

Comparative study of Sb bonding on group-IV semiconductor (001) substrates

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We present the results of *ab initio* pseudopotential density-functional calculations for the geometry and bonding of the Si(001)/Sb(2×1) and Ge(001)/Sb(2×1) surfaces. The Sb dimers are found to be symmetric, with bond lengths of 2.96 and 2.92 Å on the Si and Ge substrates, respectively. We thus concur with recent theoretical work, which concluded that the asymmetric Sb dimer model for the Ge substrate, favored by surface x-ray-diffraction studies, is incorrect. Furthermore, we calculate that the monolayer-averaged chemisorption energy of Sb on the Si substrate is 0.48 eV per dimer greater in magnitude than on the Ge substrate, and discuss the implications for surfactant-mediated growth. [S0163-1829(97)06240-1]

The realization of epitaxial growth of Ge on Si substrates, and of Si on Ge substrates, is currently a technological issue of considerable importance. Much recent work has focused on the ability of group-V elements, such as As, Sb, and Bi, to act as surfactants for such growth, changing the growth mode from Volmer-Weber (Si on Ge) or Stranski-Krastanov (Ge on Si) islanding to Frank-van der Merwe (i.e., epitaxial) growth.^{1,2}

In view of this, there have been a variety of theoretical and experimental studies of Sb adsorbed on the Si(001) surface³⁻⁷ and on the Ge(001) surface.⁷⁻¹¹ While Sb on the Si(001) substrate is well understood, the precise geometry of Sb adsorbed on the Ge(001) substrate remains a matter for debate.

At monolayer coverage, it is well known that Sb atoms adsorbed on group-IV semiconductor (001) substrates dimerize, in order to saturate one dangling bond per adatom. In the case of Ge(001), continuing discussion centers around the question of whether these dimers are symmetric or asymmetric. Surface x-ray-diffraction (SXD) experiments¹⁰ support an asymmetric dimer model, in sharp contrast to the symmetric Sb dimers formed on the Si(001) substrate. Photoemission studies by Hakansson *et al.*,⁹ however, support a symmetric dimer model, as do recent theoretical results from Takeuchi.⁷

Additionally, a detailed comparison between the bonding energetics of Sb on the two substrates is currently lacking from the literature. The aim of the present paper is to clarify the geometry of Sb adsorbed on the Ge(001) substrate, and to provide a detailed energetic comparison between the Si(001)/Sb and Ge(001)/Sb systems.

Theoretical optimization of atomic geometry was achieved iteratively within a conjugate gradient scheme,¹² with total energies and forces at each iteration provided by an *ab initio* pseudopotential local-density-functional theory calculation. The pseudopotentials used for the electron-ion interaction were those of Bachelet, Hamann, and Schlüter,¹³ and the Ceperley-Alder¹⁴ form of correlation was employed for the electron-electron exchange-correlation potential.

The calculations were performed within a supercell consisting of eight atomic layers of either Si or Ge in the (001) direction, passivated on one side with hydrogen in a dihydride arrangement. On the other side, the slab was capped by

a layer of Sb and the equivalent of four atomic layers of vacuum. The supercell dimensions were consistent with our calculated Si and Ge bulk lattice constants of 5.42 and 5.53 Å, respectively.

Electronic wave functions were expanded in terms of a basis set of plane waves, up to a kinetic-energy cutoff of 8 Ry, and Brillouin-zone summation was performed using four special **k** points in the irreducible segment of the zone. Experience with similar systems¹⁵ shows that these parameters are sufficient to calculate well-converged atomic geometries.

After bonding with a group-IV (001) substrate, each Sb adatom has three remaining electrons. In the 1×1 geometry, these electrons form a lone pair and a dangling bond on each adatom. Reconstruction to a 2×1 geometry, by formation of Sb dimers, saturates the dangling bonds and allows the lone pairs to form fully occupied π_u and π_g orbitals,⁶ leading to an overall energy benefit to the system of 0.47 eV per dimer on the Si(001) substrate and 0.70 eV on the Ge(001) substrate. Characteristic structural parameters for the 2×1 reconstructed geometries are summarized in Fig. 1 and Table I.

