Size-mismatch disorder at the surface of semiconductors

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We study the effects of size-mismatch disorder on the surface relaxation of semiconductor solid solutions. Assuming a Kirkwood-type potential, we obtain an analytic solution for the nearest-neighbor distances and their distributions as a function of the distance from the surface as well as the displacements at the (111) and (100) surfaces. This solution is also valid for bond-mismatch disorder and is checked against computer simulations for two-dimensional triangular networks along (10) and (11) surfaces. Predictions are made for the topography of the (111) surface of a SiGe alloy.

I. INTRODUCTION

The development of experimental tools to directly observe surface atoms with an accuracy of about 0.01 Å vertically has opened a new field of observation, which is very important in order to understand rapidly the technological innovations in the field of semiconductors. The surface effects, for example, become noticeable when trying to construct thinner and thinner samples. Surface studies can also provide indirect, some information on the nature of the bulk disorder, which could complement results obtained from other experimental methods like extended x-ray-absorption fine structure (EXAFS). Moreover, steady technical development in the field of scanning force microscopy (SFM) should soon permit a precision similar to that of the scanning tunneling microscope, thus allowing the direct study of the surfaces of alloys.

We propose here to extend the theory for length-mismatch disorder in the bulk, presented previously, to cover the surface problem. We will first study the surface relaxation of two-dimensional (2D) triangular lattices as a test case and then concentrate on 3D binary semiconductor alloys. In the bulk, the theory correctly predicts the local structure of ternary semiconductors, including first- and second-nearest-neighbor partial distances, the width of the nearest-neighbor distributions and the strain energy. All these results were expressed in terms of a single dimensionless parameter, the topological rigidity parameter \( a^{**} \). Regarding bulk Si-Ge alloys, there is some disagreement between theory and experiment; however, these discrepancies have already been criticized theoretically and the experiments are now in satisfactory agreement with theory.

After presenting the solution to the surface problem with bond- or site-mismatch disorder, we discuss different methods to obtain the topological rigidity parameters of lattices. We then present in Sec. IV the results for triangular lattices, and in Sec. V, those for Si\(_{1-x}\)Ge\(_x\) crystalline alloy with (100) and (111) surfaces.

II. THEORY

The formalism developed by Thorpe and collaborators was applied to crystalline and amorphous bulk alloys.
with $l$ a layer index and $x_i$ the concentration of $B$ species, which might also vary from layer to layer.

On any layer, using Eqs. (1) and (6), Végard’s law is therefore obeyed, i.e.,

$$\langle \hat{L} \rangle = (1-x)L_{AA}^0 + xL_{BB}^0 .$$  \hspace{1cm} (7)

We can now address the question of partial length average. Assuming small displacements in the solid, we have

$$L_{ij} = x_i - x_j = L_i + [(u_i - u_j) \cdot \hat{R}_{ij}] \hat{R}_{ij} ,$$  \hspace{1cm} (8)

where $X_i$ is the position of site $i$ on the lattice, $L_i = \langle \hat{L} \rangle_i \hat{R}_{ij}$, $\hat{R}_{ij}$ is the unit vector of a perfect reference lattice, and $u_j$ is the displacement from this reference lattice. Using this definition in the force equation [Eq. (3)]

$$0 = \sum_i [L_i + [(u_i - u_j) \cdot \hat{R}_{ij} - L_{ij}^0] \hat{R}_{ij}] ,$$  \hspace{1cm} (9)

one can write

$$Du = \nu ,$$  \hspace{1cm} (10)

where $D$ is the dynamical matrix of the system or the inverse Green function $G$ defined by

$$u = -G\nu$$  \hspace{1cm} (11)

and

$$\nu = -K \sum_i \langle \hat{L} \rangle_i - L_{ij}^0 \hat{R}_{ij} ,$$  \hspace{1cm} (12)

so that

$$L_{ij} = \langle \hat{L} \rangle_i + K \sum_{km} \hat{R}_{ij} \cdot (G_{im} - G_{jm}) \cdot \hat{R}_{km} (L_{km} - \langle \hat{L} \rangle_i) .$$  \hspace{1cm} (13)

Although for clarity, the layer index $l$ is not attached to $i$ and $j$, these indices are restricted to this layer. In a homogeneous bulk solid, we can drop the layer index.

