Observation of (5×5) Surface Reconstruction on Pure Silicon and its Stability Against Native-Oxide Formation

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We report the observation of a (5×5) reconstruction on the pure Si (111) surface, which is induced and stabilized by a tensile strain. The stabilization is so strong that the reconstruction survives extended exposure to air and the formation of a native oxide layer. Modeling of experimental high-resolution transmission-electron-microscope profile images indicates that the native oxide is ordered. The (5×5) reconstruction can also be induced at an initially unreconstructed Si-oxide interface by application of tension and appropriate annealing.

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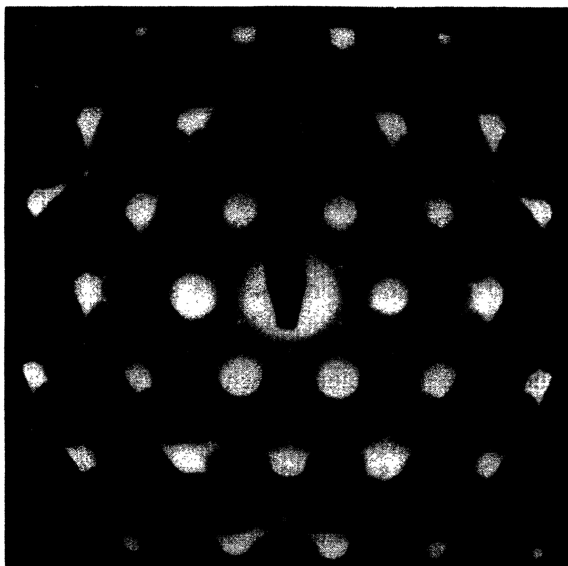
Intensive investigation of the silicon (7×7) surface reconstruction has led to a general convergence of ideas regarding its structure and the underlying mechanism responsible for its formation. A strengthened backbonding of the topmost double layer is thought to create a compression, which leads to the ejection of $\frac{1}{7}$ of the atoms in the double layer,[1] thus giving rise to the formation of the dimer–adatom–stacking fault structure.[2] The initial theoretical suggestions of the importance of strain[3] have found convincing experimental confirmation in the observation that the Ge $c(2\times8)$ structure is changed to (7×7) by means of a small compressive strain.[4] $Ge_{0.5}Si_{0.5}$ exhibits a (5×5) analog of the Si(7×7) surface.[5,6] This is thought to be consistent with the effect of a *compressive* strain, in that the larger compression in GeSi (due to the larger ionic radii) leads to the ejection of a greater fraction of the atoms ($\frac{1}{5}$ instead of $\frac{1}{7}$) from the topmost double layer.[6] In this Letter we show for the first time that a small *tensile* strain can lead to the formation of a (5×5) structure on the clean surface of pure Si, which survives extended exposure to air and the formation of a native oxide layer. We also present the first experimental high-resolution transmission-electron-microscope (HRTEM) profile images of a Si $(n\times n)$ structure and show that computer modeling of these images indicates that the oxidation of the Si(5×5) surface leads to the formation of an ordered oxide layer and a buried Si(5×5) oxide interface.

Our first sample was grown by molecular-beam epitaxy and the surface periodicity monitored *in situ* by reflection high-energy electron diffraction (RHEED). A 1000-Å-thick Si epilayer was deposited on a clean (111) Si substrate at 750 °C and exhibited a (7×7) pattern. An 80-Å-thick $Ge_{0.5}Si_{0.5}$ film was then grown at 500 ± 10 °C, showing a (5×5) pattern typical of this alloy. Finally, a 150-Å-thick Si cap was deposited at the same temperature, and also showed a (5×5) pattern with an admixture of a (7×7) pattern. Subsequent *ex situ* Rutherford backscattering measurements have yielded an upper limit of 0.1 monolayer of Ge on the final Si layer surface. We thus conclude that the (5×5) RHEED pattern observed from the sample must be ascribed to the clean topmost surface of a Si layer, grown on the buried GeSi/Si structure as described above.

