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Surface reconstruction in layer-by-layer sputtering of Si(111)

P. Bedrossian and T. Klitsner
Sandia National Laboratories, Albuquerque, New Mexico 87185
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Using scanning tunneling microscopy, we have investigated vacancy-mediated, layer-by-layer removal of surface atoms from Si(111) under 225-eV Xe-ion bombardment. We observe, with increasing substrate temperature, both the transition from vacancy-cluster nucleation to step retraction, and a transition from disruption to preservation of the 7×7 reconstruction on exposed material. We discuss the consequences of these observations for ion-beam-mediated epitaxy.

The interaction of low-energy (<400 eV) noble-gas ions with solid surfaces has recently attracted wide interest,[1] both as a result of the growing use of such ion beams to enhance epitaxial-growth processes[2,3] and of growing evidence that a substantial portion of the energy deposited by such beams can be confined to the near-surface region.[4] Indeed, diffracted intensity oscillations during sputtering in this energy regime, indicating layer-by-layer removal, have been reported for both a metal, Pt(111),[5] and a semiconductor, Si(100).[6] These and other reflection high-energy electron-diffraction (RHEED) studies of low-energy ion bombardment of Ge(100) (Ref. 7) were found to support a model which is analogous, but opposite to epitaxial growth; i.e., with mobile vacancies and "vacancy islands," assuming the roles of mobile adatoms and islands, respectively.

This picture has been supported by several recent scanning tunneling microscopy (STM) investigations of the sputtering of metal surfaces,[8,9] which have found that increasing substrate temperature during sputtering results in the nucleation of a lower density of laterally larger depressions, with step retraction at sufficiently high temperatures. We observe, however, that the usefulness of STM in illuminating the interaction of low-energy ion beams with solid surfaces extends beyond revealing the changing step structure of a surface during sputtering, for STM should also reveal the evolving, local surface reconstruction that might not be revealed by an averaging probe.

Here we present a real-space, atomically resolved study, using STM, of layer-by-layer sputtering of a semiconductor surface, with direct observation of the evolving reconstruction of that surface. Moreover, our results confirm that vacancy-mediated removal dominates the evolving step distribution, as reported for various metal surfaces.

The experiments were performed in an UHV chamber with a 7×10^{-11} torr base pressure. Samples of Si(111) were initially cleaned chemically,[10] and then transferred to the UHV chamber, where they were flashed to 1150 °C to remove the oxide left by the chemical process. A sharp 7×7 pattern was observed with low-energy electron diffraction (LEED). Sample temperatures during Xe bombardment were calibrated with an infrared pyrometer. Immediately following ion exposure, the samples were quenched to room temperature to permit imaging with the STM. The Xe flux is estimated at 0.33 μA/cm^2.

Figure 1 illustrates the layer-by-layer nature of successive stages of sputtering of Si(111) by 225 eV Xe at 250 °C. Initially [Figs. 1(a) and 1(b)], the ion beam induces the formation of monolayer-deep depressions, while the undisturbed, surrounding material retains the reconstruction of the starting surface [Fig. 1(b)]. With the further removal of most of one monolayer [Figs. 1(c) and 1(d)], the 7×7 reconstruction remains only on the monolayer-high islands, which are relics of the starting surface. The exposed material, while atomically flat, is a disordered adatom phase with no *long-range* reconstruction. The 7×7 periodicity vanishes from the LEED pattern, leaving only 1×1 spots. A similar, disordered adatom phase also occurs for laser annealed Si(111).[11]

At a higher substrate temperature (550 °C), sputtering initially creates depressions of lower density but larger extent [Fig. 2(a)]. The depressions now tend towards hexagonal shapes, bordered by monatomic steps along the unit-cell borders. A higher-resolution view [Fig. 2(b)] of the box in Fig. 2(a), showing a single-height step forming the boundary of one depression, demonstrates that now the material exposed by the sputtering process, though decorated by phase boundaries, is predominantly 7×7 reconstructed, with 7×7 domain widths exceeding 100 Å. With further sputtering [Fig. 2(c)], the depressions coalesce into larger entities, with the retraction of steps visible on a large scale. A sharp 7×7 LEED pattern was obtained from each of the surfaces represented in Fig. 2.

