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Missing dimers and strain relief in Ge films on Si(100)

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The 2×8 reconstruction of Ge films on Si(100) is shown to arise from ordered arrays of rebonded missing dimers (RMD's). Such a reconstruction was suggested by Pandey for Si(100). However, because of their large tensile stress, RMD's are much more energetically favorable in epitaxially compressed Ge films. For Si(100), RMD's have very small energy, and their presence may account for the puzzling discrepancy between theory and experiment for the stress anisotropy.

Semiconductor surfaces exhibit a bewildering variety of complex reconstructions. Typically these reconstructions serve to reduce the number of dangling bonds (DB's), but at the cost of large structural distortions; this subtle trade-off leads to the observed variety. In particular, a modest strain may tip the balance in favor of a different structure.[1] Here we show that for Si and Ge(100), a small compressive strain can transform the 2×1 dimer structure to a more complex 2×N structure. This represents an unambiguous instance of a reconstruction mechanism proposed by Pandey.[2]

When Ge is deposited on Si(100), it initially forms a film about three atomic layers thick, with excess Ge collecting in islands.[3,4] This thin Ge film has been studied with scanning tunneling microscopy (STM).[5,6] It forms arrays of what appear to be missing dimers, with roughly 2×8 periodicity. (The studies were careful to exclude Ni contamination, which can also lead to a 2×8 periodicity but with a very different structure.) The missing dimers have been assumed[5] to serve as a strain-relief mechanism by allowing room for the expansion of the Ge layer. However, our calculations indicate that they are more complex.

Simply removing a dimer creates two extra dangling bonds, raising the energy. However, Pandey proposed that by removing a dimer, and then *rebonding the second-layer atoms*, one could *decrease* the number of DB's, albeit at a considerable cost in local strain.[2] We find that such rebonded missing dimers (RMD's) are responsible for the 2×8 reconstruction of Ge films.

These RMD's have a large tensile stress, which at the proper density almost exactly cancels the compressive stress of the Ge film, as well as the anisotropic stress arising from the 2×1 dimer reconstruction of the surface. The resulting reduction in elastic energy tips the balance in the competition between elastic energy and DB's, and makes RMD's distinctly favorable in strained Ge films, in contrast to unstrained Si and Ge surfaces.

We treat 2×N reconstructions, as are seen in STM.[5,6] Every Nth dimer is removed from the surface, starting from a 2×1 dimer reconstruction. The second-layer atoms are rebonded as prescribed by Pandey.[2] The elastic energy is calculated using a Keating model, which has been modified[4] to accurately reproduce the surface stress of Si(100) 2×1. Calculations are performed for a 24-layer slab with periodic (2×N) boundary conditions in two dimensions, having one RMD per cell on each face. The resulting relaxed structure for $N=8$ is shown in Fig. 1. The strain field around the RMD is quite large, with bowing clearly visible even in the seventh layer.

The Keating model gives only the elastic energy; we must also add an energy cost for each dangling bond. The energy of Si(100) 2×1 is accurately reproduced by assuming the usual value[2] of 1.0 eV per DB. For Ge, we reduce this value in proportion to the cohesive energy, $E_{\mathrm{DB}}=0.8$ eV.

The major factor favoring formation of RMD's is the fact the each RMD eliminates two dangling bonds, relative to the 2×1 dimer structure. In addition, Pandey suggested that rebonding at RMD's leads to some enhanced π bonding within the two dimers neighboring the RMD.[2] Thus the formation energy of each RMD is $E_{\mathrm{el}}-2E_{\mathrm{DB}}-2\Delta E_\pi$, where E_{el} is the increase in elastic energy (calculated with the Keating model), E_{DB} is the dangling-bond energy (about 1.0 eV for Si, 0.8 eV for Ge), and ΔE_π is the magnitude of the enhancement of the π bonding in each neighboring dimer. We stress that no quantitative estimate of the π-bonding contribution is available; therefore we somewhat arbitrarily consider the range $\Delta E_\pi=0$–0.2 eV below, to get an idea of the possible role of this effect.