The sample was then removed from the molecular-beam epitaxy chamber, allowed to stand in air for a period of several weeks, mechanically polished from the back, chemically etched to perforation in $HF:HNO_3$ and examined in a TEM operating at 120 keV. As in previous attempts at the growth of GeSi on (111) Si,[7] the sample contains a number of defects, primarily stacking-fault tetrahedra, with an average separation of ~0.2 μm. Examination of this sample in cross section revealed the defects to originate mainly in the buried GeSi layer and at its interfaces. Figure 1 is a transmission-electron diffraction (TED) pattern of the sample in plan view, with the electron beam nearly parallel to the ⟨111⟩ foil normal. In addition to the usual (220)-type reflections from the bulk, over 250 fractional surface reflections of the type $(m/5, n/5)$ are also revealed. This diffraction pattern is observed regardless of whether the area included in the selected area diffraction aperture contains defects or not. A 20-sec sputtering of the top surface with 2.5-keV Ar ions at a glancing angle of 20° (estimated to damage and/or remove a 20-Å layer) is sufficient totally to destroy the fractional surface reflections. This confirms our earlier assignment of the (5×5) RHEED pattern to the uppermost Si surface. Our TED patterns exhibit only a (5×5) reconstruction, with no admixture of (7×7). Of the surface fractional order spots, those of the $(\frac{2}{5},\frac{2}{5})$ type are the most intense.



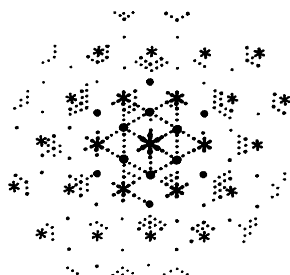


FIG. 1. Transmission-electron diffraction pattern of sample 1, after extended exposure to air, showing fractional-order reflections from the (5×5) reconstruction of the Si surface, as well as the normal (220)-type reflections from the bulk. On the schematic diagram of the observed pattern, the fractional-order spots are represented by dots, while the bulk reflections are represented by the stars.

The pattern exhibits the "star" and "$\frac{2}{5}$ hexagon" formation, normally considered a hallmark of the dimer–adatom–stacking fault structure.[6] We therefore conclude that the observed (5×5) structure is a close analog of the (7×7) structure (but see below).

We have studied this (5×5) surface reconstruction in profile,[8] both in $\langle110\rangle$ and $\langle112\rangle$ projections, by means of a JEOL 4000EX HRTEM, operating at 400 keV. The lattice images reveal normal epitaxial buried interfaces and a flat and reconstructed Si surface. The native oxide appears to be ~10 Å thick in cross section. Figures 2(a)–2(c) are respectively an experimental HRTEM profile image, the corresponding simulation, and the projected potential, in the $\langle110\rangle$ projection. Our simulations[9] and the symmetry of nearby stacking faults[10] show unambiguously that, under our imaging conditions, the tunnels are white and pairs of atom columns are black. Figure 3 is a pseudocolor representation of the experimental profile

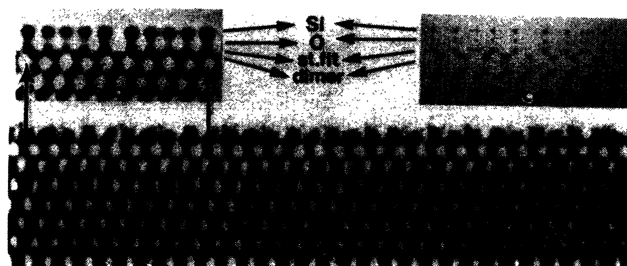


FIG. 2. (a) Experimental HRTEM profile image, (b) simulated image (Ref. 9), and (c) projected potential in $\langle110\rangle$ orientation. Scherzer defocus (-460 Å) (see Fig. 3), assumed sample thickness 70 Å. Simulation does not depend sensitively on sample thickness.