A. Bond mismatch

The previous arguments are identical for both bond- and site-mismatch disorder; the nature of the disorder appears only when averaging over Eq. (13). For a homogeneous bond-mismatch disorder problem, the surface solution of this averaging is formally identical to the bulk solution.

$$\langle L_{AA} \rangle_l = \langle L \rangle_l - x a_l^* (L_{AA}^0 - L_{BB}^0) ,$$  \hspace{1cm} (14)

$$\langle L_{BB} \rangle_l = \langle L \rangle_l + (1-x) a_l^* (L_{AA}^0 - L_{BB}^0) ,$$

except that the topological rigidity parameter $a_l^*$ now varies layer by layer via

$$a_l^* = \frac{K}{N} \sum_{ij} \hat{R}_{ij} \cdot (G_{ij} - 2G_{ij} + G_{jj}) \hat{R}_{ij} ,$$  \hspace{1cm} (15)

where $N$ is a normalization constant corresponding to the number of bonds summed over. As mentioned previously, the summation over $i$ and $j$ is restricted to the layer $l$.

With the loss of symmetry across the surface, the Green’s function cannot be obtained through the reciprocal space. In real space, the equations are not translationally invariant perpendicular to the surface, and direct calculation can become very cumbersome. We, therefore, decided to use computer simulations to obtain $a_l^*$ from Eq. (14). This may seem like a round-about route, but it works best computationally. In the process of doing this, we verified the linear dependence upon the concentration $x$ in Eq. (14).

Following the method described in Ref. 4, we can also obtain that the strain energy per bond $E_l$ is layer dependent,

$$E_l = \frac{K}{2} x (1-x)(1-a_l^*) (L_{AA}^0 - L_{BB}^0)^2 .$$  \hspace{1cm} (16)

Regarding the bond-length fluctuations, it is not possible to obtain a simple expression that can be reduced to a function of the topological rigidity parameter like in the bulk case; however, we can again show that the partial distributions are identical. This unique distribution for $A$ and $B$ length fluctuations is due to the fact that locally a bond does not know the global concentration of the layer. Appendix A sketches the derivation, which can be found in greater detail for the bulk case in Ref. 5.

B. Site mismatch

For the homogeneous site-mismatch disorder problem, the formalism is similar to the bond problem if the condition in Eq. (1) is used. After averaging over the different partial lengths, one obtains

$$\langle L_{AA} \rangle_l = \langle L \rangle_l + x a_l^* (L_{AA}^0 - L_{BB}^0) ,$$

$$\langle L_{BB} \rangle_l = \langle L \rangle_l + (1-x) a_l^* (L_{AA}^0 - L_{BB}^0) ,$$

$$\langle L_{AB} \rangle_l = \frac{1}{2} \langle L_{AA} \rangle_l + \langle L_{BB} \rangle_l ,$$  \hspace{1cm} (17)

where

$$a_i^* = \frac{K}{2N} \sum_{ijkm} \hat{R}_{ij} \cdot (G_{im} - G_{jm}) \cdot \hat{R}_{km} (\delta_{ik} + \delta_{im} + \delta_{jk}$$

$$+ \delta_{jm}) ,$$  \hspace{1cm} (18)

and where, again, $i$ and $j$ are site indices restricted to layer $l$, while $k$ and $m$ are sites on any layer. In the bulk, this equation becomes identical to the one described in Ref. 5, and independent of layer $l$.

Another quantity becomes interesting at the surface: the average site displacement $u_i$ from a reference position. In the bulk, for symmetry reasons, this quantity vanishes everywhere. At the surface, however, the symmetry is broken along $z$, so we expect the mean site displacements of the $A$ and $B$ species to be different than zero. Averaging $u_i$ over the sites $A$ of a particular layer, from Eq. (11),

$$u_i^* = -K \sum_{jk\beta} G_{ij}^\beta \hat{R}_{jk} (L_{jk}^0 - \langle L \rangle_l) ,$$  \hspace{1cm} (19)

we obtain
\[ u_{i}^{A} = \frac{K}{2N} (L_{AB}^0 - L_{AA}^0) \sum_{ij} (G_{ji}^{AA} - G_{ij}^{AA}) \tilde{R}_{ij}^2, \]  
\[ u_{i}^{B} = -\frac{K}{2N} (L_{AB}^0 - L_{AA}^0) \sum_{ij} (G_{ji}^{AA} - G_{ij}^{AA}) \tilde{R}_{ij}^2. \]

Because of symmetry,
\[ u_{i}^{A} = -u_{i}^{B} = \frac{1}{2} (u_{i}^{A} + u_{i}^{B}) = 0. \]

One can easily verify that the average over all the species indeed vanishes as it must, because of the definition of the reference lattice [i.e., \( (1-x)u_{i}^{A} + xu_{i}^{B} = 0 \)].

