Direct Observation of Atomic Structures and Reconstructions of Silicon Surfaces: A Field-Ion-Microscope Study

H. M. Liu,[a] T. T. Tsong, and Y. Liou
Physics Department, The Pennsylvania State University, University Park, Pennsylvania 16802
(Received 27 January 1987)

Well-ordered atomic structures of silicon surfaces have been obtained with the field-ion microscope for the first time. Two distinctive atomic structures coexist for the {130} surface. These two structures can be formed by slightly different lateral displacements of atoms in the (1×1) layer. The {123} surface shows a rhombic structure with an angle of $79° \pm 3°$. Two-dimensional defects can also be seen in all these surfaces. An atom-probe analysis shows that no impurity atoms are present in these surfaces.

PACS numbers: 68.35.Bs, 61.16.Fk, 61.55.Dc

During the last twenty years, silicon surfaces have been extensively studied with a wide variety of techniques as a result of fundamental scientific interest, and also of technological importance of this material. A subject of continuous intense effort has been the surface reconstruction of silicon surfaces since it is of basic theoretical interest and it may also play an important role in the epitaxial growth of different materials on silicon surfaces.[1] The best studied of silicon surfaces are the {111} and {001} planes. The study of the reconstruction of these surfaces has recently gained a powerful microscopic tool, the scanning tunneling microscope, and many interesting results have been obtained.[2] There seem to be very few atomic-resolution-microscope studies of other silicon surfaces. We report here a field-ion-microscope (FIM) observation of atomic structures of silicon surfaces, particularly the {130} and {123} planes.

It is well known that FIM is capable of imaging metal and alloy surfaces and some other compound surfaces with atomic resolution.[3] Most early studies, however, focused on the atomic structures of field-evaporated surfaces. Only very recently the (1×2) reconstruction of the Pt(110) and Ir(110) planes[4,5] and the (1×5) reconstruction of the Ir(001) plane[6] have been clearly observed in the FIM for annealed and thermally equilibrated surfaces. For semiconductors such as silicon, field evaporation is somewhat sporadic because of the large field-penetration depth, ~10 Å or several atomic layers,[7] and the nature of chemical bonds, covalent, of this material. No atomically well-ordered FIM images of Si have so far been obtained despite considerable effort of many investigators for over the last 25 years. Here we will show for the first time that atomically well-ordered images of Si can be obtained with the FIM for thermally annealed Si emitter surfaces. We also report observation of new reconstructions of some surfaces.

Silicon tips are prepared from [111]-oriented high-purity silicon whiskers by electrochemical etching in $HNO_3+CH_3COOH+HF$ mixed solution.[3] For best results one must install a freshly etched tip into the FIM and then pump it down to good vacuum quickly to minimize the problem of oxide layers. Also, not only does the etched tip have to be sharp, but also the surface has to appear very smooth in the optical microscope. The FIM is then subjected to an overnight bakeout to achieve vacuum in 10^{-10} Torr range. Our FIM is equipped with a Displex refrigerator and the tip temperature can be varied from 15 to 300 K. The Si tip is first field evaporated at 60 K in Ne, then at 15 K in He until the surface is well developed to show low-index planes. It is necessary to shine a beam of light on the tip shank to reduce the resistivity of the tip by the photoconductivity effect. In order to obtain atomically well-developed images of the Si tip, a very elaborate cleaning procedure of the sample must be followed. Usually the tip has to be

