Structure of Ge(113): Origin and Stability of Surface Self-Interstitials

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Using atomic-resolution scanning tunneling microscopy and first-principles calculations we show that Ge and Si(113) are structurally similar, contrary to previous reports. Both surfaces have (3×2) and (3×1) reconstructions stabilized by surface self-interstitials, with the (3×2) lower in energy on Si but degenerate with the (3×1) on Ge. Statistical analysis of fluctuations observed between the two structures on Ge, combined with calculations for bulk interstitials, indicate that the surface (not the bulk) is the likely source and sink of the surface self-interstitials for both materials. [S0031-9007(98)07858-2]

High-index surfaces are of increasing interest as substrates for electronic device applications. Their inherent structural anisotropy reduces antiphase domain formation, threading dislocation pileup, and surface roughness during heteroepitaxy, leading to improved epitaxial layers and novel electronic properties [1–3]. Of the few high-index Si and Ge surfaces with stable planar reconstructions [4], the (113) orientation, about midway between (001) and (111), is particularly interesting. Si(113) has a (3×2) surface reconstruction at room temperature, and undergoes a phase transition to (3×1) around 800 K [5]. There is evidence that both phases are stabilized by highly unusual *sixfold* coordinated surface self-interstitials [6,7] that are structurally similar to the [110]-split interstitial bulk defects ("{311} defects") important in transient enhanced diffusion [8]. Both (3×2) and (3×1) periodicities have also been reported for Ge(113), (3×2) in diffraction below $\sim$120 K, and (3×1) for all higher temperatures [9–11], but the atomic-scale structures on Ge are in dispute [11,12].

Three structural motifs appear to stabilize the Si(113) surface [6]. As illustrated in Fig. 1, the bulk-truncated surface consists of alternating rows of twofold-coordinated (001)-like atoms and threefold (111)-like atoms. The first model proposed for the Si(113)-(3×1) reconstruction was the adatom-dimer (AD) structure [10]. In this model every third (001)-like atom is removed and the adjacent (111)-like atoms rebond. The remaining twofold atoms dimerize, and the resulting dimer-plus-two-nonrebonded-atom structures are denoted tetramers. For the (3×2) reconstruction, Dabrowski *et al.* introduced a novel third structure to the Si(113) surface, the sixfold coordinated surface self-interstitial, justified in part by the stability of the similar bulk interstitial defect [6]. The (3×2) adatom-dimer-interstitial (ADI) model, incorporating an interstitial Si within every other tetramer, has a low theoretical surface energy and produces simulated scanning tunneling microscopy (STM) images that closely resemble the experimental ones. If an interstitial is placed in every tetramer to make

a (3×1) reconstruction, denoted the adatom-interstitial (AI) model, the energy is slightly higher. Although it has been suggested the (3×1) phase has the AI structure, and that the transition from (3×2) to (3×1) occurs via migration of the additional surface interstitials from the bulk [5,7], to our knowledge the (3×1)-AI structure has not been confirmed experimentally.

Ge(113) should provide further insight into the stability of the unusual surface interstitial, but its structure remains controversial. A recent x-ray diffraction study concluded that Ge(113)-(3×1) has a structure similar to Si(113)-(3×2)-ADI, but with the interstitials randomly distributed on the surface (accounting for the missing half-order diffraction) [11]. In contrast, an STM study of Ge(113) concluded the room-temperature structure is fundamentally different from that of Si [12]. In this Letter we describe the structure of Ge(113) as determined by a combination of atomic-resolution STM and first-principles calculations. We show that Ge and Si(113) are
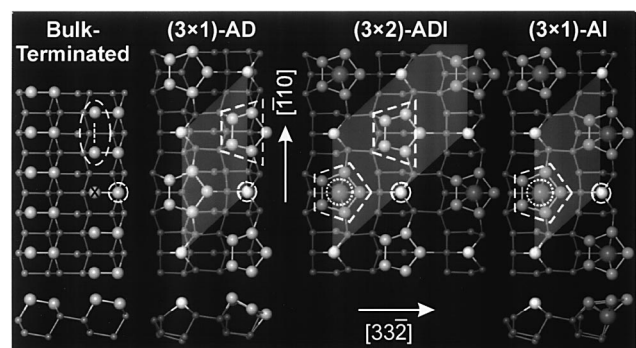

FIG. 1. Top and side views of model bulk-terminated and reconstructed Si or Ge (113) surfaces (based on first-principles equilibrium coordinates). The (3×1) adatom-dimer (AD) unit cell has two structural elements, a rebonded adatom (dashed circle) and a tetramer (dimer-plus-adjacent threefold atoms, dashed polygon). The (3×2) adatom-dimer-interstitial (ADI) model adds a third structure in every other tetramer, the surface self-interstitial (dotted circle). The (3×1) adatom-interstitial (AI) unit cell has only an adatom and a tetramer+interstitial. Primitive unit cells are shadowed.