Results for energy versus the period N of the 2×N reconstruction of a Ge film on Si(100) are shown in Fig. 2(a). We assume a three-layer film, as is actually observed,[3,4] denoting this structure as Ge$_3$Si(100) for con-

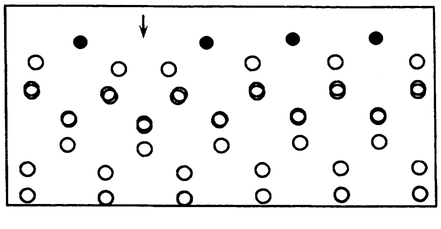

FIG. 1. Calculated structure of the Ge$_3$Si(100) 2×8 surface [i.e., a three-layer Ge film on Si(100)] projected onto a [011] plane. Solid circles are surface dimers whose bond is perpendicular to the page. The arrow indicates the position of the missing dimer. Second-layer atoms below the arrow are pulled together to form a bond. There are two inequivalent atoms per row in the third and fourth layers.

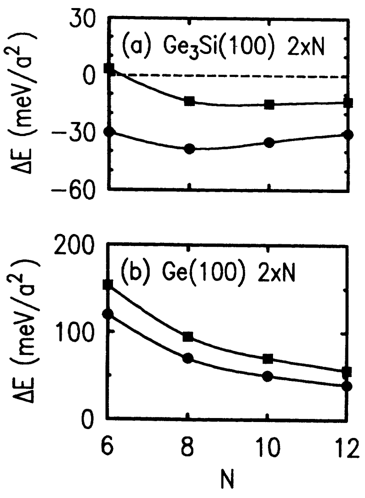

FIG. 2. Surface energy of $2\times N$ surfaces, relative to ideal 2×1, plotted vs period N. Squares are calculated assuming $E_{\mathrm{DB}}=0.8$ eV for Ge; circles include an additional contribution $\Delta E_\pi=0.2$ eV, as discussed in the text. Solid curves are splines to guide the eye. (a) Ge$_3$Si(100); (b) unstrained Ge(100).

venience. The surface lattice constant [3.84 Å for Si(100)] is denoted as a.

Even without including the π-bonding contribution, for $E_{\mathrm{DB}}=0.8$ eV the formation of RMD's lowers the energy, giving a minimum energy for $N=9$ or 10. Assuming even a modest 0.2 eV contribution from enhanced π bonding moves the minimum to $N=8$. Doubling ΔE_π to 0.4 eV would only move the minimum a bit further, to $N=7$. This range of $N\sim 8$ is in good agreement with experiment.[5,6] In each case the minimum is rather flat, with relatively little difference in energy between $N=8$ and 9, which may account for the lack of strict periodicity seen in experiments.

Because the 2×8 reconstruction occurs for Ge epitaxially grown on Si, Köhler *et al.* inferred that the reconstruction is related to relief of compressive strain at the surface.[5] This conclusion is supported by a crucial observation. Mo and Lagally found that at the tops of large Ge islands, where the strain is relaxed, flat (100) facets do not exhibit the reconstruction, but instead show a perfect 2×1 dimer reconstruction.[6]

To examine the role of strain, we calculate the energy of $2\times N$ reconstructions of an unstrained Ge(100) surface. The results are shown in Fig. 2(b). The $2\times N$ reconstructions are not energetically favorable in this unstrained case. This result is consistent with the absence of RMD's on relaxed islands,[6] and corroborates the crucial role of compressive strain.

We can gain further insight by explicitly calculating the surface stress. The surface stress tensor σ^{surf} is defined as

$$\sigma_{ij}^{\mathrm{surf}}=\frac{1}{A}\frac{dE^{\mathrm{surf}}}{d\epsilon_{ij}}\ . \tag{1}$$

Here E^{surf} is the surface energy, A is the surface area, and ϵ is the two-dimensional strain. Thus a positive value corresponds to tensile stress. Because of the symmetry of the surface, this tensor is diagonal, and we need only consider σ_{xx} and σ_{yy}, where x is the direction of the dimer bond (the 2 of $2\times N$), and dimer rows run in the y direction.

Results for σ_{xx} and σ_{yy} vs N are shown in Fig. 3(a), for $2\times N$ reconstructions of Ge$_3$Si(100), i.e., the three-layer Ge film on Si(100). While σ_{xx} is essentially constant, σ_{yy} varies dramatically with N. The latter stress essentially vanishes at $N=8$, accounting in part for the occurrence of an energy minimum near $N=8$.

One expects that these stresses represent, to a good approximation, the sum of the stress of the ideal 2×1 surface and the stress of the RMD's. This expectation is confirmed in Fig. 3(b), which shows the extra stress (relative to the 2×1) per RMD. The excess stress is essentially independent of N, and represents the stress of a RMD, $\sigma_{ij}^{\mathrm{RMD}}=A^{-1}dE^{\mathrm{RMD}}/d\epsilon_{ij}$, where E^{RMD} is the formation energy of a RMD, and A is the area per missing dimer.