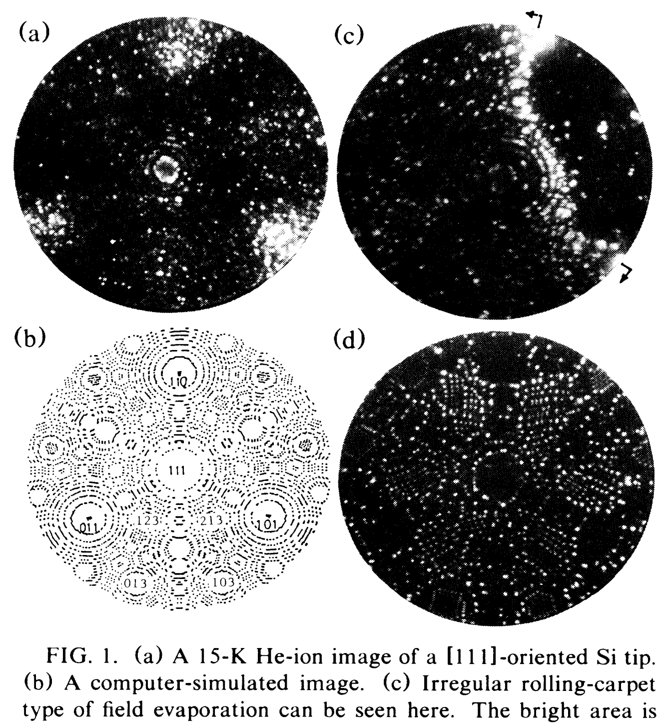

FIG. 1. (a) A 15-K He-ion image of a [111]-oriented Si tip. (b) A computer-simulated image. (c) Irregular rolling-carpet type of field evaporation can be seen here. The bright area is the field-evaporating boundary. (d) A 60-K Ne-ion image of the same tip after annealing in UHV to $800\pm50\,°C$ for ~5 min.

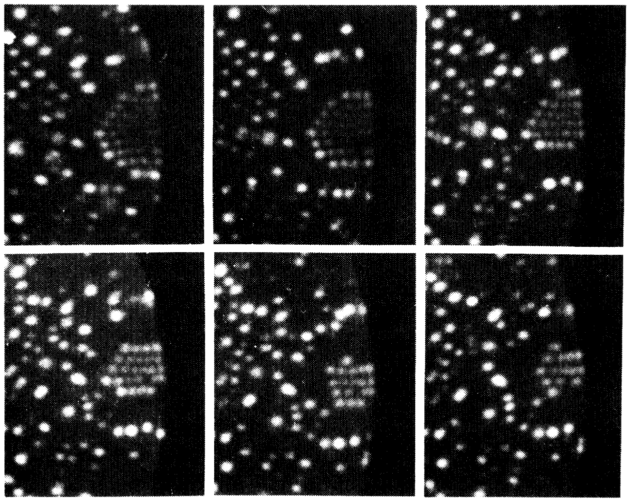

FIG. 2. Field-evaporation sequence of a reconstructed surface of the Si(130) plane developed by thermal annealing at 800 °C.

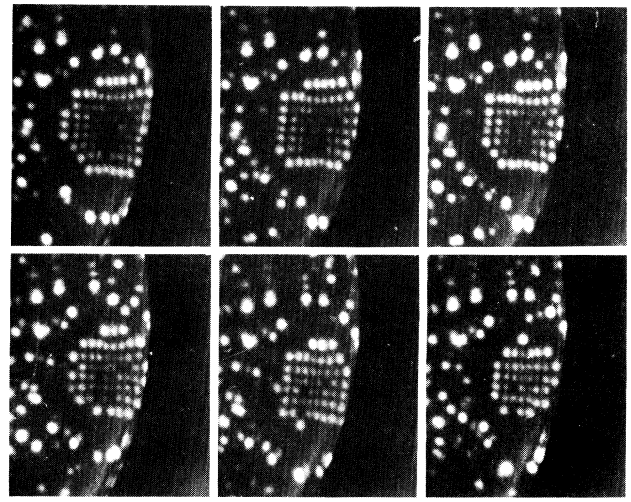

FIG. 3. Field-evaporation sequence of another reconstructed Si(130) plane formed by thermal annealing at 800 °C.

degassed to 800 °C for several to ~30 min and the system is then baked again. Good results are obtained only after repeating this procedure several times to achieve high cleanness of the tip and the shank.

