

Tunneling images of the 5×5 surface reconstruction on Ge-Si(111)

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Germanium-silicon alloys can be prepared on crystalline silicon (111) substrates and have been observed to have 5×5 surface reconstructions. We present tunneling images of this surface which show that it has strong similarities to the Si(111) 7×7 reconstruction. A model related to that proposed by Takayanagi, Ytanihiro, and Kobayashi accounts for the general features of the observed reconstruction. In addition, the surface is observed to have periodic vertical modulations which indicate an ordered Ge-Si surface alloy.

The surfaces of semiconductors have presented one of the severest challenges to our understanding of crystal physics. As new experimental techniques have been applied to probe this region, more and more information bearing on questions of geometrical and electronic structure is obtained. Nevertheless, in spite of rather intense effort extending over many years, the state of our understanding here is significantly inferior to that for the bulk which these surfaces terminate. This situation may be viewed as resulting from the fact that deducing the detailed atomic arrangement of atoms on the surface and in the near-surface region with certainty has proved to be an excruciatingly difficult task.

A good example of this situation is the silicon (111) surface which has been observed to adopt a 7×7 superlattice. This phase was first discovered by low-energy electron diffraction¹ (LEED) and was later studied in detail by this method as well as transmission and reflection electron microscopy,^{2(a),2(b)} channeling,³ helium-atom scattering,⁴ and x-ray standing waves.⁵ Recently, Binnig, Rohrer, Gerber, and Weibel⁶ have presented tunneling images of this surface that have provided additional information about structure in the outermost layer. It seems clear, however, that the major complications in this surface structure lie beneath the outermost atomic layer, where significant reorganization is required to account for the results of all the experiments mentioned above. The structural model of Takayanagi, Ytanihiro, and Kobayashi^{2(b)} appears to explain these observations the most satisfactorily, incorporating stacking faults and adatoms to satisfy diffraction, channeling, and tunneling constraints, but the situation is not yet certain.

We were originally attracted to study the Ge-Si alloy system because it has recently been shown to reconstruct with a 5×5 LEED pattern.⁷ This pattern is quite similar to the 7×7 pattern observed on clean silicon and one might suspect that a close relationship between the two surfaces exists. The 5×5 structure is more amenable to theoretical investigations since the unit mesh contains roughly half as many atoms. Hence were the close relationships established experimentally; insights gained from calculations on the smaller structure might be extrapolated to the larger with more confidence. Finally, we note that in our recent studies⁸ of the germanium (111) surface using a tunneling microscope, the normal $c2 \times 8$ reconstruction is observed to bear little resemblance to the 7×7 case and it is not obvious what habit the intermediate alloy case might actually adopt. We therefore decided to obtain tunneling images of Ge-Si alloy to resolve this question.

The sample was prepared in a UHV chamber containing sputtering and annealing facilities for sample preparation, a LEED apparatus to verify the presence of the 5×5 reconstruction, and a tunneling microscope which generates the images and scans we present below.

The sample consisted of a Si(111) wafer with several hundred angstroms of Ge grown by molecular-beam epitaxy (MBE). This sample was placed in the vacuum chamber, where it was prepared according to the recipe of McRae and Malic.⁹ First, it was Ar-ion sputtered back to the original interface to obtain an approximately equal concentration of Si and Ge atoms in the near-surface region (due to the atomic mixing that accompanies the sputtering process). This was followed by a brief anneal at 650°C which caused the 5×5 LEED pattern to develop. We rely on the detailed LEED-Auger studies of McRae *et al.*,⁹ which show that the 5×5 is obtained only within a small range of nearly equal Ge-Si surface concentration. After a period of six hours thermal drifts had decayed to acceptable levels, and the sample was placed in the tunneling microscope.

The conditions under which data were taken were similar to those reported in Ref. 8. Figure 1 is a gray scale tunneling image of the Ge-Si(111) 5×5 , where the high areas appear light and the depressed areas dark. The range of heights is of order 0.5 Å and will be discussed in more detail in connection with Fig. 2. The lateral scale of the figure is $\sim 100 \times 80$ Å.

The most striking feature in the figure is an ordering of large depressions, each surrounded by a hexagonal array of protrusions. The depressions are themselves in a triangular array with a 19.2-Å nearest-neighbor distance. These depressions may be looked upon as defining the corners of a rhombohedral unit mesh whose long diagonals point along $\langle 211 \rangle$ directions in the surface, and whose short diagonals are along $\langle 110 \rangle$ directions in the surface. Each unit mesh is then seen to contain six large protrusions.