It has been proposed that low-energy sputtering of both metals[5] and semiconductors[6,7] is dominated by the creation of mobile surface vacancies. A close analogy therefore exists between deposition and sputtering in this regime. Epitaxial growth involves mobile adatoms which nucleate islands and migrate to steps; removal by low-energy sputtering involves mobile vacancies which nucleate "vacancy islands," or depressions, and annihilate at step edges. Just as Si *deposition* at the temperature represented in Fig. 1 is associated with island nucleation and RHEED oscillations,[12,13] the removal in Fig. 1 involves the nucleation of a high density of small depressions. We note that this observation is consistent with the observation of RHEED oscillations during sputtering of Si(100) at comparable temperatures and incident Xe energy.[6] The observed lack of preservation of the 7×7 reconstruction in Fig. 1 after sputtering parallels previous STM studies of Si(111) homoepitaxy, in which Si deposited at comparable temperatures nucleated small unreconstructed islands.[14]

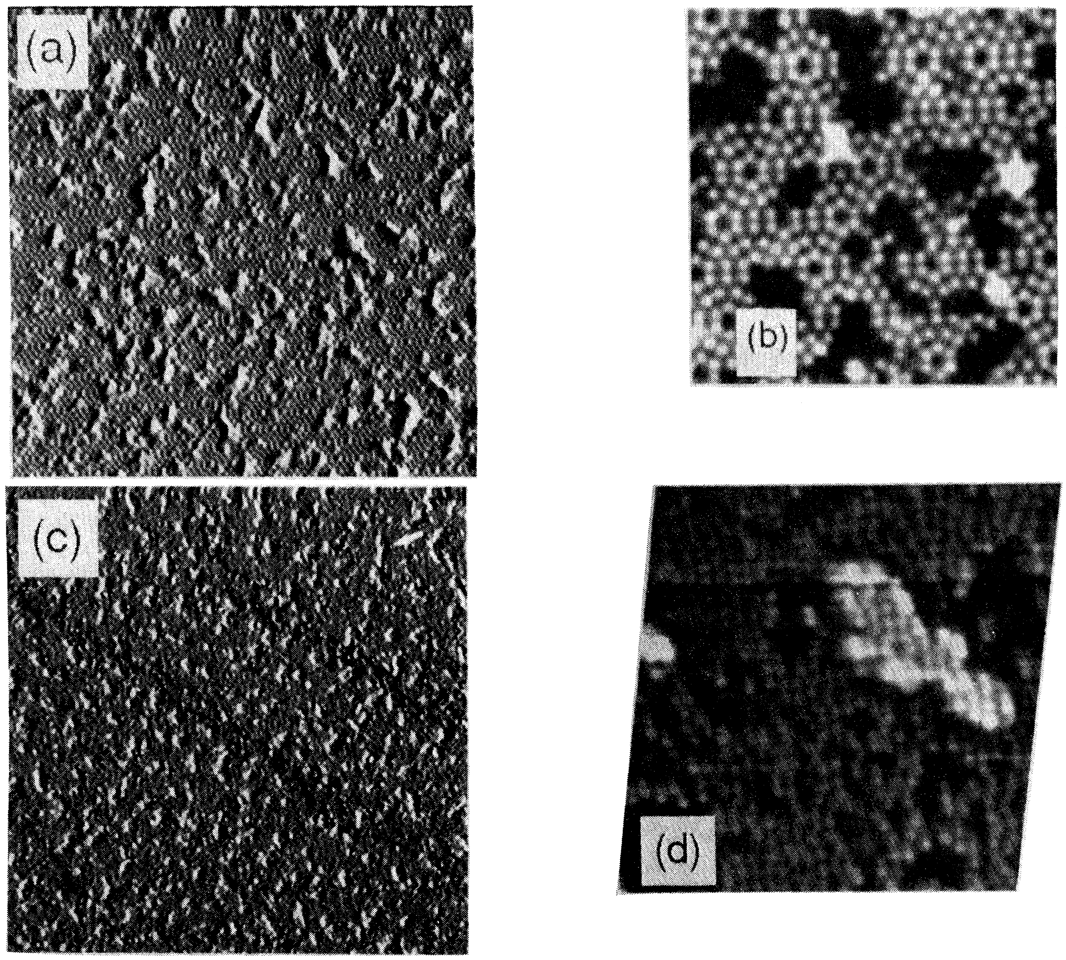

FIG. 1. (a) 500-Å STM image, displayed with the grey scale keyed to the height gradient, of the initial stages of sputtering of Si(111) by 225 eV Xe at $T=250\,^{\circ}\mathrm{C}$, showing depressions within the 7×7 surface. Tip bias $=-1.8$ V. This and later gradient images should be viewed as if a light source is incident from the left. White lines represent atomic steps upward from left to right, and dark lines represent atomic steps downward from left to right. (b) 150-Å detail of Fig. 1(a), with the grey scale keyed to the height, showing the remaining adatoms of the starting surface. (c) 2000-Å gradient image after further sputtering, showing monolayer-high islands with most of one layer removed. The arrow indicates one island. (d) 150-Å detail of Fig. 1(c), with the grey scale keyed to the height, showing a one monolayer-high island and the exposed layer without long-range order. In this height image, the exposed island is brighter than the surrounding layer.

