RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 8 15 SEPTEMBER 1988-I

Oxidation of Si(111)-(7×7) as studied by scanning tunneling microscopy

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(Received 9 May 1988)

The initial stages of oxidation of the Si(111)-(7×7) surface were studied via scanning tunneling microscopy. Images of the same area of the surface were obtained for various exposures of oxygen. The results show that defect sites act as nucleation centers for the oxidation process. Straight atomic steps commonly found on this surface are relatively insensitive to oxygen exposure.

Scanning tunneling microscopy has rapidly become a useful tool for the surface scientist. It has revealed the symmetry of the Si(111)-(7×7) reconstructed surface[1] and provided strong evidence for the dimer-adatom-stacking fault model proposed by Takayanagi, Tanishiro, Takahashi, and Takahashi.[2] The scanning tunneling microscope (STM) has also revealed previously unobserved reconstructions on the Si(111) surface.[3] Another property of the STM is that it can be used to observe dynamic systems. For instance, recently Jaklevic and Elie observed the diffusion of Au atoms on a Au(111) surface as it annealed.[4]

In this study, we use a STM to do time-lapse topography and have observed the initial stages of the oxidation of Si(111)-(7×7). The adsorption of oxygen on Si surfaces has been studied with a variety of techniques.[5-8] These surfaces have technological relevance in that the preparation of thin, insulating oxide layers is of importance in the manufacture of semiconductor devices. From previous studies it is known that oxidation of Si(111) does not lead to an ordered reconstruction, and the presence of several oxidation states extending spatially beyond a monolayer at high exposures indicates that the reaction process is rather complex and nonuniform. Since most surface techniques sample a fairly large area on the sample surface, only the spatially averaged behavior is determined. Thus, important questions remain unanswered. For instance, the presence of cleavage defects on GaAs(110) is known from photoemission studies to significantly enhance the oxidation rate for this surface.[9] It is natural to speculate that defects and/or atomic steps on the Si(111)-(7×7) surface might have a similar effect. The present STM investigation with atomic resolution provides evidence for the important role of surface defects in the oxidation process.

The STM used in this study is fairly similar to that described by Demuth, Hamers, Tromp, and Welland in that the sample is mounted on a lever which allows the sample to be moved into positions suitable for STM, high-energy electron diffraction (HEED), deposition of material, and sputtering.[10] The main difference is that in the present design, the pivot wedge pushing against the sample surface as described in Ref. 10 is replaced by two pivot wedges off the sample surface to eliminate surface damage problems. The vacuum chamber has a base pressure of about 1×10^{-10} Torr. The Si(111) samples used were cut from a commercial *p*-type waver, with a resistivity of 1–10 Ω cm, into a 6.4×18-mm^2 rectangle. The samples were etched with nitric acid. After a sample was inserted into the vacuum chamber and the base pressure was reached, the sample was outgassed at about 300 °C for many hours. Sample heating was achieved through resistive heating by passing a current through the sample itself. The clean (7×7) surface was generated by thermal annealing to roughly 1100°C for about 10 sec to remove the surface oxide layer. The reconstruction was verified with HEED. After thermal annealing, it was necessary to wait for about an hour for the thermal drift to reduce to an acceptable level for taking the STM images.

During the experiment, a given region on the sample surface was, repetitively, scanned while oxygen was allowed to enter into the vacuum chamber via a precision leak valve. The oxygen pressure could be monitored and measured via a nude ion gauge or by observing the ion current of the ion pump on the system. To avoid ionizing the oxygen the ion gauge was turned off during the course of the STM experiment. Oxygen adsorption was carried out at nearly room temperature. Each STM image typically covered a 500×500 Å^2 area with a 512×512-pixel resolution, and was acquired in about one minute. During each scan, the tunneling tip remained above a particular site only about 0.01% of the time; thus, blockage of oxygen molecules by the tip was negligible. The tungsten tip was sensitive to oxygen exposure; therefore, most of the many experimental runs had to be aborted due to sudden irreversible changes of the tip. However, the general characteristics of the sample oxidation process as discussed below were reproducible.