image and a digital diffractogram (DDM) of the surface region of Fig. 2(a), where the intensity levels are coded as colors of the rainbow, with red corresponding to the highest intensity level (white). The $(5(\times5))$ periodicity is clear in both the image and the DDM, firmly establishing that we have succeeded in retaining and imaging the reconstruction. Since the intensity distribution in TED (Fig. 1) closely resembles that of the (7×7) structure, we use the atom positions deduced by other techniques as the starting point for image simulation. This shows the major consequence of the (5×5) reconstruction in profile to be the presence of a chain of black, flat, v-shaped features of the surface [Fig. 2(b), ignoring layers marked Si and O]. Comparison of simulated and experimental images at three defocus values ($-350, -460, -600$ Å) suggests that the (5×5) reconstruction is buried under an ordered layer, characterized by a row of large white tunnels, above which a certain degree of order can still be discerned in the black atoms (Fig. 2). We find a best fit to this arrangement when we assume that the adatoms are removed and every dangling bond perpendicular to the surface is saturated with an oxygen atom, in turn bonded to another Si [see Fig. 2(c)], with the usual average bond lengths (1.6 Å) and bond angles (150°) for a Si—O—Si bridge, and with the bridges aligned such that the Si—O—Si arrangement appears straight in projection [see Fig. 2(c)]. Thus our modeling of the profile images strongly suggests the presence of an ordered oxide layer at the Si(5×5)-oxide interface.

We have so far described our observations that a pure Si surface can exhibit *a (5×5) surface reconstruction, which is stable against exposure to air and which leads to the formation of, and persists underneath, an ordered oxide layer.* We have experimentally ascertained that a 1000-Å Si layer grown on a (111) Si substrate in our system (sample 2), with the Ge oven hot but closed, exhibits a clear (7×7) RHEED pattern. We further find, both by RHEED and TED, that *the*

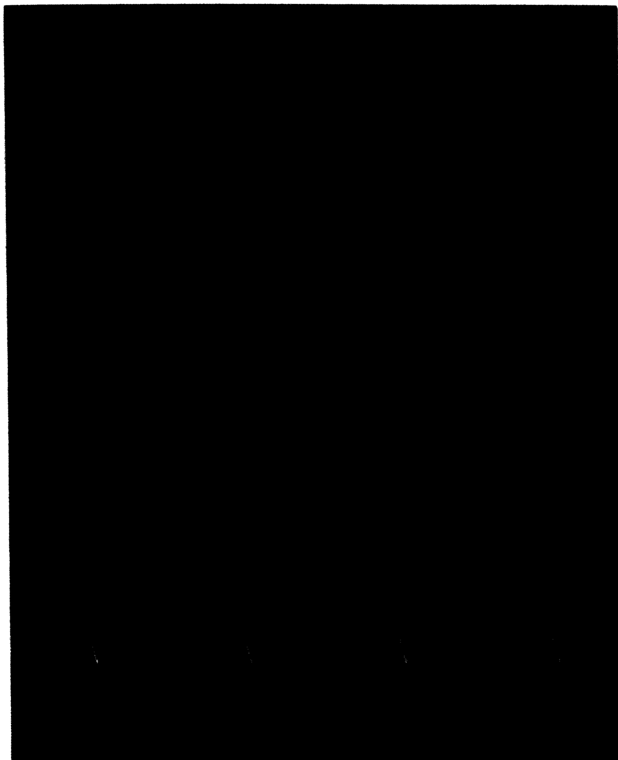


FIG. 3. Pseudocolor representation of surface region of experimental profile image of Fig. 2(a), together with its digital diffractogram (DDM). Color code is the rainbow, with red corresponding to highest intensity level (white of Fig. 2). Top inset shows the total intensity contained in each vertical column of DDM. Note the $\frac{1}{5}$-order lines between the intense long lines due to the bulk periodicity. In the profile image, note the $(5(\times 5))$ unit cell in projection, marked by arrows separated by 16.6 Å (projection of 19.2 Å).