In a surface experiment, the experimentally measured quantity would be the height difference between the two species at the surface,
\[ u_{i}^{A} - u_{i}^{B} = -\frac{K}{2N} (L_{AB}^0 - L_{AA}^0) \sum_{ij} (G_{ji}^{AA} - G_{ij}^{AA}) \tilde{R}_{ij}^2, \]

where, once again, \( i \) and \( j \) are summed only within the layer defined by \( I \). This height difference (23) turns out to be concentration independent and varies only with the layer and the size mismatch. If one also adds the difference in radius, defining the maximum height at the surface roughly as might be seen using a scanning force microscope, for example, the total distance between the two peaks in an alloy is
\[ \Delta u_s^2 = \frac{1}{2} \left[ 1 - \frac{K}{N} \sum_{ij} (G_{ji}^{AA} - G_{ij}^{AA}) \tilde{R}_{ij}^2 \right] (L_{AA}^0 - L_{BB}^0). \]

Finally, as in the bond-mismatch problem, we can get the strain energy per bond,
\[ E_I = \frac{K}{4} x(1-x)(1-a_I^*) (L_{AA}^0 - L_{BB}^0)^2, \]

and can again show that the partial bond-length distributions are all identical (see Appendix A).

For semiconductor alloys, one needs to use an interaction potential with both two- and three-body forces. We have chosen the Kirkwood potential,
\[ V = \frac{\alpha}{2} \sum_{ij} (L_{ij}^0 - L_{ij})^2 \]
\[ + \frac{\beta}{8} (L_{ij})^2 \sum_{ijk} (\cos \theta_{ijk} - \cos \theta_{ijk}^0)^2, \]

which has the advantage of separating completely the disorder in bond length from the disorder in bond angle. Therefore, in the case of bond- or site-mismatch disorder, the derivation given here remains valid, except that the Green’s function now includes regular terms and \( K \) is replaced by \( \alpha \). This is the same procedure as we have used successfully in the bulk.5-7

III. TOPOLOGICAL RIGIDITY PARAMETERS

There are many methods to obtain the topological rigidity parameters of a system. One would be to solve directly Eqs. (15) and (18), using the Green’s functions of the system. For a bulk crystal, this method can be useful, providing directly an analytical result; however, for less symmetric systems, like surfaces, clusters, or amorphous solids, obtaining these Green’s functions can require a large computational effort.

Another method is to use Eqs. (14) or (17). If one replaces a bond of length \( L_A \) by one of length \( L_B \) in a perfect crystal, the energy of this bond changes by
\[ \Delta E = K (L - L_B)^2 - K (L - L_A)^2, \]

where \( L \) is the length of the bond after relaxing the lattice. The force of this bond on the lattice is
\[ F = \frac{d}{dL} (\Delta E) = K (L_A - L_B). \]

But the force can also be expressed by
\[ F = \frac{K}{a^*} (L - L_B). \]

The topological rigidity parameter \( a^* \) describes how much more difficult it is to deform the spring in the network compared with a free spring. For a perfectly rigid lattice, \( a^* = 0 \), while for a completely floppy network, \( a^* = 1 \).

Using the two previous equations,
\[ \Delta L = L - L_B = a^* (L_A - L_B), \]

which is simply Eq. (14). It is, therefore, possible to obtain the topological rigidity parameters by applying forces on atoms of a pure system or by alloying a lattice and relaxing the whole network. In most cases, the latter method is used, because it allows a better comparison with experiment. However, for the local calculation of the topological rigidity constants (i.e., for a kink, an edge or a cluster), it is often simpler to use a local force method. For \( a^* \), a force must be applied at both ends of a bond, while it must be applied on all neighbors of a particular atom, radially, to obtain \( a^{**} \) for each bond around the central atom.