The results indicate that large defect-free areas on the surface are fairly insensitive to oxygen exposure; after an exposure of about 50 L (1 L = 10^{-6} Torr sec) the images typically show no appreciable changes except for a few atomic sites or patches randomly distributed in an area of 500×500 Å^2. Long straight atomic steps on the surface as described by Becker, Golovchenko, McRae, and Swartzentruber appear to be equally insensitive to oxgyen exposure.[11] However, if the starting surface has a substantial number of defects, then the overall oxidation rate is significantly enhanced. The details can be seen in Fig. 1, which shows a typical set of STM pseudo-grey-scale

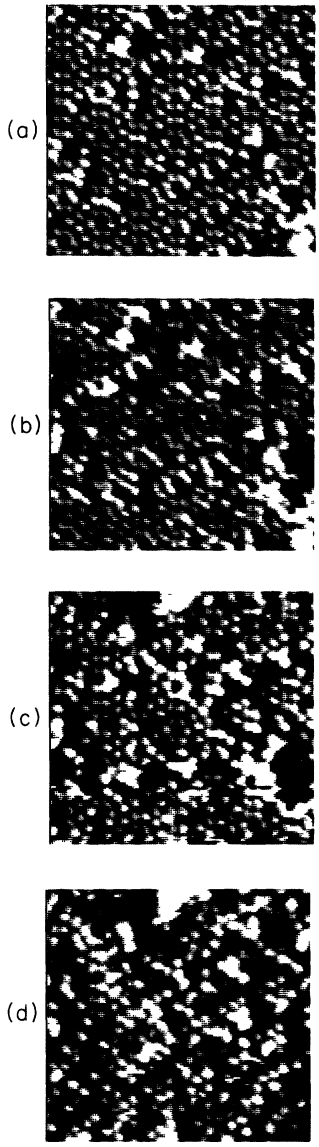


FIG. 1. STM pseudo-grey-scale images of oxygen on Si(111)-(7×7) for (a) 0-, (b) 2.4-, (c) 4.0-, and (d) 8.6-L exposure. Protrusions and depressions on the surface are represented by bright and dark regions, respectively.

images for a given area (about 160×160 Å^2) on the surface. The oxygen exposures are 0, 2.4, 4.0, and 8.6 L for the four images. For this set of data, the STM was operated in constant current mode with a tunneling current of 1 nA and the sample biased at +2 V relative to the tip.[12] The images are presented with dark areas corresponding to depressions on the surface. A slight distortion of the images in the xy plane due to thermal drift has not been corrected.

Figure 1(a) shows the STM image of the starting surface. The experimental conditions are such that the adatoms appear as protrusions in the image, and one observes many (7×7) unit cells with twelve adatoms (protrusions) in a unit cell and four deep holes at the four corners of a rhombic unit cell.[1,2,12] This particular surface had been thermally annealed for a longer time at a higher temperature than the usual conditions for generating the best surfaces. Therefore, a number of defects are present, which have the appearence of missing adatoms in the image. The nature of the defects is not known (STM shows a convoluted partial density of electronic states, not the atoms). The area of the image contains 493 adatom sites, for which 241 are corner adatom sites and 252 are center adatom sites. The corner adatoms are those adatoms surrounding a corner hole, and the center adatoms are those adatoms separated from the corner hole by corner adatoms. There are six of each kind in a unit cell. If this image is compared with that taken from a defect-free sample, a defect density of 15.4% is obtained, with 3.9% due to "missing corner adatoms" and 11.5% due to "missing center adatoms." If one examines other images of the Si(111)-(7×7) surface found in the literature,[11,13] one observes that one is more likely to see missing center adatoms than corner adatoms, consistent with our finding.

To aid viewing the oxidation process, we have recreated the images in Fig. 2 using circles to indicate the adatom sites. The outlines of the unit cells are also shown. The filled circles represent the missing adatoms on the starting surface [Fig. 1(a)]. The image in Fig. 2 does not have a square boundary due to thermal-drift distortion of Fig. 1.

When oxygen is adsorbed on the surface, the oxygen atoms do not necessarily yield protrusions in the STM images. They could appear as depressions. This is because the STM senses the local partial electronic density of states which may be either increased or decreased by adsorption depending on the nature of the chemisorption bond.[14–16] The images also appear different for different bias voltages. Lacking a detailed theory for comparison, we will not attempt to interpret the detailed changes here. Figures 1(a)–1(c) show that for the bias conditions used here, the initial oxygen adsorption causes the appearance of depressions on the surface; thus, more adatoms (pro-

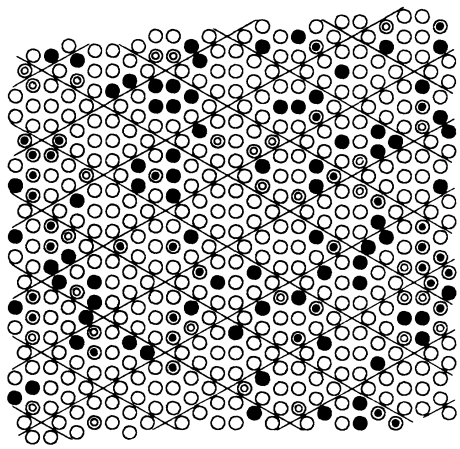


FIG. 2. Schematic diagram representing the images shown in Fig. 1. The lines indicate the surface (7×7) unit cells. The adatom sites are shown as circles. The "missing-adatom defects" in the image of Fig. 1(a) are indicated by filled circles. Newly generated "missing adatoms" in Figs. 1(b) and 1(c) are indicated by circles with a smaller filled circle at the center and circles with a smaller open circle at the center, respectively.