(7×7) *does not survive exposure to air.* It is therefore important to address the origin of the appearance and stability of the (5×5) reconstruction. The presence of defects in the buried GeSi layer in our sample is a clear indication of a relaxation of the strain in this layer, and a consequent increase of its in-plane lattice parameter from that of the Si substrate towards that of GeSi. The topmost Si layer is then grown on a substrate with an in-plane lattice parameter larger than that of Si and is likely to be in tension. These inferences are confirmed by Rutherford backscattering measurements. The GeSi retains a compressional strain of only 1.5%, compared to the normal value of over 3% for $Ge_{0.5}Si_{0.5}$ layers, which are commensurate with, and exhibit an in-plane lattice parameter equal to that of, the Si substrate.[11] The topmost Si layer exhibits a tensile strain of $(0.2\pm 0.2)\%$. Such small strains are comparable with those needed to bring about a $c(2\times 8)$ to (7×7) change in Ge.[4] We therefore propose that the tensile strain present in the Si layer is responsible for favoring the (5×5) over the (7×7) surface.[12] Further evidence of the role played by a tensile strain is provided by the following two experiments. First, a sample of similar structure to that of the first sample, grown at a higher temperature (570 °C), contained a different defect density and its topmost Si layer exhibited a (7×7) reconstruction in the molecular-beam epitaxy chamber. TED examination of this sample after careful thinning at room temperature again showed that the (7×7) reconstruction does not survive exposure to air. Since most of the Si substrate is removed in the electron-transparent regions of a thinned sample, the in-plane lattice parameter in such regions is able to relax towards that of the GeSi alloy layer, thus putting the topmost Si layer in tension. We find that annealing such a thinned sample in the range 200–300 °C, in UHV, Ar, or O_2, gives rise to a (5×5) pattern in TED. Second, we have grown on a Si substrate a $Ge_{0.25}Si_{0.75}$ alloy layer, whose thickness (1200 Å) exceeds the critical value for defect-free strained epitaxy [$\sim$750 Å (Ref. 11)], allowing its in-plane lattice parameter to relax substantially towards that of the unstrained alloy. We find that a 125-Å-thick Si layer deposited on this alloy layer (i.e., grown in tension) exhibits a (5×5) pattern in RHEED and subsequently in TED. These experiments clearly show that the application of a tensile strain, during or after growth, is able to *induce* a *stable* (5×5) reconstruction in both a clean Si surface and an unreconstructed Si-oxide interface. This is qualitatively different from the *preservation* of a surface reconstruction in a *metastable* state under an amphorous Si overlayer.[13]

In the following we speculate on the significance of our observations. The strain-induced stabilization of the (5×5) surface appears so strong as to enable the surface to maintain a reconstructed arrangement after attack by oxygen. This implies that the (substantial) energy released upon the formation of a Si—O bond may be used to bring about an ordered rearrangement of the atoms so as to retain a (5×5) periodicity at the Si-oxide interface. Also, the observation of a (5×5) reconstruction brought about by tension seems to require a rethinking of the precise role that strain plays in surface reconstruction. In view of the general idea that the compression brought about by a strengthened back bond leads to the ejection of $\frac{1}{7}$ of the atoms from the topmost double layer, it is surprising that a tensile strain brings about the ejection of a larger fraction of the atoms and hence a (5×5) arrangement. Also, since the growth of an oxide is accompanied by a substantial expansion, a Si surface underneath an oxide layer may in many cases be in tension. It is therefore possible that the stable configuration of a Si-oxide interface is that possessing a (5×5) configuration. Thus it may be possible to achieve a highly ordered interface by appropriate formation of the oxide. This may have

exciting implications for the fabrication of devices, which require interfaces of exceptional perfection.

In conclusion, we have shown that a tensile strain leads to the formation of a (5×5) structure on the Si (111) surface, which survives extended exposure to air and the formation of a native oxide layer, which appears to be ordered. The (5×5) arrangement can also be induced at an originally unreconstructed Si-oxide interface by the application of tension and appropriate annealing. The most likely structure deduced from RHEED, TED, HRTEM, and Rutherford backscattering consists of bulk Si, (5×5) reconstructed Si double layer, ordered monolayer of SiO, and disordered oxide.