In Fig. 1(a), a 15-K He field-ion image of a field-evaporated (111)-oriented Si tip surface is shown. Although no well-developed atomic structures of the surface can be seen, ring structures are well developed and identification of crystal planes can be reliably made. Figure 1(b) is a computer simulation image of this surface. In high-purity He, field evaporation of Si is sometimes quite irregular. It may start from a high–defect-density region near the tip shank, and several surface layers may evaporate together like a rolling carpet, as seen in Fig. 1(c). By a quick lowering of the tip voltage, a new surface similar to Fig. 1(a) can be obtained again. Figure 1(d) shows an atomically well-developed Ne-ion image of a Si surface right after annealing to ~800 ± 50 K for about five minutes of a field-evaporated surface. No field evaporation of the surface layers is done. To make sure that this atomically well-ordered annealed surface is not images of compound layers of Si, we have analyzed these surfaces in the pulsed-laser time-of-flight atom probe.[8] No impurity atoms are detected. We must conclude that the atomic structures seen represent those of pure Si surfaces.

For the annealed surface shown in Fig. 1(d), the central (111) plane is too large, and the atomic structures cannot be seen. Presumably it is a (7×7) reconstructed surface. As field evaporation is somewhat sporadic, we are unable to derive the structure of this surface by field evaporation. Atomically well-ordered image structures are, however, found for most high-index planes, such as the {130} and {123} planes as shown in Figs. 2, 3, and 4. Two distinctively different atomic structures coexist as can be seen in Fig. 1(d). One (Fig. 2) shows a rhombic structure of angle 60° ± 3° and sides of approximately 5.5 ± 1.1 Å and 6.5 ± 1.3 Å. The other (Fig. 3) shows a rectangular structure of sides 6.5 ± 1.3 Å and 5.5 ± 1.1 Å. The size is estimated from the tip radius and the best image voltage, and also the expected resolution, and is no better than ± 20% since field-ion images suffer large image distortions and large variations in magnification. Angles are measured from enlarged images and the uncertainty is estimated to be ± 3°. Both of these structures do not fit the (1×1) structure of the Si{130} plane which is shown by dots in Fig. 5. However, a good agreement with the two image structures can be obtained if one allows surface atoms to make lateral displacements of 0.68 Å from dotted positions to the grid points shown in Fig. 5. In Fig. 4, the image structure of the Si{123} plane is shown. It has a paired rhombic structure of unit cell size ~11 ± 2.2 Å by 6.6 ± 1.3 Å with an angle of 79° ± 3°. The (1×1) structure of the Si{123} plane is also shown in Fig. 5. It has also paired rhombic structure, but the unit-cell size is 9.40 Å by 6.65 Å, and the angle is 61.9°. Although the unit-cell sizes agree

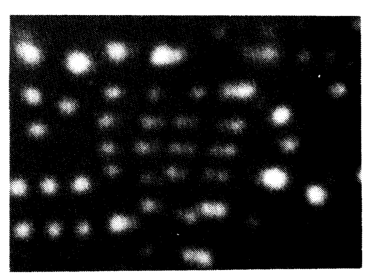

FIG. 4. Ne image of a reconstructed Si(123) plane.

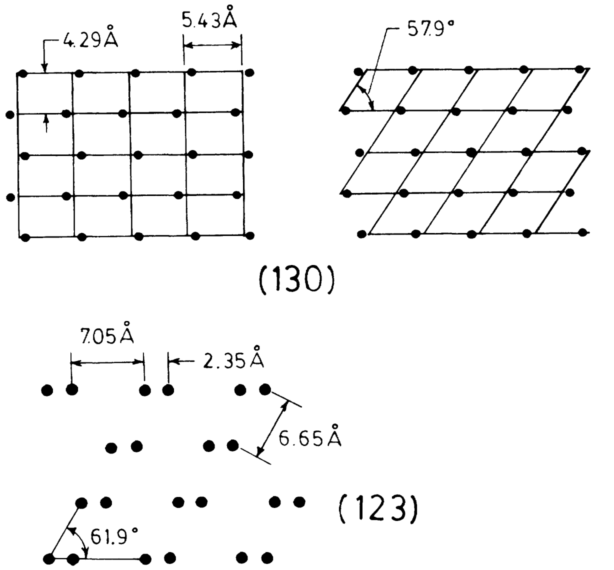

FIG. 5. The (1×1) structure of the Si(130) surface is shown by dots. By two different sets of lateral displacements of atoms, two structures resembling the image structures are obtained as shown by the rectangular and rhombic grids. The (1×1) structure of Si(123) plane is rhombic with paired atoms. Displacements in both cases are ~0.68 Å.