We have confirmed numerically the equivalence between using alloying or local forces to obtain the topological rigidity parameter. In two dimensions, the local force method in unstable under relaxation close to the surface. As discussed in the next section, there is nothing surprising about this because of the divergences associated with positional fluctuations in two dimensions. We have also verified, both analytically and numerically, that the arguments given above for \( a^* \) also work for \( a^{**} \) on a diamond structure. It is, therefore, possible to extend the concepts and formalism developed in the previous section to almost any disordered configuration.

Although the application of the force method is straightforward for a bond case, even near a surface, it becomes more complicated when trying to obtain \( a^{**} \) at the surface. In the bulk, one can pull on all bonds symmetrically, thus involving only the pair term of the Kirkwood potential. At the surface, the symmetry is broken and if one pulls only on the neighbors, a net force would result, moving the system as a whole. One solu-
FIG. 1. Layer indices for a two-dimensional cut of a Si(111) structure. The numbers refer to the bond layers, while the small letters identify the position of some atoms.

The local value of the topological rigidity parameter $a^{**}$ of a particular bond depends on the position of the reference atom. Using the notation of Fig. 1, for a Si(111) network, $a_{bc}^{**}=0.85$ (defect on site b), which is different from $a_{cb}^{**}=0.80$ (defect on site c). In a homogeneous sample, the $a^{**}$ value for a bond in layer 2 is simply the arithmetic average,

$$a_2^{**} = \frac{1}{2}(a_{bc}^{**} + a_{cb}^{**}).$$

IV. TRIANGULAR LATTICE

The first system looked at is the triangular lattice. Although it does not exist in nature, it provides a useful test for the theory, both because of its simplicity and of its two dimensionality, which allows a simple graphical representation.

We have done the simulation using slabs with periodic-boundary conditions along x and surfaces perpendicular to y. The relaxation was performed using a conjugate-gradient algorithm presented in Numerical Recipes. We consider two directions, (11) and (10). Figures 2(a) and 2(b) shows these two surfaces in a disordered state. The (10) surface has a low coordination number, three-nearest neighbors, while the sublayer has five. This very low coordination leads to a floppy surface. By comparison, the (11) surface, which is closer to the (111) surface of semiconductors, is more stable, due to its higher coordination: a fourfold coordination at the surface and all the sublayers perfectly coordinated. Note that the plane argument used to justify Eq. (4) remains valid for (11) orientation, provided that we rephrase it along the following line. We cut each surface bond by half and measure the force on this point due to, say, the right half of the bond. Since the system is symmetric in x, the total force must be zero and Eq. (4) is still valid in this special case.

For this work, we have used the straightforward definition of the topological rigidity,

$$a^{**} = \frac{\langle L_A \rangle - \langle L_B \rangle}{L_A^2 - L_B^2},$$

which, via Eq. (14), is independent of the concentration x. This definition has the merit of being simple to implement and remains valid in almost any geometry. Figure 3 shows the value of $a^{**}$ as a function of the layer index l in a $100\times100$ slab (with periodic-boundary conditions), averaged over 100 configurations. As expected, the surface presents a much flippier configuration than the bulk; from $a^*=\frac{1}{2}$, in the bulk, it reaches 0.82 for the first interlayer and 0.80 for the top intralayer along the (11) sur-

FIG. 2. Triangular network cut along the (a) (11) and (b) (10) direction. Bonds with 50% mismatch are distributed at random with equal probability.

$$a^{**} = \frac{\langle L_A \rangle - \langle L_B \rangle}{L_A^2 - L_B^2},$$

FIG. 3. Variation of the topological rigidity parameter $a^{**}$, as a function of depth in a triangular slab cut along (11) direction. The results are an average over 100 configurations of a $200\times200$ sites cell with a 2% mismatch.
The difference in topological rigidity between the first interlayer and intralayer can be understood in the following manner. Inside the top layer, bonds are confined along $x$, due to in-layer symmetry. However, interlayer bonds have an important component along $y$, which is almost free of topological constraint close to the surface. It is, therefore, easier for a bond in the first interlayer to keep its natural length than for an intralayer bond.

Besides the topological constant, it is important to look at the fluctuations in height at the surface. Since we are interested in probing the surface itself, such a quantity should provide us with useful information. However, the position fluctuations diverge in two dimensions, as was first demonstrated by Peierls (1934) and Landau (1937). We can see the effect of fluctuations in the large averaging needed to obtain an accurate value for the topological rigidity (a hundred samples for Fig. 3).