We find the Sb dimers to be symmetric on both substrates. Thus we concur with Takeuchi⁷ that the SXD observation of asymmetric Sb dimers on Ge(001) (Ref. 10) appears to be incorrect. Our calculated Sb dimer bond lengths of 2.96 Å on Si(001) and 2.92 Å on Ge(001) are in good agreement with

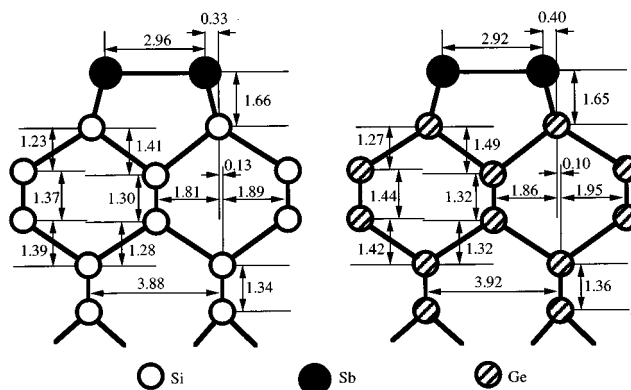


FIG. 1. Schematic side views of the Si(001)/Sb(2×1) and Ge(001)/Sb(2×1) surfaces. All dimensions are in Å.

TABLE I. Structural parameters of the Si(001)/Sb(2×1) and Ge(001)/Sb(2×1) surfaces.

Si(001)/Sb(2×1)	Sb-Sb (Å)	Sb-Si (Å)
SEXAFS—Ref. 3	2.88	2.63
Theory—Ref. 4	2.93	2.61
Theory—Ref. 5	2.94	2.59
Theory—Ref. 6	2.87	2.53
Theory—Ref. 7	2.95	2.62
This work	2.96	2.56
Ge(001)/Sb(2×1)	Sb-Sb (Å)	Sb-Ge (Å)
SXD—Ref. 10	2.90	2.47,2.49
XSW—Ref. 11	3.06	
Theory—Ref. 7	2.95	2.62
This work	2.92	2.59

previous theoretical results, as are our calculated Sb-Si and Sb-Ge backbond lengths of 2.56 and 2.59 Å, respectively. Comparison with experimental bond lengths is also favorable in the case of the Si substrate. For the Ge substrate, however, there is some disagreement between theory and experiment, as we predict a longer Ge-Sb backbond than the 2.47–2.49 Å found in SXD,¹⁰ but favor the SXD dimer bond length of 2.90 Å over the x-ray standing wave (XSW) figure of 3.06 Å.¹¹ Further experimental work to clarify this point would be invaluable.

In view of the role of Sb as a surfactant both for Ge growth on Si and for Si growth on Ge, it is important to compare the energetics of the Sb monolayer on the two different substrates. A suitable starting point is the chemisorption energy per dimer, which we shall define as the energy change when two isolated atoms of species *A* form a dimer at surface *X*. Since this energy depends on the local environment at which chemisorption takes place, it is a function of coverage, θ .

For a system of P primitive surface unit cells with a total of $N = \alpha P \theta$ adsorbate atoms (i.e., α per cell per monolayer), the chemisorption energy per dimer may be written as

$$\Delta_{\text{Chem}}^{X/A_2}(\theta) = \alpha P \int_{\theta(N)}^{\theta(N+2)} \mu_A^{X/A}(\theta) d\theta - 2E_{\text{isolated}}^A, \quad (1)$$

where $\mu_A^{X/A}(\theta)$ is the chemical potential for species *A* on surface *X/A* at coverage θ , and E_{isolated}^A is the energy of an isolated atom of species *A*.

In the limit as P tends to infinity, we can consider $\mu_A^{X/A}(\theta)$ to be constant over the range of integration, and putting α equal to 2 for our 2×1 geometry, we get

$$\Delta_{\text{Chem}}^{X/A_2}(\theta) = 2\mu_A^{X/A}(\theta) - 2E_{\text{isolated}}^A. \quad (2)$$

So the *difference* between the Sb chemisorption energies on our two substrates is simply related to the difference in the chemical potentials,

$$\Delta_{\text{Chem}}^{\text{Si/Sb}_2}(\theta) - \Delta_{\text{Chem}}^{\text{Ge/Sb}_2}(\theta) = 2[\mu_{\text{Sb}}^{\text{Si/Sb}}(\theta) - \mu_{\text{Sb}}^{\text{Ge/Sb}}(\theta)]. \quad (3)$$