trusions) on the surface appear to be missing with increasing exposure. The newly-oxygen-induced "missing adatoms" in Figs. 1(b) and 1(c) are indicated in Fig. 2 by circles with a smaller filled circle at the center and circles with a smaller open circle at the center, respectively. The observation of depressions induced by oxygen adsorption is consistent with the expectation based on the theoretical model of Ref. 14. Oxygen is more electronegative than Si, and its adsorption causes a reduction in the state density at energies significantly above the Fermi level. The reduction of the state density requires the tunneling tip of the STM to move closer to the surface in order to keep the tunneling current constant during scanning; thus, a depression appears in the image. Oxygen-induced depressions have also been observed previously for the GaAs(110) surface.[15,16]

An examination of Fig. 2 reveals details about the role of defects in the oxidation process. After 2.4 L exposure [Fig. 1(b)], 35 new "missing" adatoms are generated, with 16 being corner adatoms and 19 being center adatoms. All of these new missing adatoms, except one, are near neighbors to the original surface defects. Thus, the regions with missing adatoms appear to expand with oxygen adsorption. The result clearly establishes that the defects on the starting surface serve as nucleation sites for the oxidation of Si(111). This observation also holds when comparing Figs. 1(c) with 1(b); after an additional oxygen exposure of 1.6 L for a total of 4.0 L, 30 new missing adatoms are generated, with 20 being corner adatoms and 10 being center adatoms. All of these are near neighbors of existing missing adatoms.

The above analysis shows that comparable numbers of center and corner adatom sites are affected by oxygen adsorption after 2.4-L oxygen exposure. Since there are about equal numbers of center and corner adatom sites neighboring existing defects, the result indicates no significant chemical selectivity during the initial oxidation between the two kinds of adatom sites. In contrast, a recent study of NH_3 on Si(111)-(7×7) reveals noticeable chemical selectivity between the two kinds of sites.[17] On further oxygen exposure to a total of 4.0 L, there is a factor of 2 difference between the numbers of the two kinds of adatoms affected by the oxygen; however, the difference is not large enough to draw a definitive, statistically significant conclusion.

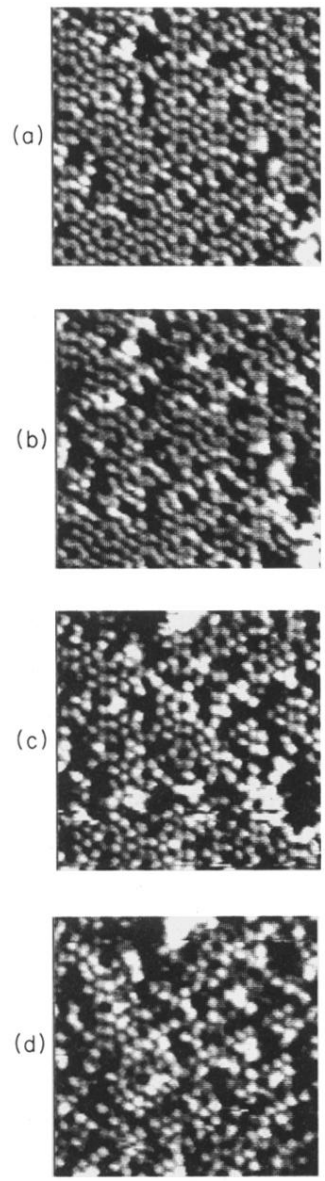
Figure 1(d) shows the surface at a total of 8.6 L of oxygen exposure. As in previous images, additional adatoms become missing. However, portions of the surface which had previously "disappeared" due to oxygen exposure now reappear, but the positions of the reappeared adatoms (protrusions) are distorted. The loss of position registry causes the impression of considerable disorder on the surface. The apparent heights of the reappeared adatoms also show considerable variations, but typically lower than the unaffected adatoms on the surface. In fact, the reappearance can be detected already in Fig. 1(c), where three previously missing adatoms have reappeared. The effect is much more apparent in going from Fig. 1(c) to 1(d). These reappearances can be explained by two reasons. One reason has to do with the manner in which these STM images were acquired. The average grey scale of each image was automatically set at a fixed level. Thus, when more adatoms (protrusions) are depressed relative to the original surface, the automatic resetting of the average grey scale tends to bring out the details of the depressed regions. Another reason is that increasing oxygen exposure leads to more apparent height variations in the protrusions; this observation is consistent with the fact that oxidation of Si(111) does not lead to an ordered structure.