Pursuing the analogy with growth, we note that *deposition* at successively higher temperatures has been associated with the nucleation of islands of successively larger width but lower density, eventually reaching a transition to growth by step flow when the elevated mobility of a deposited adatom enables its migration to a step edge before nucleating a new island. This regime has been associated with a disappearance of RHEED oscillations,[15] and the associated increase in island size has been observed with STM on Si(100).[16] Elevated substrate temperature has also been associated with the disappearance of RHEED oscillations during sputtering of Si(100),[6] indicating a transition to step retraction by analogy with growth.

The larger size of the depressions in Figs. 2, compared with Fig. 1(a), is consistent with elevated vacancy mobility at these temperatures. Moreover, both the shape of the depressions in Fig. 2 and their atomic reconstruction closely parallel STM studies of Si(111) homoepitaxy, which reported an increasing tendency toward both hexagonal island shapes and 7×7 reconstruction of the deposited islands with increasing temperature.[14] In Fig. 2(a), we observe the depressions only on the widest terraces; their absence on the narrower terraces indicates that a vacancy created on such a terrace can reach a step edge before nucleating a new depression. Therefore, we observe sputter-removal dominated by step retraction on such terraces. While bunching of steps appears in Figs. 2(a) and 2(c), the absence of true double steps is consistent with previously observed interstep repulsion on Si(111).[17]

We note here that a picture of mobile vacancy-mediated sputtering, as explained above, does not *uniquely* account for layer-by-layer removal, which could also result, for example, from preferential sputtering of atoms from step edges. However, the latter mechanism would

