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Modification of HF-treated silicon (100) surfaces by scanning tunneling microscopy in air under imaging conditions

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The modification of HF-etched silicon (100) surface with a scanning tunneling microscope (STM) operated in air is studied for the first time in samples subjected to the standard HF etching without the follow-up rinsing in H_2O. The modifications are produced in air under normal STM imaging conditions ($V_t=-1.4$ V and $I_t=2$ nA). The simultaneous acquisition of topographical, current image tunneling spectroscopy and local barrier-height images clearly shows that the nature of the modification is not only topographical but also chemical. The features produced with a resolution better than 25 nm are attributed to a tip-induced oxidation enhanced by the presence of fluorine on the surface.

Silicon surfaces have been widely studied in ultrahigh vacuum (UHV) with scanning tunneling microscopy (STM) and atomic resolution is regularly obtained after cleaving the sample and removing the contamination and the native oxide by high-temperature annealing.[1] But in air, the imaging of silicon surfaces by STM is much more difficult because of the quick oxidation and contamination of the surface. Most of the work that has appeared in the literature[2–7] showing images of silicon in air have been done with the hydrogen passivation of the surface using an HF etching.[8–10] Nevertheless, atomic resolution has been rarely achieved.[6,7] Recently, several letters have appeared in the literature concerning the modification of H-passivated silicon surfaces by STM.[11–13] While these works are made in extreme conditions: electrochemical ambient,[12] UHV,[13] or applying high voltage in air,[11] we report the modifications of silicon surfaces in air under normal STM imaging conditions ($V=-1.4$ V sample negative, $I=1$–2 nA). We have found that modifying the cleaning method by drying the sample with nitrogen immediately after the HF etching and skipping the final rinsing in deionized (D.I.) H_2O produces always a surface which is more easily modified by STM than conventional H-passivated silicon surfaces. Moreover, the surface can be modified with a precision better than 25 nm.

The STM used in the experiments is a pocket-size with PZT tube-shape piezoelectric giving a maximum scanning range of 1.5×1.5 μm. The acquisition of current image tunneling spectroscopy (CITS) and local barrier height are made simultaneously to the acquisition of the topographical images, cutting the feedback for 3 ms. For CITS, a voltage ramp is applied to the sample starting at the feedback condition in order to avoid undesirable transient effects (the initial sample voltage and tunnel current of the ramp are the same as the ones used for imaging). The same method is applied for local barrier-height imaging, where a voltage ramp starting with null voltage is added to the z-piezo voltage given by the feedback in order to calculate the barrier height. In both cases, 10 to 50 curves are averaged in the post-acquisition analysis. PtIr tips were employed.

The samples used were n-type (100) silicon with a surface resistivity of 0.02 Ω cm. The samples were first cleaned with H_2SO_4 (95%):H_2O_2 (30%) and rinsed with D. I. H_2O for 10 min. After this, a thermal oxide of 15 nm was grown on the surface. Immediately before its imaging with STM, the samples were first degreased with thicloretan, aceton, and D. I. H_2O, and then etched by dipping in HF 40% for 1 min. The sample was not rinsed again in H_2O, but directly dried with nitrogen.

In Fig. 1 we show the effect of scanning twice a region of the surface and then imaging a larger area without changing the experimental conditions. The image shows a depression on the upper-left corner of the surface (about 1 nm depth), or more rigorously, a region where the piezo is elongated to maintain the tunneling current constant. This behavior is very similar to that found in an electrochemical medium by Nagahara *et al.*[12] We have also found that the modification is deeper when the tip velocity over the surface is slower. In Fig. 2 we show another modification of the surface consisting in two parallel 25-nm-width lines separated by 25 nm, fabricated scanning one line after the other in order to establish the resolution and precision of the technique.

These modified regions are also distinguishable in the

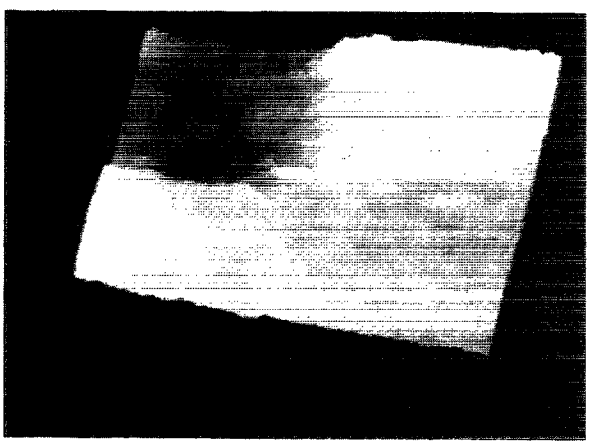

FIG. 1. STM topograph of a silicon surface (250 nm$\times$250 nm) showing the depression produced by scanning first a smaller area of (100 nm$\times$100 nm) on the upper-left corner. The depth of the depression is 1 nm. $V_t=-1.4$ V. $I_t=2.25$ nA.