From Fig. 3(b), we see that the RMD contributes a very large tensile stress in the y direction. This is easily understood from the structure (Fig. 1). The second-layer atoms must be pulled together from their bulk positions in order to form a bond. Because they are much more strongly constrained than the dimer atoms, this results in a correspondingly large tensile stress, compared to the modest tensile stress resulting from surface dimerization.

For comparison, Fig. 4 gives the same information as Fig. 3, for an unstrained Ge surface. The RMD's contribute nearly the same stress as for the epitaxial film. However, in this case the initial 2×1 surface is on average tensile, with only a slight compression in the y direction. The result is that (except perhaps for very large N) the RMD's increase the stress rather than reduce it, which leads to the less favorable energies shown in Fig. 2(b).

As a final test of our understanding of the strained Ge films, we consider films thinner than three atomic layers. Köhler *et al.*[5] found that a monolayer film of Ge formed a $2\times N$ reconstruction, but with $N\sim 11$. Repeating the calculations above for a monolayer film, we find that RMD's

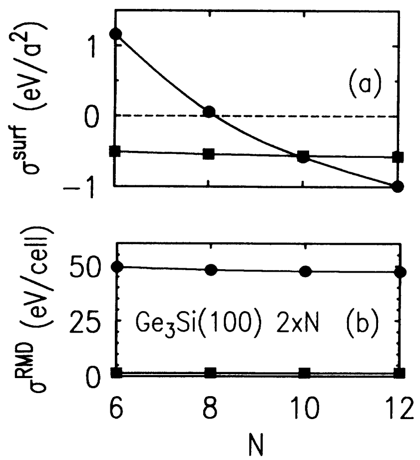

FIG. 3. Surface stress of Ge$_3$Si(100) $2\times N$ surfaces vs N. Squares and circles correspond to x and y directions, respectively. Solid curves are splines to guide the eye. (a) σ^{surf} is the total surface stress, shown per 1×1 cell. (b) σ^{RMD} is the net stress relative to the ideal 2×1, per $2\times N$ cell.

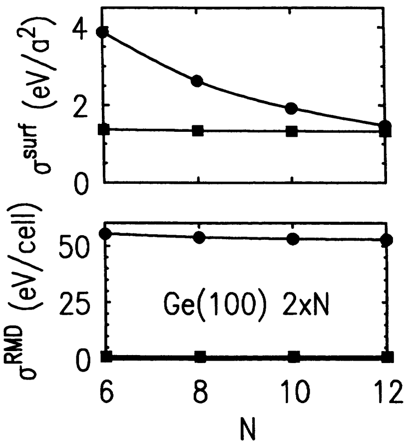

FIG. 4. Same as Fig. 3, for unstrained Ge(100) $2\times N$ surfaces.

are energetically unfavorable in this case, *unless* the four rebonded atoms in the second layer are also Ge atoms. Because these atoms are under tremendous tensile stress, substituting Ge atoms (which are both larger and less rigid than Si) results in an energy lowering of roughly 0.6 eV per RMD.

For a monolayer Ge film, including Ge atoms in the rebonded second-layer sites, RMD's are still less favorable than for the three-layer film. But $2\times N$ structures are found to be a bit lower in energy than the ideal 2×1, with the minimum energy occurring for larger N than in the three-layer case, consistent with the observations of Köhler *et al.* The precise value of N is, however, very sensitive to the exact value assumed for $E_{DB}+\Delta E_\pi$.

While Ge films exhibit high densities of ordered RMD's, missing dimers are also observed in STM images of Si(100).[7] In that case, some of the missing dimers may be associated with contamination, but we expect that some may be RMD's. It is not clear whether RMD's on Si(100) are endothermic defects, or exothermic but highly repulsive, with the minimum energy occurring at such low densities that ordering does not occur.

To address this question, we repeat the calculations of energy and stress for a plain Si(100) surface. Since the RMD's have negligible stress in the x direction (the direction of the dimer bonds), we expect their interaction in that direction to be weak. We therefore continue to use $2\times N$ structures, recognizing that this is only a rough model for the actual structure in this case.

The results for Si(100) are shown in Fig. 5 vs $1/N$, to facilitate extrapolation to large N (low densities). While we cannot expect such extrapolation to be highly accurate, it permits us to obtain a qualitative picture of the behavior at low densities of RMD's. The point for $N=\infty$ in Fig. 5 corresponds to the ideal 2×1 structure. As before, results are shown for E_{DB} alone (here 1.0 eV) and for $E_{DB}+\Delta E_\pi$, with $\Delta E_\pi=0.2$ eV. The solid curve represents a least-squares quadratic fit.