Closer inspection of Fig. 1 shows a remarkable feature. As one proceeds around the hexagonal array of protrusions surrounding any large depression, one observes a periodic oscillation in protrusion height. This oscillation also manifests itself by breaking the apparent reflection symmetry of the unit mesh with respect to its short diagonal. In order to demonstrate this effect more clearly, we present a line scan of the data in Fig. 1 along a long diagonal. The asymmetry in left- and right-hand peak heights is apparent with the difference amounting to approximately 0.1 Å. Careful measurement of the height difference averaged on eight unit meshes gives 0.15 ± 0.07 Å, which is 25% of the max-

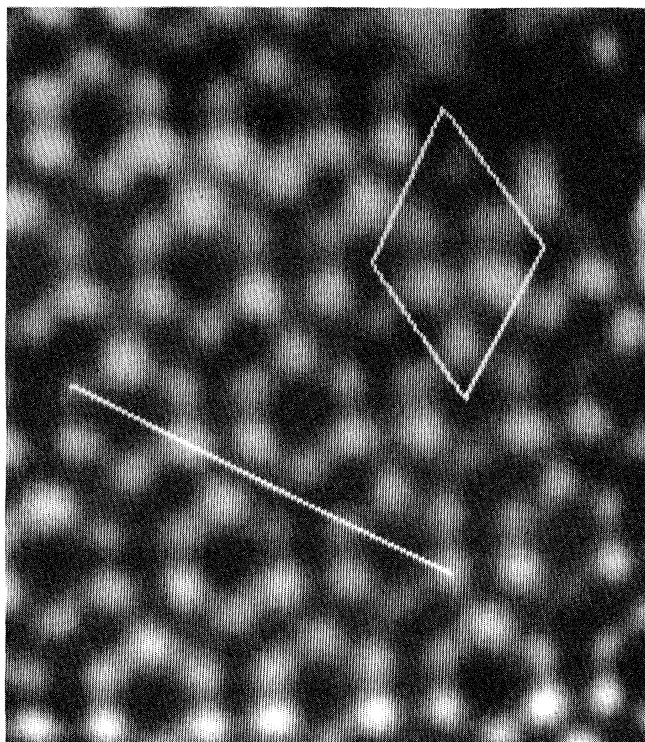


FIG. 1. Tunneling image of Ge-Si(111) 5×5 surface reconstruction. Total height variation from the highest (white) areas to the lowest (black) areas is ~ 0.5 Å. A unit mesh is outlined, of which the length of one side is 19.2 Å. The straight line indicates the direction of the tip height plot shown in Fig. 2.

imum corrugation observed in the unit mesh.

These results may now be compared with those for the Si(111) 7×7 which were originally obtained by Binnig *et al.*⁶ Both structures are characterized by deep depressions at the corners of a rhombohedral mesh. The cells in the 7×7 case have 26.9-Å edges, however, and each cell contains 12 pro-

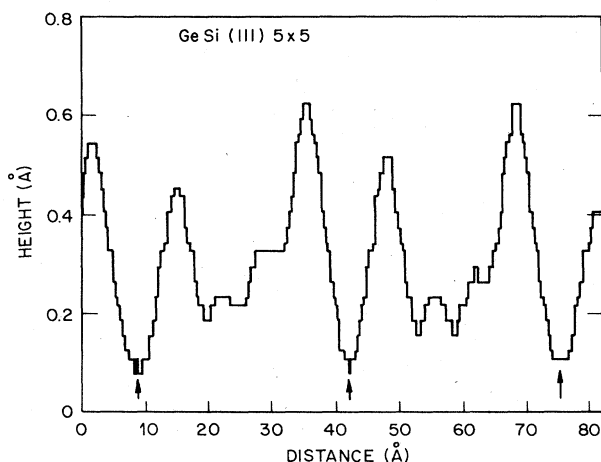


FIG. 2. Tip height plot across two unit meshes along the long diagonal as indicated in Fig. 1. The arrows mark the location of the unit mesh corner holes. The asymmetry between the two halves of the unit mesh is clearly visible.

trusions. Six of these serve to surround the deep corner protrusions. Thus if the 7×7 cell is shrunk to have the proper size for a 5×5 geometry by eliminating all noncorner protrusions, the two structures are seen to be very closely related indeed.

All models of the 7×7 structure which are serious contenders for explaining this structure (of which we are aware) can be reduced in this manner and we conclude that calculated total energy comparisons for the analogous 5×5 structure will be an invaluable aid in selecting the physically realized 7×7 structure. Efforts along this direction taken by Chadi¹⁰ on silicon, for example, seem totally justified. Such calculations would be even more realistic were they performed for Ge-Si alloys.

We believe that the strongest current model of the 7×7 structure is that proposed by Takayanagi *et al.*^{2(b)} This model appears to account for electron microscopy, channeling, and tunneling microscope observations on Si(111) 7×7 . It explains the large holes at the corners of the unit cell by having alternating surface regions of different stacking merge at the corners. This is accomplished by taking each unit mesh to have a stacking fault on one side of the short diagonal in the topmost double layer, which accounts for the asymmetry across the cell short diagonal originally observed by Binnig *et al.*⁶ Adatoms, which account for the protrusions in the tunneling images, are then placed above the top double layer directly above the nonhollow threefold sites. Figure 3 depicts a similar model for the 5×5 reconstruction modified by foreshortening the 7×7 mesh to eliminate all noncorner protrusions. The model seems quite satisfactory, but fails to account for the oscillation in adatom height.