within experimental uncertainties, the difference in angle is much too large. We must conclude that the {123} planes are also reconstructed. To determine atomic structures by micrographs alone is, in general, not accurate. We therefore hope that our result will stimulate interest in studying surface reconstruction of high-index planes of silicon by other techniques. When such information is available, more reliable structures and atomic arrangements can then be made from the field-ion images.

Another interesting observation that we have made of these surfaces is the existence of a very high density of two-dimensional defects in all these surfaces as shown in Fig. 6. Defects observed include vacancies, a missing atom in a pair, variations in atom-row spacing, etc. When a plane is large, atoms near the center of the plane appear much dimmer and can be mistaken for vacancies. Only if an atom image does not show up after the plane is gradually reduced in size by field evaporation is it a true vacancy.

We would like to point out that although most studies of atomic structures of silicon surfaces focus on the {111} and {100} planes, the {130} plane and some other high-index planes may also be interesting and important. Our recent studies indicate that thin layers of silicides of Rh, Ir, Pt, and Pd are grown preferentially on the Si{130} plane, also with well-ordered interfaces.[9] It is well known that the electronic and atomic properties of Ohmic contacts and Schottky barriers in semiconductor devices and very large-scale integrated circuits depend mainly on the interface atomic structures.[10] Our finding that two distinctively different atomic structures can be formed on the same plane at the same annealing temperature is also interesting. This is the first time that atomically well-resolved images of Si have been obtained with the FIM, even though many attempts have been made by many people over the last 25 years. A unique capability of field-ion microscopy is the ability to analyze the composition of these surfaces. We did not detect impurity atoms in these surfaces with our pulsed-laser atom probe.

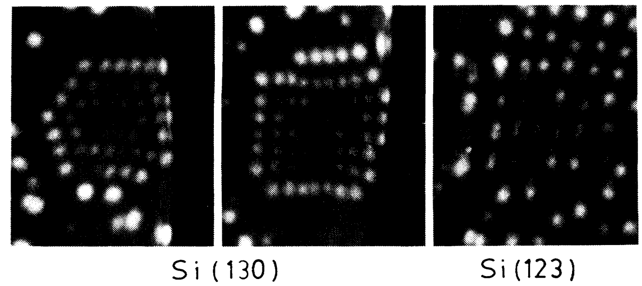

FIG. 6. Two-dimensional surface defect structures seen on the {130} and {123} surfaces of Si.

This work was supported by the National Science Foundation under Grant No. DMR-86-09269. We thank Dongli Feng for her help in the (1×1) structure of silicon surfaces.

[a]Visiting scholar from Dalian Marine College, Dalian, The People's Republic of China.

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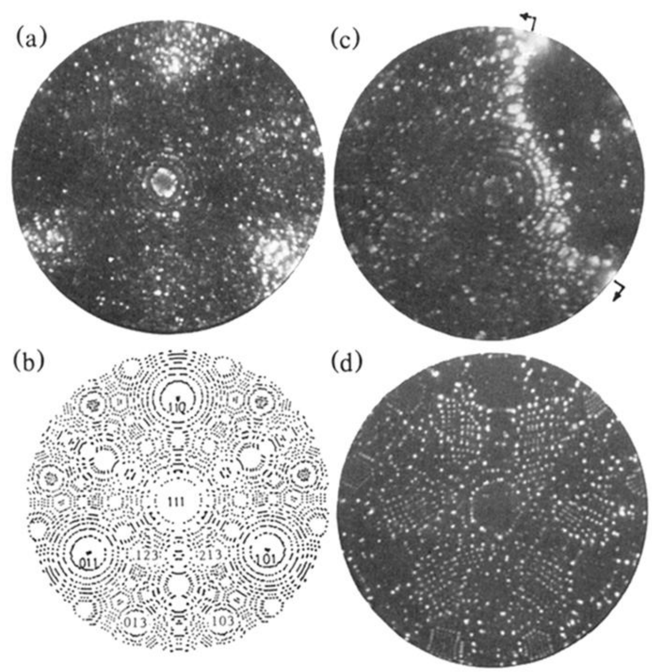