V. SILICON-GERMANIUM ALLOYS

For SiGe alloys, we have used the Kirkwood potential [Eq. (26)]. The same elastic constants ($\alpha$ and $\beta$) are used for all interactions. As discussed in previous papers, the use of different elastic constants for the three different interactions (Si-Si, Ge-Ge, and Si-Ge) leads to almost identical results, since they differ by only 20%;$^6$,$^7$ we chose a ratio $\beta/\alpha=0.2$, which is typical for semiconductors. The other approximation we use is the Pauling's radii in order to obtain the equilibrium mixed bond length $L^0_{\text{SiGe}} = 1/2(L^0_{\text{SiSi}} + L^0_{\text{GeGe}})$, with $L^0_{\text{SiSi}} = 2.347$ and $L^0_{\text{GeGe}} = 2.4364$. EXAFS measurements and $ab\ initio$ calculations have shown that this is indeed a very good approximation.$^{14,15}$

We used periodic-boundary conditions along $x$ and $y$, leaving the two surfaces perpendicular to $z$ and examined for two orientations: the (100) and (111) surfaces. As for (10) in the triangular network, the atoms at the surface (100) have few neighbors (only two), they are relatively unstable and hence, reconstruct easily. One method to prevent surface reconstruction is to satisfy the surface dangling bonds with hydrogen. With only two bonds attached to the bulk, the surface Si atoms are easily etched away during this process. Atoms at the surface (111), on the other hand, have three neighbors and form a relatively stable structure.$^{11-13}$ The hydrogenation process leaves a perfect surface with no reconstruction and should allow measurement that can compare with the theory and simulations presented here. All the results can be understood in terms of the formalism developed in Sec. II.

The relaxation process is much faster in 3D than in 2D. Without averaging over many configurations, the $a^{**}$ value of the bulk shows only very small fluctuations. The averaging has been made over 5-20 configurations of cells containing between 16000 (20x20x20 units cells) to 33152 atoms (26x26x26 unit cells). The relaxation has been obtained using a conjugate-gradient method.$^{10}$

Because the subsurface atom is tied to the bulk by only one bond, we expect $a^{**}$ to be very floppy at the surface and even more in the subsurface layer. Figure 4 shows the variation of $a^{**}$ as one moves closer to the surface (111). For the first two interlayers, $a^{**}$ is about 17% larger than in the bulk. The surface effect decreases very quickly, the third interlayer already gives a $a^{**}$ value only a few percent larger than the bulk value; even at a few layers under the surface, it becomes difficult to distinguish the environment from that of the deep bulk. Figure 5 presents the topological rigidity parameter as a function of the distance from a (100) surface. Since the coordination at the surface is lower than for (111), the variation of $a^{**}$ is greater by about 27%. The same results are obtained for $a^{**}$, using the local force method instead of alloying.

Table I shows the value of $\Delta a$ along different directions and for two concentrations 15-85 and 50-50. As predicted by Eq. (23), the partial displacements vanish in the bulk and are nonzero only for the layers close to the surface, along the $z$ direction. Due to the symmetry of the

FIG. 4. Topological rigidity parameter $a^{**}$, as a function of the layer number from a surface (111) in SiGe alloy containing 26x26x26 unit cells, averaged over five configurations.

FIG. 5. Topological rigidity parameter $a^{**}$, as a function of the layer number from a surface (100) in SiGe alloy containing 26x26x26 unit cells.
TABLE I. Displacement \( \langle u_{Ge} \rangle \)-\( \langle u_{Si} \rangle \) perpendicular (z) and parallel (x and y) to the surface at various depths for two concentrations of SiGe alloys. The small nonzero results in all rows, except the third, represents the small statistical errors, due to the configuration averaging.

