Formation of atomically smooth terraces during cleavage of bismuth crystals; dynamics of the terrace boundaries

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Scanning tunneling microscopy has been used to study a basal-plane surface of Bi formed by *in situ* cleavage in a vacuum of 10^{-9} torr. The cleavage face has atomically smooth terraces ranging in size from a few nanometers to a few hundred nanometers. In most cases the terrace boundaries are blurred over two or three interatomic distances, even at room temperature. This blurring increases to tens of angstroms upon heating to 520–530 K. The activation energy for the motion of the boundaries can thus be estimated to be about 700 K. However, the straight boundaries oriented along atomic rows are atomically smooth at room temperature.

Scanning tunneling microscopy has established that the boundaries of monatomic steps on several metals[1–6]—Ag, Au, Cu, and Pb—are extremely mobile even at moderate temperatures, and that they vibrate around their average positions with an amplitude of several interatomic distances over times shorter than (at most) a millisecond. Estimates in Ref. 1 put the time scale on the order of 10^{-10} s. Steps of vicinal faces were studied in the experiments of Refs. 1–3. The distance between steps was not very large in comparison with the thermal blurring of the steps, so in principle there should have been a distortion of their motion. Furthermore, the surface was etched by an ion beam, and the crystals were annealed for a long time, in order to produce an atomically clean surface and atomically smooth terraces. In the course of this treatment, radiation defects arise, and impurities may segregate at the surface. These effects have been linked with the onset of a large number of pinning centers at boundaries.[4]

It is accordingly worthwhile to study terraces at a surface produced by breaking a single crystal along a cleavage plane, since in this case there is the hope that the concentration of impurity atoms at the surface will be low for pure metals. We have accordingly carried out scanning tunneling microscopy of a cleaved surface along a basal plane of a Bi single crystal.

Samples with dimensions $\approx 1\times2\times5$ mm were cut by electric discharge machining from Bi single crystals grown by crystallization from the melt of a material with a purity $\approx 10^{-5}$ %. An analysis showed that no additional impurities entered the material during the growth. The trigonal axis was parallel to the long edge of the sample. A notch 0.2–0.3

mm deep was cut halfway along one of the 2× 5-mm faces. This notch, which ran parallel to the basal plane, set the position of the test surface after the cleavage of the sample. The sample was etched in nitric acid to remove the outer layer damaged during the machining. It was then washed in water and mounted in the holder of the scanning tunneling microscope, which was described in Ref. 7. The sample could be heated *in situ* to the point of melting.

After the microscope was placed in a vacuum chamber, an outgassing was carried out by heating to $\approx 150°$C. The tungsten tip of the microscope was heated by an electron beam, and the sample was annealed for several hours at $\approx 250°$C. The duration of this annealing was chosen in such a way that there was no appreciable degradation of the vacuum when the sample was reheated to the same temperature. After the vacuum in the apparatus reached a level better than 10^{-9} torr, the sample was broken by means of a spring, which was released by burning a wire holding it. The tip of the scanning tunneling microscope was then brought up to the new surface. We selected a position which appeared smooth through a 10× telescope.

According to the results of Ref. 8, a monatomic layer of contaminants forms on a Bi surface over a time of more than 100 days because of the very low ($\approx 10^{-4}$) sticking factor of residual-gas molecules such as H_2O and O_2 in a vacuum of 10^{-9} torr. Our experiments with one sample usually took several days; we observed no effects which might have been attributed to the appearance of contaminants on the surface.

Figure 1a is a typical scanning tunneling micrograph of a freshly cleaved face. We see two long, atomically smooth terraces. On these terraces there are a few islands and depressions with sizes ranging from a few tens of angstroms to several hundred angstroms. There is a small island on one of the large islands at the center of the frame. This region is shown in larger scale in Fig. 1b; a cross section along the line indicated by the arrows is shown in Fig. 1c. Within the error of the measurements and the calibration, which was carried out with the help of monatomic Pb steps in Ref. 6, the height of all steps is $C_1/3 = 3.95$ Å, where C_1 is the height of the hexagonal cell of the Bi crystal. The unit cell contains six atomic layers separated by alternating distances of 1.874 and 2.080 Å. There are accordingly two layers within the height of a step; it is natural to assume that these two layers lie closer to each other in the interior.