This modulation brings us to the main difference between the Si and Ge-Si alloys. The height of the protrusions in the 7×7 data of Ref. 6 were nominally all equal. We obtained this result in detailed studies performed in our laboratory over a range of negative bias voltages, tip with respect to sample. The observed modulation in the 5×5 data is truly significant. If one accepts the explanation of ing from individual adatoms, then a natural explanation for ing from individual adatoms then a natural explanation for the observed peak height variations is that an ordered alloy with germanium and silicon atoms occupying alternate positions around the deep depressions exists on the surface. The difference in covalent radii between germanium and sil-

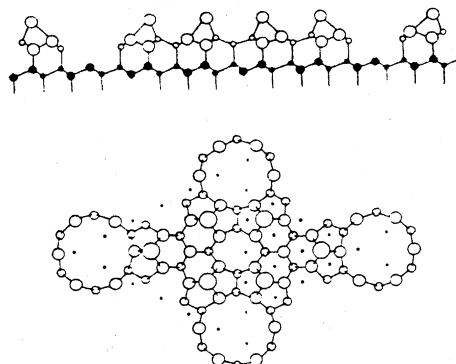


FIG. 3. A schematic of the dimer-adatom-stacking fault (DAS) model of Takayanagi *et al.* [Ref. 2(b)] foreshortened for the smaller unit mesh of Ge-Si(111) 5×5 .

icon amounts to 0.05 Å (Ref. 11), in reasonable agreement with our observed peak height differences. The discrepancy can be accounted for by assuming that the surface modulations of atoms lies above a similar modulation below. In addition, tunneling effects dependent on the detailed local density of states may also affect the apparent height observed by the tunneling microscope. For these reasons the data must be looked upon as a qualitative rather than a quantitative indication of alloy order.

From previous diffraction measurements on bulk Ge-Si the alloy has always been considered to be disordered. These samples were always prepared by coevaporation of both silicon and germanium in a MBE apparatus. Our sputter-mixing method of preparation may account for the observation of surface order. Recent studies of specially heat-treated samples have, however, indicated that an ordered bulk phase may, in fact, exist.¹² While we do not believe that our samples are necessarily an ordered bulk alloy, since the thermodynamic conditions for ordering may be more favorable at the surface than in the bulk, the possibility of such a phase in the bulk certainly enhances the possibility of its existence at the surface. It would be extremely interesting to calculationaly see how much energy can be

gained from ordering different models of the 5×5 surface and then determine under what conditions ordering makes thermodynamic sense.

Alternatively, an explanation for the vertical modulations in our data is simply that the surface is buckled due to compressive stress at the surface, with no ordering regarding germanium or silicon site occupation. However, we have studied 7×7 pure germanium layers grown on silicon substrates⁸ and observed no such buckling, although similar stresses might be expected here.

In conclusion, we have observed the Ge-Si(111)5×5 surface reconstruction in the tunneling microscope and found it to be a close relative of the 7×7 structure observed on pure silicon surfaces. This observation justifies the use of this reduced structure in calculations attempting to describe this class of reconstruction. In addition, we present the first evidence for ordered surface alloys in the Ge-Si system.

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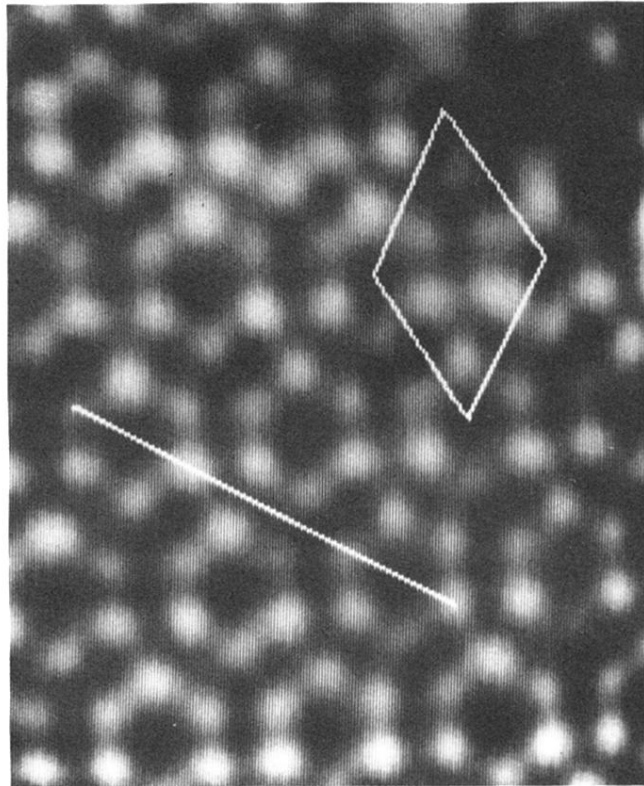


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