<table>
<thead>
<tr>
<th></th>
<th>Si(<em>{25})Ge(</em>{75})</th>
<th>Si(<em>{15})Ge(</em>{85})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>( \langle u_{Ge}^z \rangle )-( \langle u_{Si}^z \rangle )</td>
<td>(-0.001) (-0.001)</td>
</tr>
<tr>
<td></td>
<td>( \langle u_{Ge}^x \rangle )-( \langle u_{Si}^x \rangle )</td>
<td>(-0.002) (-0.001)</td>
</tr>
<tr>
<td></td>
<td>( \langle u_{Ge}^y \rangle )-( \langle u_{Si}^y \rangle )</td>
<td>(0.043) (0.045)</td>
</tr>
<tr>
<td></td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
<tr>
<td>Bulk</td>
<td>( \langle u_{Ge}^z \rangle )-( \langle u_{Si}^z \rangle )</td>
<td>(-0.001) (-0.002)</td>
</tr>
</tbody>
</table>

system, \( \Delta u \) vanishes along x and y. The difference between the average height of each species is independent of the concentration.

The height at the surface is described by Eq. (24), where Pauling's atomic radius of each species is also included. From Table I, and considering a mismatch of about \( L_{AB}^0 - L_{AB}^0 = 0.09 \) Å for SiGe, the separation between the centers of the height distributions at the surface should be around 0.085 Å. The species of each individual atom could be determined from this single quantity only if the partial distributions were completely separated. Figure 6 shows the height distribution at the surface; it also presents the partial distributions. As one can see, these partial distributions are Gaussian like (Fig. 7), where the width of the distribution follows more or less a \( \sigma^0 \), i.e., when \( \sigma^0 \) increases, the width increases also. The overlap between the peaks is too large to permit an atom by atom distinction between species at the surface. Although the accuracy of SFM is still too crude to be able to distinguish this height distribution, one can hope that in the next few years, experimentalists will be able to measure this quantity with a precision of about 0.01 Å.\(^3\)

Although the fluctuations are isotropic in the bulk, they are not at the surface, as we could expect (Figs. 8 and 9). On the top layer, the width of the displacement distribution along x, y, and z is almost the same, with z being only slightly larger. However, on the subsurface layer, the difference is very important. The width of distribution along x and y is bulklike, while along z, it retains almost the surface value. The effect of the layer directly over it does not seem to have any noticeable effect on the z relaxation. It is easy to understand this phenomenon directly from the geometry of the layers. The bond between the second and third layers is initially only in the z direction, because there is little influence from the top layers, it relaxes almost fully by disturbing the second layer, which is relatively free, but not the third one, which has all the bulk behind it.

As seen in Sec. II, all the quantities described previously are only functions of the length mismatch and of the concentration of species. We have, therefore, performed relaxation at two different concentrations (x=0.20 and 0.50 in Si\(_{15}\)Ge\(_{1-x}\)) and verified that all quantities behave.

**FIG. 6.** Height distribution at the surface (111) of Si\(_{25}\)Ge\(_{75}\) (solid line). The dashed and dot-dashed lines are the Si and Ge height distributions, respectively. The curves are results from a 35,152 site cell.

**FIG. 7.** Gaussian fit (solid line) for partial z displacement distribution in Si\(_{25}\)Ge\(_{75}\) (a). The dashed and dot-dashed lines are the Si and Ge distributions, respectively; the solid lines are two Gaussians with identical width.

**FIG. 8.** Ge displacement distribution along z at the surface (111), the subsurface, and the center of a slab of Si\(_{25}\)Ge\(_{75}\) (solid, dashed, and dot-dashed lines). The distribution represents an average over 20 configurations from a 16000 site cell.
as they should. From the results presented in this section, the so-called z plot (Fig. 10) is indeed obeyed for every layer, with a topological rigidity parameter $a^{**}$, depending on the layer, but independent of the concentration $x$.

VI. CONCLUSION

Although reconstruction is often present at the surface, it is interesting to be able to develop a phenomenological theory that would allow some understanding of the relaxation phenomenon at the surface, due to alloying. We have presented such a theory here and applied it to the 2D triangular lattice, and to the SiGe(111) and (100) surfaces. Experimentally, the (111) surface of Si$_{1-x}$Ge$_x$ alloy remains chemically disordered, but reconstructs into a 5x5 structure for $x > 0.1$ or a 7x7 structure at lower Ge concentration. However, it should be possible to isolate the effect of length mismatch by studying samples maintained at large enough temperature to destroy the reconstructed surface or by saturating the dangling bonds at the surface with hydrogen. Because the displacements associated with both alloying and reconstruction are relatively small, the two effects should add up linearly to give the final surface topography. Figure 11 presents the topography of an unreconstructed (111) Si$_{0.5}$Ge$_{0.5}$ surface, as obtained relaxing the alloy with the Kirkwood potential. The situation is more complicated for the (100) surface, since the use of hydrogen simply etches the surface away and there appears to be some kind of chemical ordering on this surface.