To raise the image contrast in Fig. 1b, the window along height was chosen to bring out only the surfaces of the large island at the upper left of the frame and the terrace at the upper right, which is at the same level. Everything lower is black, and everything higher is white. Accordingly, we can clearly see the edges of the visible regions, and we can clearly see their atomic structure. According to the crystallography of Bi, the atoms form a hexagonal lattice and are separated by a distance which agrees with the expected value of 4.546 Å. (The agreement here is within the error—on the order of a few percent—of the calibration of the scanning tunneling microscope on the basis of the atomic structure of lead.[6]) We see that the island has three atomically smooth boundaries, whose directions coincide with the directions of atomic rows. At the rounded corners of the island, near the terrace, and near the small island, the edges are ragged. In these regions, the visible structure of the boundaries corresponds to the circumstance that, in the course of the scanning, the tip of the microscope finds the boundary in a new place on each successive line of the scan. The circumstance that atomic rows can be seen clearly

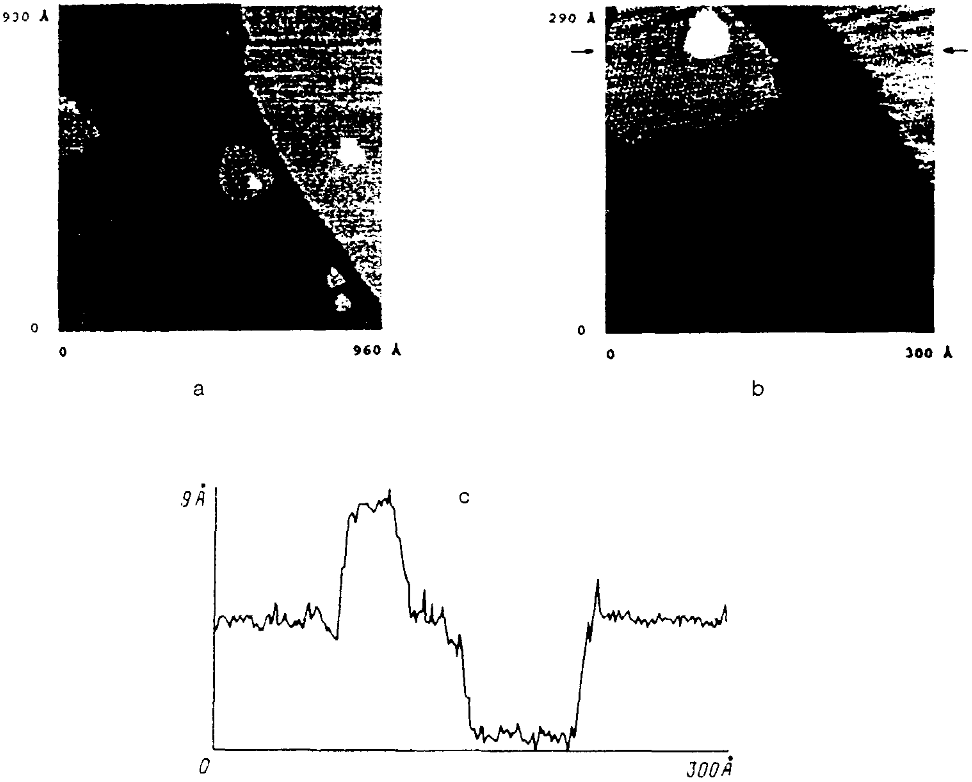

FIG. 1. a: Topogram of a cleavage surface before annealing of the sample. The change in level from black (depression) to white (elevation) is 9 Å . The time taken to record one line was 3.8 s. b: Topogram of the boxed region in frame a. The drop in level from black to white is 1 Å . The amplitude of the atomic corrugation is 0.57 ±0.05 Å , according to a 2D Fourier analysis. The recording was begun after 38 min; the time taken to record one line was 1.2 s. c: Cross section of frame b along the line defined by the arrows. The voltage on the tip of the scanning tunneling microscope was 4 mV; the tunneling current was 0.1 nA. The experiment was carried out at room temperature. a—There are 128 lines in the frame; b—256. a) There are 128 points on a line; b) 256.

on the image resolves the question of the noise of the microscope. Over a time shorter than the period of the line scan, ≈1 s, a boundary, which deviates from the exact direction of the atomic rows, moves in a random manner over a distance on the order of two or three interatomic distances.