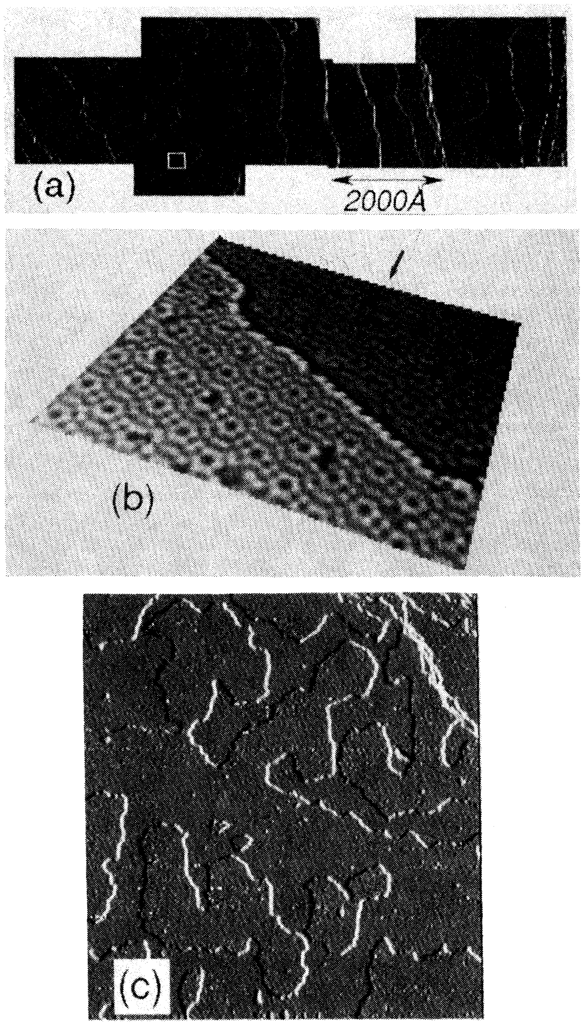

FIG. 2. (a) Collage of 2000-Å gradient images showing large depressions on the widest terrace, after 225-eV Xe sputtering at $T=580\,^{\circ}\mathrm{C}$. The bright lines represent upward steps from left to right. (b) 150-Å detail of the boxed region in Fig. 2(a), showing the 7×7 reconstruction on either side of the monolayer-high depression boundary. The arrow indicates a 7×7 phase boundary in the exposed layer. (c) 2000-Å gradient image after further sputtering, showing the coalescence of depressions.

not imply a strong dependence of depression width on sample temperature; therefore, our observation of such a temperature dependence confirms that a mobile species, rather than preferential sputtering, dominates layer-by-layer removal. The observation of depressions indicates that the mobile species is a vacancy, rather than an adatom.

The transition from growth dominated by nucleation to growth dominated by step flow can be driven to lower temperature by decreasing the terrace lengths on the substrate material. Samples with higher misorientations will therefore exhibit step flow at lower temperatures.[18] By analogy, a similar terrace-length dependence for the onset of step flow would apply to vacancy-mediated sputtering. However, the temperature range over which sputtering preserves the 7×7 reconstruction would not be expected to depend strongly on the sample misorientation for terrace widths larger than several 7×7 unit cells. We find that, as a consequence of this, for a misoriented Si(111) sample, the onset of step flow can be driven below the temperatures required to preserve the 7×7 reconstruction during sputtering.

This is shown in Fig. 3, where brief sputtering exposes unreconstructed material adjacent to a step edge that has been retracted. In the figure, a sharp boundary in the vicinity of a step separates a region of apparently undisturbed 7×7 periodicity, characteristic of the starting surface, from a band containing a variety of local, metastable reconstructions but no long-range order. The step edge, the unreconstructed band, and the sharp boundary can be followed across the available scanning range of the instrument. In the context of vacancy-mediated sputtering, the unreconstructed band represents material exposed by the sputtering process, and the sharp boundary can be identified with the path of the original step edge, before sputtering. We observe here that the structure pictured is unlikely to be accessible easily with growth alone. Therefore, such an image underscores the possibility of using ions both alone and in concert with deposition to produce similarly novel structures, as well as the capability of the STM to characterize such structures.

Epitaxial growth on 7×7 reconstructed Si(111) involves a sequence of complicated rearrangements, including the breaking of dimers and the removal or upward propagation of the stacking fault in one-half of each 7×7 unit cell. However, the images in Figs. 1 suggest the possibility of using sputtering to remove the long-range reconstruction, hence, to lower the activation barrier for epitaxial growth. Moreover, Fig. 3 demonstrates that the surface can be dereconstructed locally and preferentially near a step edge. In view of the profound influence that surface reconstruction can have on film growth,[19] this observation suggests that the mode of epitaxial growth might be altered deliberately in the vicinity of a step edge by ion bombardment.