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[12]The presence of an admixture of (7×7) in RHEED may be due to nonuniformities in strain brought about by the inhomogeneous defect distribution. Since TED of sample 1 only reveals a (5×5) pattern, the (7×7) reconstruction presumably does not survive exposure to air, a result confirmed by our second sample.

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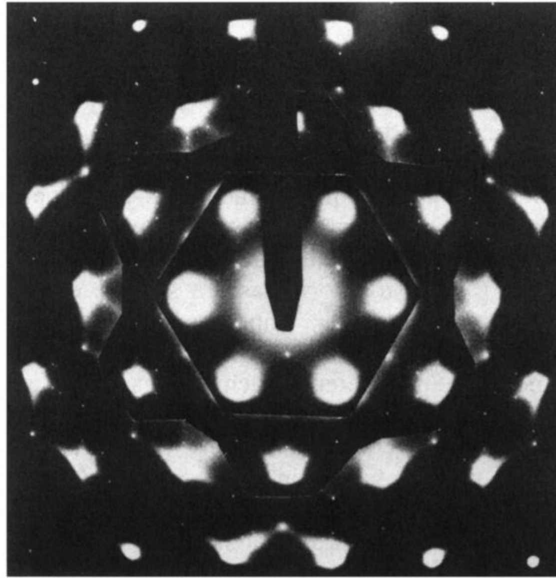

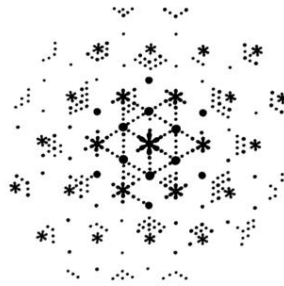

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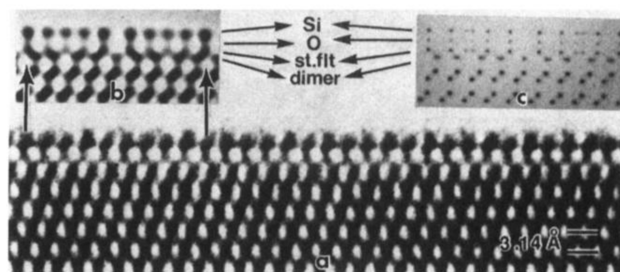

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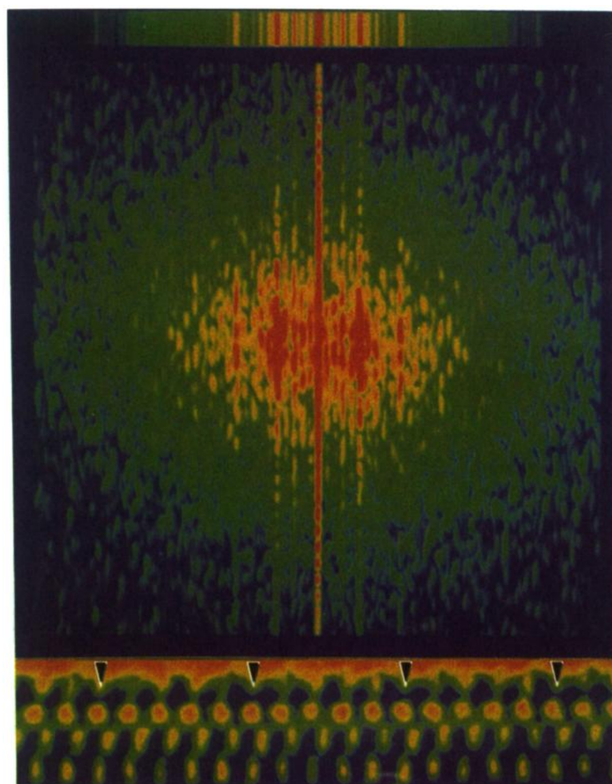

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