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structurally similar, with the exception that at room temperature Ge is composed of an equilibrium mixture of degenerate (3×2)-ADI and (3×1)-AI domains. Moreover, our results suggest that the surface interstitials originate on the surface (not in the bulk), and that transitions between (3×2)-ADI and (3×1)-AI on both Si and Ge occur via adatom migration.

The experiments were performed in ultrahigh vacuum using commercial Ge wafers oriented to within 0.3° of (113). After an initial degassing, the samples were cleaned by multiple cycles of ion bombardment and annealing (850 °C). All STM images were acquired at room temperature with a constant current (0.1–1 nA) and bias voltages of 1–3 V. To determine the equilibrium surface geometry and surface energy of various structural models, we performed first-principles calculations within the local-density approximation (LDA) to density-functional theory. The calculations used a slab geometry consisting of five double layers of Si or Ge, with the bottom surface passivated by H atoms. The upper three double layers were completely relaxed until the surface energy was converged to within 1 meV/Å^2. Total energies and forces were calculated using Troullier-Martins pseudopotentials in a plane-wave basis with kinetic-energy cutoffs of 8 and 15 Ry for Si and Ge, respectively, as implemented in the FHI96MD code [13]. Simulated STM images were then created from calculated surfaces of constant energy-integrated local density of states.

Experimental STM images of the Ge(113) surface reveal distinct (3×1) and (3×2) domains, as shown in Fig. 2(a). Consistent with the previous STM study [12], we find the (3×1) domains cover $55 \pm 5\%$ of the surface. In contrast to the previous results, however, our atomic-resolution images of the (3×2) areas [Fig. 2(b)] strongly resemble experimental and theoretical images of Si(113)-(3×2) [6]. The three structural elements within the (3×2)-ADI reconstruction, adatoms, tetramers, and interstitial-filled tetramers, all give rise to characteristic features in the filled-state topography. The adatoms are observed as a simple (3×1) array of spherical bumps, and the two-lobed tetramers are the highest features. On Si the addition of an interstitial to a tetramer alters both its physical and electronic structure, flattening the four surface atoms and shifting electron density inward towards the interstitial [6]. In images of Ge(113)-(3×2) these interstitial-filled tetramers appear as diffuse pentagons. Empty state images of Ge(113)-(3×2) domains (not shown) also strongly resemble Si(113)-(3×2)-ADI.

The high resolution of our Ge(113)-(3×2) images makes the interpretation of the coexisting (3×1) domains straightforward—*they have the AI structure.* As seen in Fig. 2(c), only two types of features are observed in the filled-state images of the (3×1) regions. One is the spherical protrusion characteristic of an adatom, appearing in a (3×1) array spanning the surface.
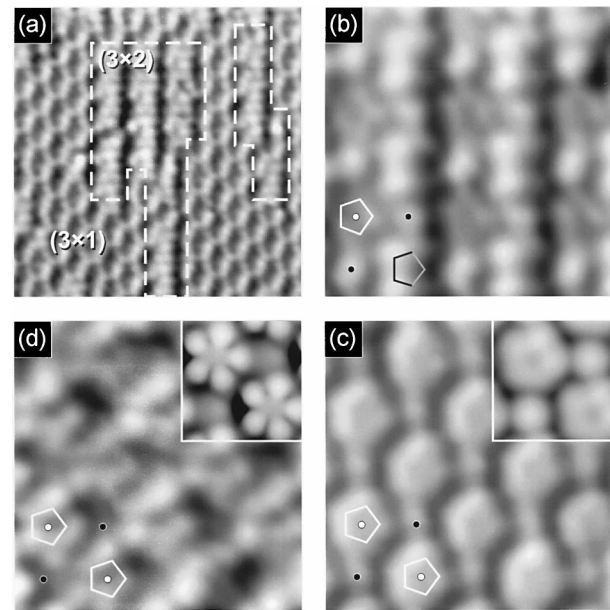

FIG. 2. STM images of clean Ge(113). (a) 100 Å × 100 Å filled-state image showing the distinct (3×1) and (3×2) domains (1.5 V). (b) 30 Å × 30 Å filled-state image of a (3×2) area (2 V). Atomic-scale features characteristic of the ADI structure are indicated: rebonded atom (black dot), tetramer (black/gray lines), tetramer+interstitial (white pentagon+dot). (c) Filled-state image of a (3×1) area at the same magnification and bias voltage. Inset is a theoretically simulated image of a relaxed (3×1)-AI structure. (d) Empty-state image of a (3×1) area with the corresponding simulated image inset (1.5 V).