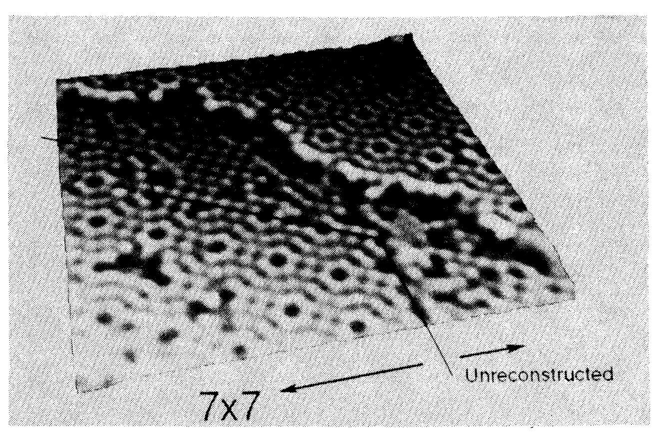

FIG. 3. 150-Å image showing step retraction at 400 °C. The line separates the 7×7 region from newly exposed, unreconstructed material.

We have used Xe ions in this work in order to maximize the mass difference between the incident noble gas ions and the target Si atoms, with the aim of minimizing the energy transfer to the silicon for a given incident beam energy. The ratio of bulk to surface damage would be expected to increase with the energy transfer. Indeed, calculations have predicted a greater ratio of energy deposited on the surface to that deposited in bulk for Xe ions incident on Si than for Ar ions.[4] Further experimental work might address the effects of the incident ion mass on vacancy-cluster nucleation, step retraction, and preservation of the surface reconstruction during sputtering.

In summary, we have investigated layer-by-layer sputtering of Si(111) on the atomic level. The gross features of depression size and distribution and step retraction support a picture of vacancy-mediated sputtering of a semiconductor surface, and the evolution of the reconstruction at various temperatures parallels previously reported, analogous growth processes. Within a specific temperature window, the width of which will depend on the substrate misorientation, sputtering by step retraction can be observed together with the disruption of the 7×7 reconstruction.

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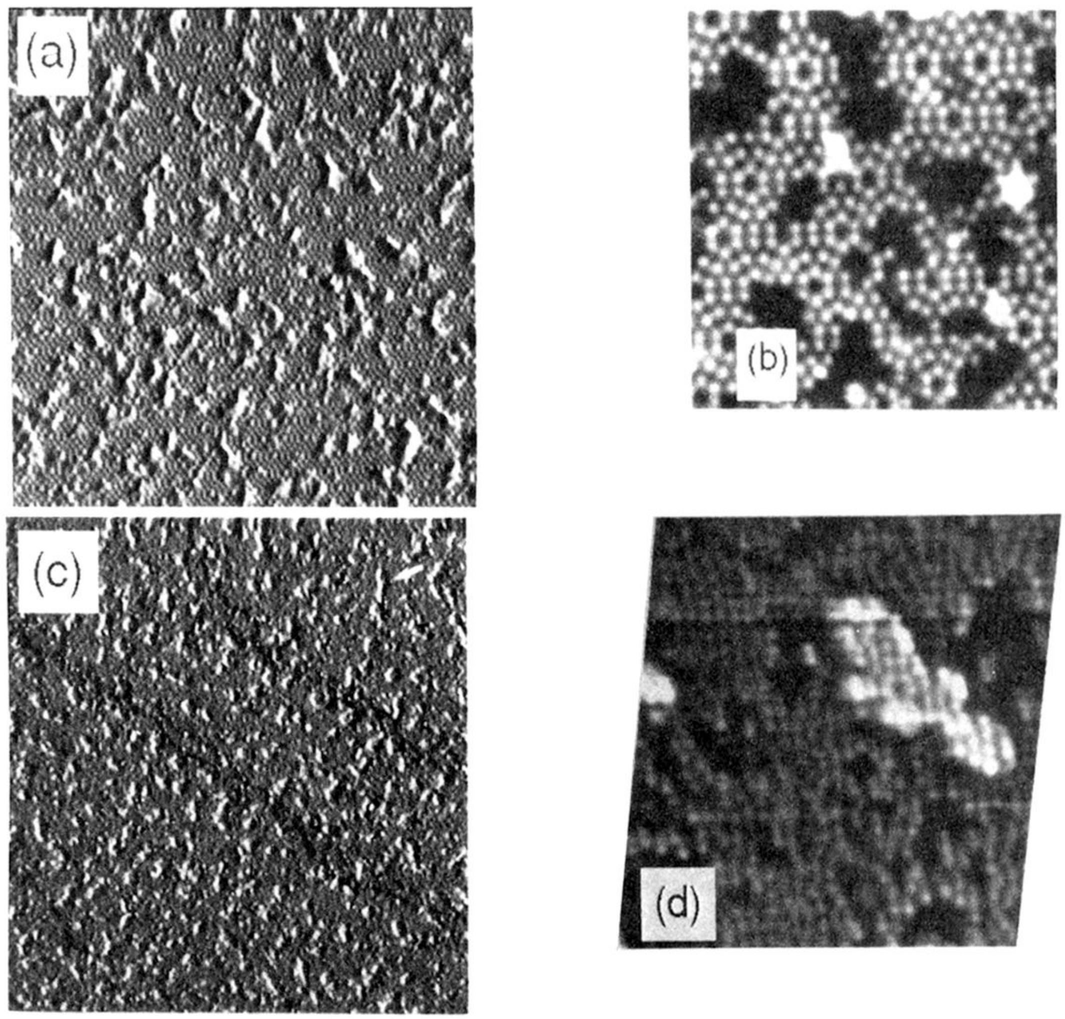