The results indicate that, for reasonable values of $E_{DB}+\Delta E_\pi$, formation of RMD's may be either weakly endothermic or exothermic for low densities of RMD's. In the limit of low density, the formation energies inferred from Fig. 5(a) (from the linear term in the quadratic fit) are 150 and -250 meV per RMD for $E_{DB}+\Delta E_\pi=1.0$ and 1.2 eV, respectively. Regardless of sign, these are extremely small energies for a defect involving such drastic strain and rebonding.

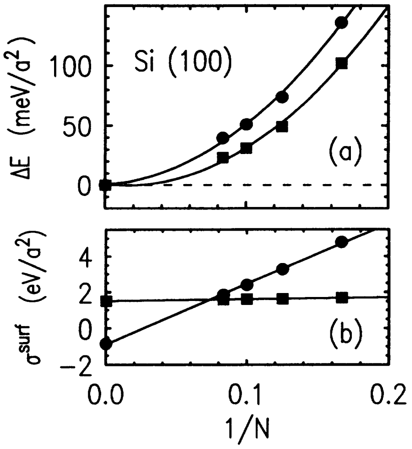

FIG. 5. (a) Surface energy of Si(100) $2\times N$ surfaces, relative to ideal 2×1, plotted vs $1/N$. Circles are calculated with $E_{DB}=1.0$ eV for Si; squares include an additional contribution $\Delta E_\pi=0.2$ eV, as discussed in the text. Solid curves are least-squares quadratic fits. (b) Surface stress for the same structures as in (a). Squares and circles correspond to x and y directions, respectively.

Repeating this analysis for the case of Ge(100), using the data of Fig. 2(b), we obtain formation energies of 370–770 meV per RMD. The higher formation energy on Ge(100) appears to explain the observation of Mo and Lagally, that Ge(100) facets of large islands are relatively free of missing dimers, compared to Si(100).

Figure 5(b) shows the surface stress of Si(100) $2\times N$ vs $1/N$. The stress asymmetry $(\sigma_{xx}-\sigma_{yy})$ is crucial in determining the behavior of steps on Si(100),[8,9] and has been the subject of intense interest.[10,11] However, the best theoretical calculations[10] give anisotropies of around 2.5 eV/a^2, while experimental measurements[11] give 1.0 eV/a^2. The failure of theory and experiment to agree on such a fundamental property represents a major obstacle in the quantitative understanding of surface steps and related properties.[9]

Our results suggest an explanation for this discrepancy. The stress asymmetry calculated here decreases linearly from 2.4 eV/a^2 to zero as the number of RMD's increases from zero to about 7% of all dimers, as seen in Fig. 5(b). Thus a density of only 4% missing dimers would suffice to account for the discrepancy between theoretical calculations for the ideal 2×1 surface, and measurements on the real surface.

Even without any contribution from π bonding, the calculated formation energy is only 150 meV per RMD. If we neglect interactions, then the equilibrium density of RMD's would be 4% at a temperature around 550 K, reducing the stress anisotropy to around the observed value. While such numbers should not be taken too seriously as *quantitative* results, they clearly show that RMD's can account for the puzzling discrepancy between theory and experiment for the stress anisotropy of Si(100).

We should stress that the equilibrium density of RMD's is expected to depend sensitively upon temperature. Since the stress anisotropy is measured indirectly, via its effect on steps,[11] the relevant temperature is that at which the step positions equilibrate. A small amount of subsequent atomic diffusion at lower temperatures might reduce the number of RMD's observed at room temperature, without allowing the steps to significantly readjust to the resulting larger anisotropy.

In conclusion, our calculations explain the $2\times N$ reconstruction observed in Ge films on Si(100). The reconstruction represents the first unambiguous confirmation of energy lowering by Pandey's mechanism[2] of rebonding at a missing dimer. The second-layer rebonding entails large tensile stress, and is stabilized in this case by the compressive strain of the film. For unstrained surfaces, rebonded missing dimers are expected to be present in low densities on Si(100), and to be virtually absent on Ge(100), in qualitative agreement with STM observations. Finally, the anisotropic tensile stress contributed by the RMD's provides a reasonable explanation of the discrepancy between theory and experiment for the stress anisotropy of Si(100).

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