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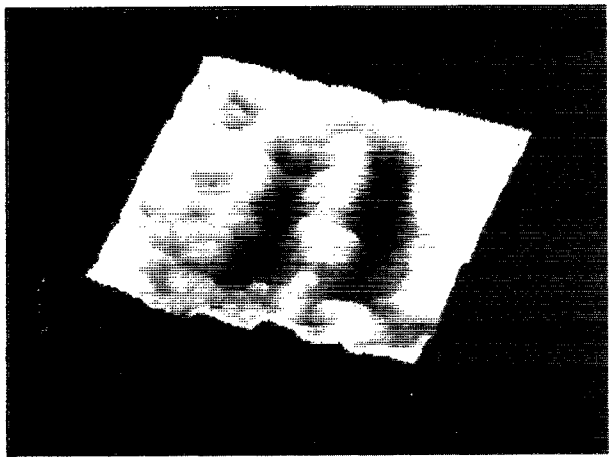

FIG. 2. STM topograph of a silicon surface (200 nm×200 nm) showing two parallel lines fabricated by scanning one line after the other. The dimensions of the lines are 100 nm×25 nm and 0.5-nm deep, and the separation between lines is 25 nm.

CITS images where the same features clearly appear in a voltage range between −1.4 and −0.6 V. In Fig. 3 we show *I/V* curves acquired simultaneously with the topographic image of Fig. 1: (a) corresponds to the depressed area (inside the square) and (b) to the nondepressed area. The differences between curves (a) and (b) clearly state that a chemical modification of the surface has occurred. In order to study the behavior of this chemical modification of Fig. 4, we show the evolution with time of the *I/V* curves while scanning the same region of the surface [curve (a) is taken while making the first image, of the area; curve (b) while scanning for the third image, and so on]. Note that the change is not abrupt but gradual. Local barrier-height measurements in every point were also simultaneously acquired and a barrier height of 0.2 eV in the modified area and 0.7 eV in the nonmodified region is

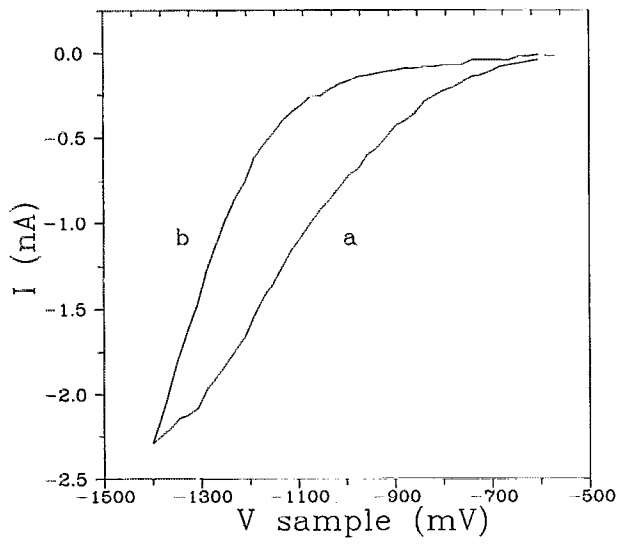

FIG. 3. *I/V* curves corresponding to Fig. 1. (a) is taken over the modified region (square) and (b) is obtained over the nonmodified region.

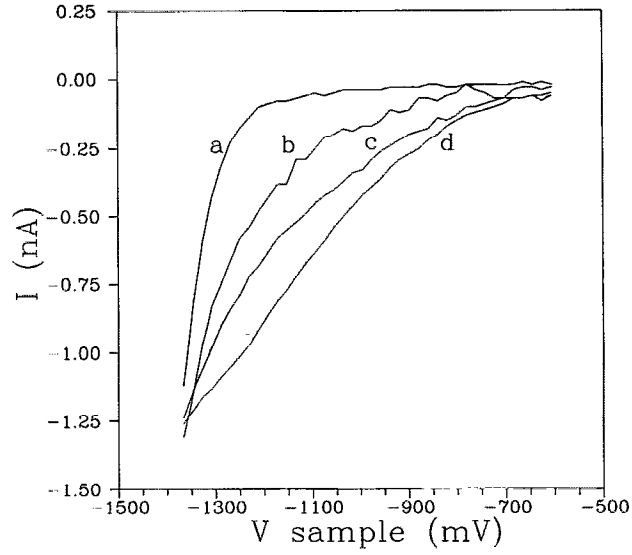

FIG. 4. Four *I/V* curves taken in the same region showing the evolution with time of the modification of the surface. Curve (a) is taken while scanning a small region for the first time, curve (b) is taken while scanning the same small region for the third time, and so on.

found. These results also indicate that the modification has a chemical character.