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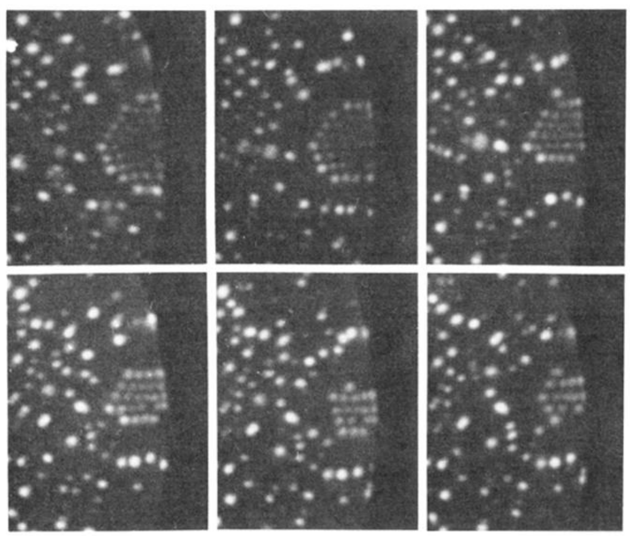

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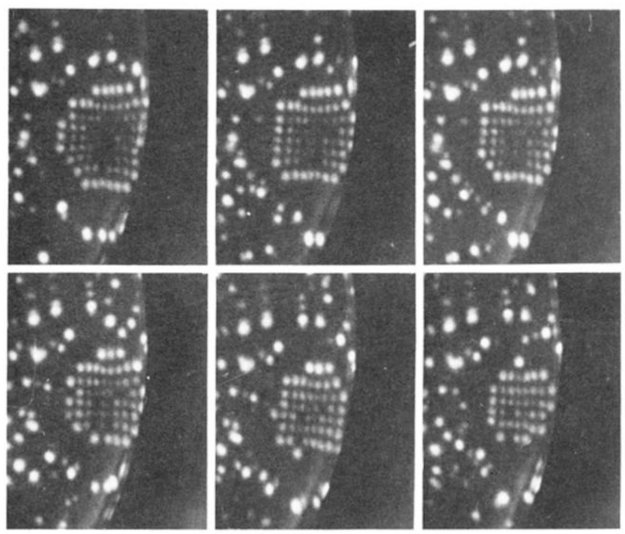

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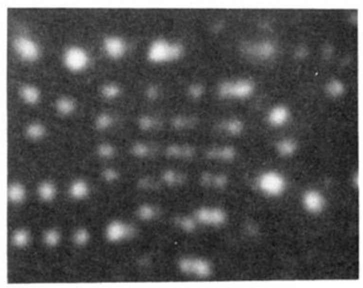
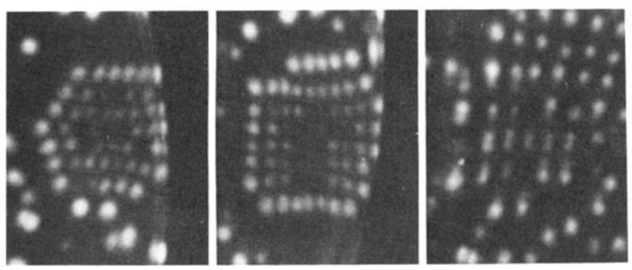


FIG. 4. Ne image of a reconstructed Si(123) plane.



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