57**, 4649 (1998).