In the experiment by Nagahara *et al.*[12] it is concluded that the modification could be produced by a tip-induced oxide formation and a subsequent chemical etching by the HF solution which produces the depression. In our case, we propose that the modification is an oxidized area produced by a tip-induced oxidation at the surface enhanced by the presence of the fluorine. In fact, x-ray photoelectron spectroscopy measurements made with an analogous cleaning method reveal the existence of fluorine in a concentration up to 1×10^{14} cm^{-2}.[9,10] The interaction between water and silicon surfaces dipped in HF produces, as a first step, the exchange of Si-F with H_2O to form Si-OH groups, reducing the concentration of the fluorine on the surface.[10]

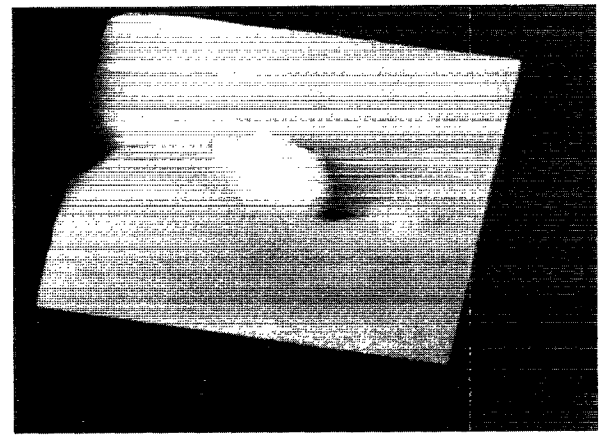

FIG. 5. STM topographical image (350 nm×350 nm) of a mound formed by scanning a small area in the middle of the surface at high voltage (−3 V, current 2 nA) and then imaged at −1.4 V, 2 nA. The height of the mound is 2 nm.

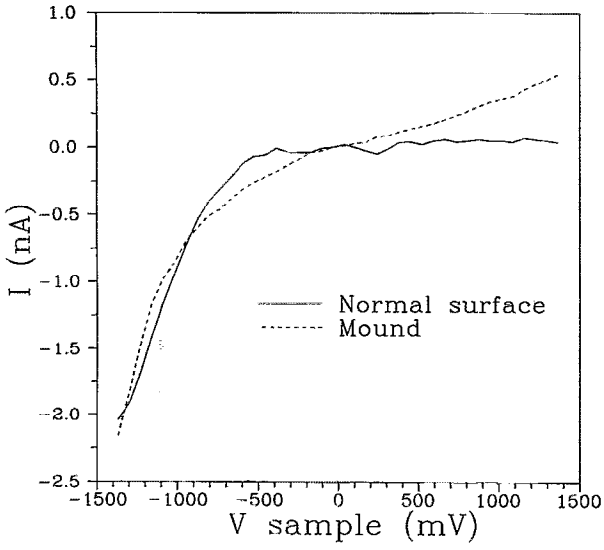

FIG. 6. I/V characteristics corresponding to Fig. 5. The I/V curve obtained over the mound shows a less rectifying behavior than the I/V curve acquired over the nonmodified surface.

Experimentally we have found that it is easier to produce the modification immediately after the cleaning of the surface than 2 or 3 h later. This could be due to the reaction of the fluorine with vapor water of the air which produces a reduction of the fluorine coverage. Thus the features observed in Figs. 1 and 2 correspond to oxidized regions. On the other hand, the extremely low barrier height found in the modified area could be due to the embedding of the tip inside the grown oxide, which does not allow a free oscillation of the tip.

The modification of the surface applying a higher voltage than that usually used for imaging has also been done. In contrast to the results of Dagata *et al.*[11] which produced a hole while scanning at -3.5 V, we found that not a hole but a mound is created most of the time.

In Fig. 5 we show a mound fabricated by scanning a small area during 2 min with a tunnel voltage of -3 V and a tunnel current of 1.5 nA and imaged with -1.4 V and 1.5 nA. It is important to note that in this case no reproducible scans were obtained while scanning at -3 V. The modified region is distinguishable in the CITS image but now in all the voltage range. I/V curves taken on two different points of the image of Fig. 5 are shown in Fig. 6. The I/V curve acquired over the mound created shows a less rectifying behavior and an appreciable increasing of the current level for positive voltage. As both, the topographical and CITS images in this case are different from the modification produced under normal conditions, a different mechanism would occur, perhaps a deposition of material from the tip over the surface due to the high applied voltage.

In conclusion, the modification of HF-treated silicon (100) surfaces with STM in air when the sample has not been submitted to a rinsing in D. I. water after the etching in HF has been presented. Topographical images show the creation of stable depressions on the surface produced by scanning a small region in normal imaging conditions ($V_t = -1.4$ V, $I_t = 1$ nA). CITS and local barrier-height images show that a chemical change of the surface has been produced. We propose that the features are oxidized areas of the silicon surfaces and that a fluorine coverage of the surface is responsible for an enhancement of the tip field-induced oxidation. It is also reported the creation of a protuberance when the surface is scanned with high voltage ($V_t = -3$ V).

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