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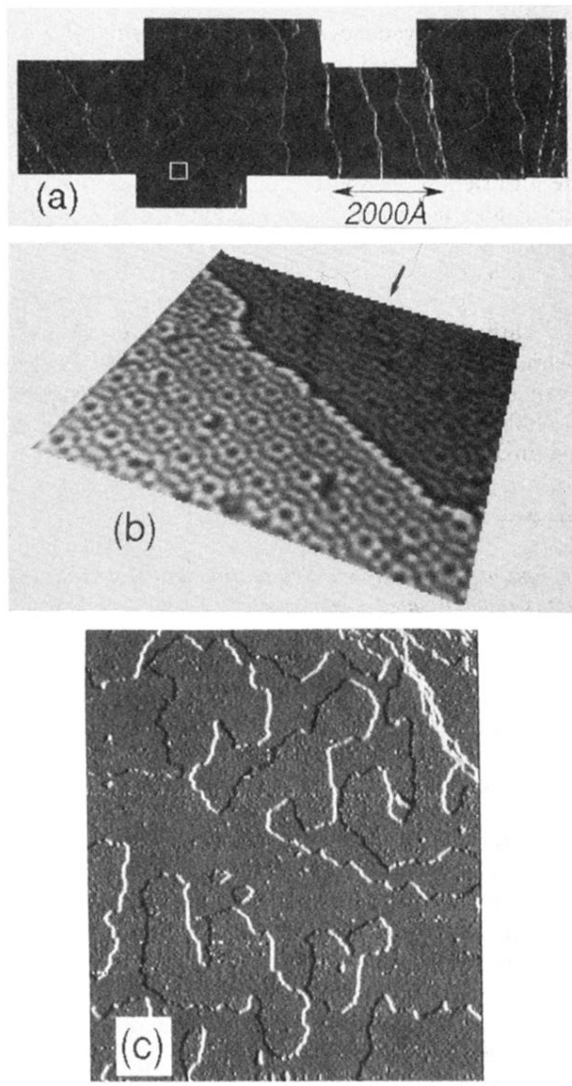

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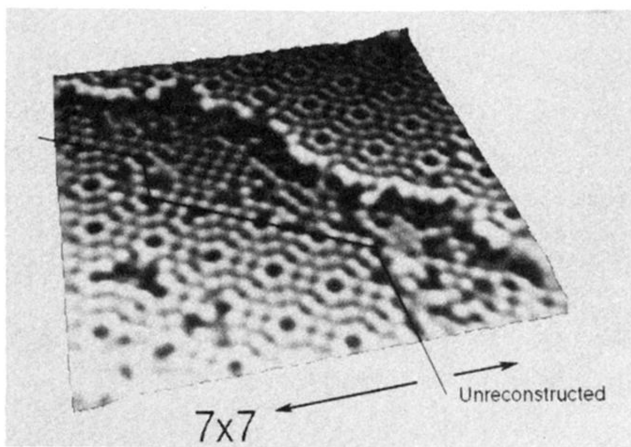

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