face. The other is the pentagonal ring associated with a tetramer+interstitial, which is relatively prominent when not between interstitial-free tetramers. The pentagonal structure is somewhat more distinct in the empty states [Fig. 2(d)], just as observed with the tetramer+interstitial on Si(113). Note that the tetramer+interstitial structures appear asymmetric (with the upper halves in this image higher), indicating they are buckled. The degree of the asymmetry is dependent on the tunneling conditions (and somewhat tip dependent as well), and is also observed in a variety of different buckling configurations across the surface. In some images the high side of the buckled pentagonal rings and the adatoms are very prominent, resembling diagonal chains on the surface as in Fig. 2(a) (where the bottom halves of the pentagons are higher). Overall, the experimental results lead us to propose that Ge(113) is composed of a mixture of energetically equivalent (3×2)-ADI and (3×1)-AI domains. Moreover, the occurrence of the AI reconstruction on Ge provides the strongest evidence to date that Si(113)-(3×1) indeed has the AI structure.

In order to confirm our structural assignments and provide insight into the origin of the surface self-interstitials, we have performed LDA calculations for a variety of fully relaxed Si and Ge structures, with and without interstitials.

As tabulated in Table I, we have computed the surface energy for (3×2)-ADI, (3×1)-AD, and (3×1)-AI reconstructions of Ge(113), along with the different structures proposed by Gai *et al.* For purposes of comparison we have also performed calculations for Si(113). Our surface energies for Si(113) closely agree with the previous results of Dabrowski *et al.* [6], showing that the (3×2)-ADI structure (interstitial in every other tetramer) is 4% lower in energy than (3×1)-AD (no interstitials), and slightly lower in energy than the (3×1)-AI (interstitial in every tetramer). Adding surface self-interstitials has an even more dramatic effect on Ge(113), lowering the surface energy by 12%. In accord with experimental observations, in the Ge calculations the (3×1)-AI and (3×2)-ADI structures are energetically degenerate. We find the relaxed Ge structures also reproduce the observed buckling, and provide simulated STM images that accurately reproduce the experimental ones [Figs. 2(c) and 2(d)]. It has been proposed that on Si(113) the (3×1)-AI structure is higher in energy than the (3×2)-ADI because the prior requires electrons to occupy conduction states [6]. This idea could account for the degeneracy of the two models on Ge, where the smaller band gap should reduce the energy penalty for conduction band occupation.

It has been suggested that the self-interstitials lower the (113) surface energy by relieving surface stress along the $[3\,3\,\bar{2}]$ direction [6]. In order to test this theory, we have calculated this component of the LDA surface stress tensor for the AD, ADI, and AI structures (Table I). (Because of computational expense we have calculated the stresses for Si only, but expect qualitatively similar results for Ge.) The calculations show that the interstitials do *not* lower the surface stress; adding an interstitial to every tetramer (the AI structure) actually *increases* the stress significantly. Hence, the relative stability of the interstitials must arise from some other effect, probably electronic in nature.

Although our results have not revealed the mechanism responsible for the stability of the interstitials, they do provide new insight into the origin of the interstitials, with implications for the nature of the (3×2)-to-(3×1)

transitions in Si and Ge (113). As recently reported [14], over the course of minutes individual units cells on Ge(113) can be seen to switch between (3×1) and (3×2) with the apparent addition or removal of a single surface interstitial. This phenomenon is illustrated in Fig. 3, where two consecutive images of the same area are shown with each tetramer and tetramer+interstitial denoted. When an interstitial occupies a tetramer, it takes on the characteristic pentagonal shape; similarly, when one leaves a tetramer, the dimer end becomes more prominent in the image. When this transition happens midscan a "glitch" is observed, with the dimer bright on one side of the glitch and dark on the other.

We have systematically analyzed the state of each tetramer (with vs without an interstitial) in an area encompassing 360 tetramers over the course of 60 min, observing 351 tetramers change state [15]. On average an equal number of interstitials leave and enter the tetramers, as required by the equilibrium distribution, at a rate for either case of 1.4×10^{-4} s^{-1} per tetramer. Surprisingly, the pair distribution function for interstitial migrations reveals they are spatially anticorrelated; i.e., when an interstitial disappears from one tetramer, there is a relatively high probability that an interstitial appears in another one nearby (within ~ 30 Å, or about four unit cells). If the transitions were occurring randomly via interstitial migration into or out of the bulk as previously proposed [7,14], one would expect the anticorrelation probability to be the overall transition probability, which is what we find for in-in and out-out correlations (and for in-out correlations at large distances). For the enhanced in-out correlation to transpire by bulk diffusion, a complex reaction pathway must be invoked involving lateral bulk diffusion followed by rapid migration back to the surface. A much simpler interpretation is that the room-temperature transitions observed on Ge(113) take place *via short hops by interstitial atoms across the surface.*

TABLE I. Calculated surface energies (meV/Å^2) for different reconstructions of Si and Ge (113). The $[3\,3\,\bar{2}]$ component of the surface stress tensor for each Si reconstruction is also listed (eV/Å^2), calculated as described in Ref. [18].