The study of surfaces is also important because it enhances the effects of mismatch. All the distributions are widened and, therefore, easier to observe, the strain being reduced at the cost of increasing the distortions in the crystalline lattice. As we have seen, the concept of topological rigidity allows us to describe quantitatively the floppiness of the network as we approach the surface. In both the 2D and 3D cases, effects of surface on the relaxation die out very quickly in the bulk, after only a couple layers. We have also shown that it is possible to calculate the topological rigidity parameter locally simply by applying a force on a few atoms. This method is much simpler than trying to obtain $a^*$ or $a^{**}$ directly from the Green's functions, particularly in low-symmetry situations.

Although all structural quantities at the surface do not reduce to simple function of the topological rigidity parameters $a^*$ or $a^{**}$ as is the case for the bulk, the same theoretical approach applies at the surface as in the bulk. If the experimental surface results are in agreement with the theory, then one can infer that the theory is also valid in the bulk. Therefore, a measurement of the surface relaxation can give important clues about the volume strain in the limits of this theory.

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APPENDIX A: NEAREST-NEIGHBOR DISTANCE FLUCTUATIONS

In this appendix, we follow closely the derivation for site-mismatch disorder presented in Ref. 5 for the length probability distributions. Similar results can be obtained for bond mismatch on a triangular lattice. It is possible to write the length probability distribution as

$$P_{e_i e_j}(L) = \left( \frac{1 + e_i \sigma_i}{2} \right) \left( \frac{1 + e_j \sigma_j}{2} \right) \delta(L_{|a|} - L),$$  \hspace{1cm} (A1)

where the greek and latin indices are associated with the different fcc sublattices of the diamond structure. The average is over the layer to which $i$ and $a$ belong. Using the integral form of the $\delta$ function, the probability distribution becomes
\begin{equation}
A_{\alpha\beta} = \frac{K}{4} \sum_{i} \hat{\mathbf{r}}_{i\alpha} \cdot (\mathbf{G}_{i\beta} + \mathbf{G}_{i\alpha}) \cdot \hat{\mathbf{r}}_{i\beta} . \tag{A7}
\end{equation}

Inserting these results into Eq. (A3), we obtain
\begin{equation}
F_{\varepsilon_{1} \varepsilon_{2}}(q) = e^{-i q \left[ (L) + (2x - 1) \Delta_{AB} \left[ \sum_{i} A_{ii} + \sum_{\beta} A_{\alpha\beta} \right] \right]}
\times I_{\varepsilon_{1}}(q) I_{\varepsilon_{2}}(q) , \tag{A8}
\end{equation}

where we can separate the averaging on each sublattice,
\begin{equation}
I_{\varepsilon}(q) = \left( \frac{1 + \varepsilon_{1} \varepsilon_{1} - i \varepsilon_{1} \varepsilon_{2} \varepsilon_{2} \Delta_{AB}}{2} \right)
\times [ \cos q A_{ii} - i (1 - 2x) \sin q A_{ii} ] . \tag{A9}
\end{equation}

And so the solution becomes
\begin{equation}
F_{\varepsilon_{1} \varepsilon_{2}} = \frac{1 + \varepsilon_{1} (1 - 2x)}{2} \frac{1 + \varepsilon_{1} (1 - 2x)}{2}
\times f(q) e^{-i q \left[ (L) + (2x - 1) \Delta_{AB} \right]} . \tag{A11}
\end{equation}

The function $f(q)$ contains the higher moments and is concentration independent:
\begin{align}
&f(q) = e^{-i q \left[ (L) + (2x - 1) A_{ii} + A_{\alpha\beta} \right]}
\times \Pi_{i \neq \alpha} \left[ \cos q A_{ii} - i (1 - 2x) \sin q A_{ii} \right]
\times \Pi_{\beta \neq \alpha} \left[ \cos q A_{\alpha\beta} - i (1 - 2x) \sin q A_{\alpha\beta} \right] . \tag{A12}
\end{align}

Therefore, all the partial lengths $AA$, $AB$, and $BB$ will have the same distribution, but of course appropriately shifted and have the respective weights $(1-x)^2$, $2x (1-x)$, and $x^2$.