Over the time between sequential recordings of the image of the small island in Fig. 1, a and b, this small island is displaced about 50 Å with respect to the large island, without any visible change in dimensions. This is not the only observed case of a motion of nanometer-scale formations. For example, we observed the motion of a circular pit two atoms deep with a diameter of about 35 Å at a velocity on the order of 0.04 Å /s and also the disappearance of this pit as it approached the edge of a long two-atom step. The typical scale of the drift correlates with the blurring of the boundaries of these regions. If we assume that an island (depression) retains its integrity as the boundary moves, then it

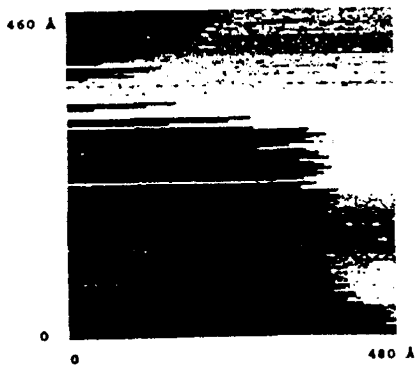

FIG. 2. Topogram recorded at a sample temperature of 535 ±3 K. The change in level from bright to dark is 4 Å. The voltage at the tip was 4 Å, and the tunneling current was 0.1 nA. The time taken to record one line was 2 s, the number of lines was 128, and the number of points in a line was also 128.

may diffuse a distance on the order of 150 Å over 10^3 s if the mean square displacement of the boundary over 1 s is on the order of 5 Å.

For a heated sample, the boundary has qualitatively the same structure as at room temperature, but the blurring of the boundary is about three times as great (Fig. 2). The bright horizontal lines crossing the entire frame in this figure apparently correspond to the trapping of an individual atom (or dimer) at the end of the tip as the latter intersects the boundary on its return path. Although the noise and drift of the scanning tunneling microscope increase as the sample is heated, the blurring of the boundary is not due to this heating, since we can clearly see the atomic picture in the atomically smooth regions even in this case. On only one of several tens of surface regions studied did we reproducibly observe a straight boundary, about 300 Å long, whose blurring did not exceed the resolution of the microscope for the given recording (about 5 Å). The stability of the boundary in this case apparently resulted from a pinning of the boundary.

The motion of a boundary is generally believed to be due to a thermal generation of slope changes at the boundaries of steps and their motion along the boundary.[1-4] Adopting that model for the long boundaries, and comparing the blurring of the boundaries at various temperatures, we can estimate the activation energy for this process: ≈700 K. To find a more accurate value we would have to significantly increase the statistical base of the experiment, so that it would become possible to compare boundaries in a common orientation. The reason is that the qualitative differences in the behavior of the boundaries oriented along rational directions and of disoriented boundaries is clear evidence of a significant anisotropy in the process.

After a sample was annealed at ≈530 K for several days, its surface took the form of extended, atomically smooth terraces on which there were essentially no small features characteristic of a freshly cleaved surface (compare Figs. 1a and 3). This result indicates a high diffusion rate of the microscopic regions. The boundaries of the extended steps also become smoother, but they do not become straight, and we do not observe a tendency for these boundaries to become oriented along a rational direction.

We note in conclusion that the formation of terraces with nanometer dimensions observed by us during the cleavage is of interest from the standpoint of the dynamics of cleavage. These islands and depressions cannot be due to impurities, whose concentration

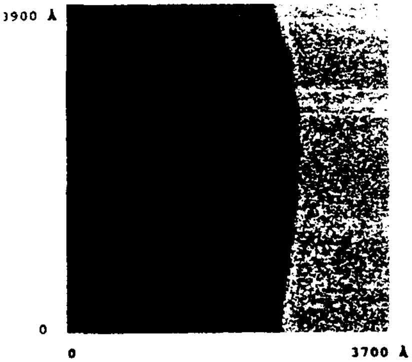

FIG. 3. Topogram recorded at room temperature after annealing of the sample at ≈535 K. The change in level from bright to dark is 8 Å. The voltage on the tip was 2 mV, and the tunneling current was 0.1 nA. The time taken to record one line was 12 s, the number of lines was 256, and the number of points in a line was also 256.

per atomic plane is on the order of 1 μm^{-2}, i.e., two or three orders of magnitude smaller than the concentration of the nanometer-scale formations (Fig. 1a). These islands and depressions are furthermore unrelated to the emergence of dislocations of the surface, since they lie on atomically smooth terraces. Our test samples were of fairly high quality; in no case were we able to observe the emergence of dislocations at the surface. For example, there are no dislocations in Fig. 3, over an area ≈ 0.1 μm^2. The high mobility of the islands and depressions indicates that the underlying region is free of defects. It thus seems plausible that the nanometer-scale regions form because of an interference of intense sound waves generated during the cleavage. The velocity of the vertex of the crack during the cleavage of Bi, which ranges up to[9] 1080 m/s, is significantly lower than the sound velocity, and such an interference would be possible in principle. Judging from the dimensions of the terraces, the frequencies of the sound waves should be an order of magnitude lower than Debye frequencies.

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