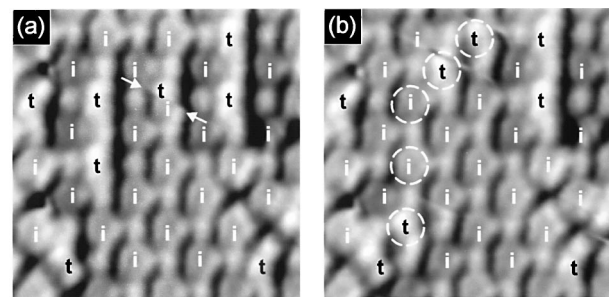| Structure (See Fig. 1)	Ge(113) Energy	Si(113) Energy	Si(113) Stress
Bulk terminated	111	143	
(3×1)-AD	73	97	0.29
(3×2)-ADI	64	93	0.29
(3×1)-AI	64	95	0.33
(3×1)-Gai (Ref. [12])	86		
(3×2)-Gai	85		

FIG. 3. Images of a 60 Å $\times$ 60 Å area recorded 600 s apart illustrating the occasional migration of surface interstitials (from two larger images; filled states, 2 V). The state of every tetramer is indicated—those with an interstitial are labeled "i," those without, "t." The "glitch" between the arrows in (a) occurred when the t above the glitch gained an interstitial between two scan lines, appearing as an i below the glitch. Tetramers that changed state from (a) to (b) are circled.

To further elucidate which of these two mechanisms dominates interstitial transport, we have calculated the fully relaxed energy of a Si(113)-(3 × 1)-terminated slab containing a [110]-split interstitial as a function of its depth below the surface. When the interstitial is moved from the AI surface layer to the first subsurface layer, the energy jumps from 95 to 116 meV/Å^2. Moving the interstitial to yet deeper layers does not lead to any further increase. Thus, there is a large barrier for migration of interstitials from the surface into the bulk, and only an extremely short-ranged gradient to drive migration from the bulk to the surface layer. These theoretical results indicate that migration of surface interstitials into the bulk is unlikely, and that there is no driving force for those beneath the surface to re-emerge, supporting the interpretation of our experimental results in terms of surface migration of interstitials on Ge(113).

What then is the nature of the (3 × 2)-ADI to (3 × 1)-AI transitions in Si and Ge(113)? Because our evidence indicates that bulk diffusion of interstitials is not as facile as previously suggested, surface diffusion must play an important role. For the case of Si, where the transition occurs at relatively high temperature (~800 K), it is possible that the bulk is also a source for some of the interstitials. We propose, however, that step edges and other surface defects are the main source and sink for the extra interstitial atoms during that phase transition. For Ge, we propose the surface self-interstitials observed at room temperature come from a similar source, and are trapped on the surface in an equilibrium mixture of the two structures while the sample cools. The very low surface diffusion barrier for Ge adatoms [16] then allows the interstitials to occasionally "hop" across the room-temperature surface.

The report that Ge undergoes a transition to (3 × 2) at ~120 K is puzzling [10,11]. Given that little bulk or surface diffusion is expected at such a low temperature, we suspect that this transition is fundamentally different from the high-temperature AI to ADI transition. Upon close inspection of the relaxed coordinates calculated for Ge(113)-(3 × 1)-AI, we find a number of energetically similar buckling configurations for the surface atoms (consistent with the variations seen in our images). Rather than a phase transition based on interstitial migration, we predict that the low temperature (3 × 1) to (3 × 2) transition on Ge occurs via correlated buckling of the tetramer+interstitials in the AI structure. This effect would be similar to the well-known dimer buckling that occurs at low temperature on Si(001) and near room temperature on Ge (001) [17], and the correlated tetramer buckling observed on Si(114)-c(2 × 2) [18]. Note that a similar "puckered" (3 × 2) structure, but without interstitials, has been shown to be theoretically stable for Si(113) [19]. Additional calculations and STM measurements are planned to test this prediction.

In conclusion, we have determined the structure of Ge(113) using STM and first-principles LDA calculations, finding that a surface self-interstitial stabilizes degenerate (3 × 2)-ADI and (3 × 1)-AI reconstructions. Our results provide strong evidence that the high-temperature Si(113)-(3 × 1) reconstruction also has the AI structure. Observations of room-temperature transitions between the two structures on Ge, combined with calculations for bulk interstitial structures, indicate that the surface rather than the bulk is the source of the surface interstitials during (3 × 2)-ADI to (3 × 1)-AI transitions on both Ge and Si. This report provides a further indication that the surface self-interstitial may be a common defect on semiconductor surfaces.

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