At higher oxygen exposures (up to 300 L), one can see, from the loss of position registry of the reappeared adatoms (protrusions) and the apparent height variations, that the oxidation continues to affect more adatom sites on the surface in the same manner as discussed above. The lateral expansion of the oxidized parts of the surface progresses to cover up the entire surface at an exposure of about 20 L. The disorder becomes quite severe beyond this exposure so that the corner holes can no longer be identified. However, if a large area of the image is viewed from a distance, one can barely recognize the original underlying (7×7) unit-cell tile pattern. This observation seems to imply the existence of residual (7×7) reconstruction underneath the oxide layer. This is possible, for instance, if the stacking fault on one-half of the (7×7) unit cell is not completely suppressed by oxygen adsorption.[2,8] At even higher coverages, the surface appears to consist of atoms (or protrusions) fairly randomly distributed while maintaining a minimum separation between neighboring protrusions. The average number of protrusions over a sizable area is however still quite close to the original adatom density of the (7×7) surface. The protrusions also appear to ride on fairly random "waves" on the surface, resulting in considerable variations in the apparent height of these protrusions.

In conclusion, this STM study of the oxidation of the Si(111)-(7×7) surface reveals that defect sites with the appearance of missing adatoms act as nucleation sites for the oxidation process. The oxidation progresses by expanding the oxidized area around the defects. Large defect-free regions and straight atomic steps commonly found on this surface seem to be quite insensitive to oxygen exposure. The oxidized surface is highly disordered.

This material is based upon work supported by the Department of Energy, Division of Materials Sciences, under Contract No. DE-AC02-76ER01198. Some of the personnel and equipment support was also derived from grants from the National Science Foundation (Grants No. DMR-8352083 and No. DMR-8614234), the IBM Thomas J. Watson Research Center (Yorktown Heights, New York), and the E. I. du Pont de Nemours and Company (Wilmington, Delaware). We acknowledge the use of central facilities of the Material Research Laboratory of the University of Illinois, which was supported by the Department of Energy, Division of Materials Sciences, under Contract No. DE-AC02-76ER01198, and the National Science Foundation under Contract No. DMR-8316981.

[1]G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).
[2]K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).
[3]R. S. Becker, J. A. Golovchenko, G. S. Higashi, and B. S. Swartzentruber, Phys. Rev. Lett. **57**, 1020 (1986).
[4]R. C. Jaklevic and L. Elie, Phys. Rev. Lett. **60**, 120 (1988).
[5]G. Hollinger and F. J. Himpsel, Phys. Rev. B **28**, 3651 (1983).
[6]M. Nishijima, K. Edamoto, Y. Kubota, H. Kobayashi, and M. Onchi, Surf. Sci. **158**, 422 (1985).
[7]J. E. Rowe, J. M. Seo, D. S. Black, and H. Holloway, Bull. Am. Phys. Soc. **33**, 570 (1988).
[8]I. K. Robinson, W. K. Waskiewicz, and R. T. Tung, Phys. Rev. Lett. **57**, 2714 (1986).
[9]T. Miller and T.-C. Chiang, Phys. Rev. B **29**, 7034 (1984); and (unpublished).
[10]J. E. Demuth, R. J. Hamers, R. M. Tromp, and M. E. Welland, J. Vac. Sci. Technol. A **4**, 1320 (1986); IBM J. Res. Dev. **30**, 396 (1986).
[11]R. S. Becker, J. A. Golovchenko, E. G. McRae, and B. S. Swartzentruber, Phys. Rev. Lett. **55**, 2028 (1985).
[12]R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).
[13]R. S. Becker, B. S. Swartzentruber, and S. Vickers, J. Vac. Sci. Technol. A **6**, 472 (1988).
[14]N. D. Lang, Phys. Rev. **58**, 45 (1987); Bull. Am. Phys. Soc. **33**, 272 (1988).
[15]J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **58**, 1668 (1987).
[16]J. A. Stroscio, P. M. Feenstra, D. M. Newns, and A. P. Fein, J. Vac. Sci. Technol. A **6**, 499 (1988).
[17]R. Wolkow and Ph. Avouris, Phys. Rev. Lett. **60**, 1049 (1988).



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