Although we cannot determine the chemical potential at a particular coverage, we *can* calculate an average chemical

potential during growth of the first layer, which we shall call the monolayer-averaged chemical potential

$$\bar{\mu}_{\text{Sb}}^{X/\text{Sb}} = [E_{X/\text{Sb}}(1) - E_X]/n_{\text{Sb}}(1), \quad (4)$$

where $n_{\text{Sb}}(1)$ is the number of Sb atoms per supercell at 1-ML coverage, and $E_{X/\text{Sb}}(1)$ and E_X are the supercell energies of the *X*(001)/Sb(1 ML) and *X*(001) systems, respectively.

Taking the energies of the covered surfaces from the present work, and those of the clean Si(001) and Ge(001) surfaces that we have studied previously,¹⁵ we calculate

$$\bar{\mu}_{\text{Sb}}^{\text{Si/Sb}} = -152.17 \text{ eV}, \quad \bar{\mu}_{\text{Sb}}^{\text{Ge/Sb}} = -151.93 \text{ eV}, \quad (5)$$

both of which are lower than our calculated chemical potential for bulk Sb [−151.02 eV (Ref. 16)], confirming that an epitaxial monolayer of Sb is energetically preferable to the formation of three-dimensional Sb islands on both substrates.

Consequently, from Eq. (3), we find that the monolayer-averaged chemisorption energy of Sb on Si is 0.48 eV per dimer greater in magnitude than on the Ge surface. Since this is a binding energy, this means that Sb is more strongly bound to the Si surface than to the Ge surface. This indicates that the Sb adsorbate stabilizes Si-terminated surfaces to a greater extent than it does Ge-terminated surfaces.

This difference in the monolayer-averaged chemisorption energies is largely attributable to the difference in the energies of formation of Sb-Si and Sb-Ge backbonds, since the Sb-Sb dimer bond itself is almost identical on the two substrates. Thus we may estimate that each of the four Sb-Si backbonds on the Si substrate is approximately 0.1 eV stronger than each of the four Sb-Ge backbonds on the Ge substrate.

In the absence of Sb, the different strengths of the bonds between group-IV atoms (Si-Si strongest, Si-Ge intermediate, and Ge-Ge weakest) means that Ge termination is favored whenever both species occur near the surface, whatever the substrate. Thus, Ge adlayers on Si(001) diffuse only moderately into the substrate,¹⁵ while a monolayer of Si grown on Ge(001) may diffuse almost entirely into the first subsurface layer, depending upon growth conditions.^{17,18}

On the monolayer Si-covered Ge(001) substrate, the stable Ge-terminated Ge(001)/Si/Ge surface is only 0.38 eV per dimer lower in energy than the metastable Si-terminated Ge(001)/Si surface¹⁹ (calculated with stoichiometrically equivalent supercells). Thus the extra stability of 0.48 eV per dimer conferred by Sb on the Si-terminated surface as compared to the Ge-terminated surface is likely to be sufficient to suppress interdiffusion of Si into the substrate. This question will be addressed in some detail in a future publication.

On the Si substrate, however, the difference between the stable Si(001)/Ge and metastable Si(001)/Ge/Si surfaces amounts to 0.51 eV per dimer¹⁹ (again calculated with stoichiometrically equivalent supercells). Thus the 0.48 eV per dimer additional stability contributed by Sb to the Si-terminated surface is insufficient to reverse the natural ordering.

In summary, our calculations show the Sb dimers on both Si(001) and Ge(001) substrates to be symmetric. Our calculated geometry for the Si substrate is in close accord with previous experimental³ and theoretical^{4–7} work. For the Ge

substrate, our results are again in accord with previous theoretical work,⁷ but contrast sharply with aspects of SXD (Ref. 10) and XSW (Ref. 11) studies, suggesting that existing experimental investigations do not tell the whole story.

The greater binding energy for Sb on the Si(001) substrate, as opposed to the Ge(001) substrate, suggests that the adlayer will suppress interdiffusion of Si into the Ge(001)

substrate. It is, however, promising to note that the effect is not sufficient to reverse the natural ordering of Ge on the Si(001) substrate.

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