Flatness and shape of (111) facets of equilibrated Pb crystals

S. Surnev, P. Coenen, B. Voigtländer, and H. P. Bonzel
Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich, D-52425 Jülich, Germany

P. Wynblatt
Department of Materials Science and Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
(Received 11 July 1997)

Scanning tunneling microscopy has been used to study the (111) facets of μm-sized Pb crystallites produced on a Cu(111) substrate, and equilibrated at temperatures ranging from 430 to 570 K. The results show that most of the (111) facets are atomically flat in the sense that they contain no monatomic steps over a distance from several hundred nanometers to about 1 μm. The facet edge is clearly seen by the bounding monatomic step. The shape of facets deviates from being circular, indicating the presence of the threefold anisotropy of the step energy. A corresponding anisotropy is also evident in the shapes of monatomic adatom and vacancy islands occasionally observed on the facet. The step energy ratio of B to A steps was derived from the shape as 0.91 at 520 K. [S0163-1829(97)08444-0]

The theory of the equilibrium crystal shape (ECS), as developed by Gibbs[1] and Herring,[2] predicts that flat facets will develop on crystals at those orientations which correspond to cusp-shaped singularities in a plot of the anisotropy of surface free energy. This *continuum* thermodynamics view implies a mathematical flatness of the facets, but it is not clear how flat a facet will be produced experimentally on a real crystal. Analyzing such facets on the atomic scale will provide an answer to this important fundamental question.

Previous experimental studies of equilibrated crystals have made use of scanning electron microscopy (SEM) to obtain the ECS of crystals having dimensions of the order of 10 μm.[3–6] This technique produces two-dimensional images of the three-dimensional ECS. As a result, it is only possible to obtain detailed shape information along sections through the ECS. In addition, the resolution of the SEM is not sufficient to allow imaging of atomic scale features. The ECS of pure Pb has been investigated in some detail in previous studies.[4,5,7] At temperatures where Pb crystals can approach the ECS in reasonable times, they display (111) and (100) facets and roughened curved surfaces. Below about 580 K, the facets are smoothly connected to the curved surfaces, i.e., there are no missing orientations on the ECS of Pb.[7]

The purpose of the present study is to report aspects of facets on the ECS, here via the example of Pb on a Cu(111) substrate. Data are obtained using scanning tunneling microscopy (STM) of crystals equilibrated in the temperature range 430–570 K. In contrast to SEM, this technique allows the direct acquisition of three-dimensional shape information, and can be operated under conditions where monatomic surface steps can be resolved, even in crystals measuring a few μm in size. Specifically, we address the following questions: How flat is a facet on the ECS of Pb? What is the shape of a (111) facet, and to what extent does it deviate from a circle, given the inherent threefold symmetry of a face-centered-cubic (fcc) crystal in the direction normal to this facet? What are the shapes of adatom and vacancy islands on a (111) facet?

Experiments were carried out in an UHV chamber (base pressure $<1\times10^{-10}$ Torr), with facilities for Auger electron spectroscopy (AES) and STM. The STM used in these studies was a home-built instrument of Besocke type,[8] operating at room temperature. The tunneling tip is mounted on a piezoelectric tube of length 25.4 mm, thus allowing scans of up to 25 μm in x and y to be performed. Atomic resolution can presently not be achieved in the x and y directions with this microscope because of the long piezoelectric tubes. On the other hand, monatomic steps can easily be detected as the vertical (z direction) resolution is 0.05 nm.

The Pb crystals were produced by a method described previously in Ref. 9. Briefly, a Pb film about 200 nm in thickness was deposited, *in situ* in the UHV chamber, from a well outgassed water-cooled Knudsen cell (Al_2O_3 crucible), at rates of 0.6 Å/sec, onto the clean (111) surface of a Cu crystal. During Pb deposition the pressure in the chamber increased up to 1×10^{-9} Torr. Following deposition, carbon, oxygen, and sulfur at the sample surface were always below the detection limit of AES. The crystal and Pb thin film were heated to a temperature just above the melting point of Pb. Upon melting, the Pb film dewets from the Cu substrate to form discrete Pb droplets. Immediately after melting, the Cu crystal was cooled rapidly to freeze the Pb droplets, which solidified into single crystals of Pb ranging in size from a few nanometers to a few micrometers. Pb and Cu are essentially immiscible, so that a negligible amount of Cu dissolves into the Pb. It has also been previously demonstrated by AES measurements performed on the Pb crystallites in a scanning Auger microprobe,[9] that no Cu segregates to the Pb surface, within the detection limits of AES.

The Pb crystallites were equilibrated in the temperature range 430–570 K and then cooled to room temperature before imaging. Sample temperature during equilibration was measured by an IR pyrometer. Typically during STM examination of the samples, the tunneling current was 1 nA, with a tunneling voltage of $+100$ mV applied to the sample. No influence of the voltage polarity on the quality of the images was observed. The scanning speed was chosen between 400

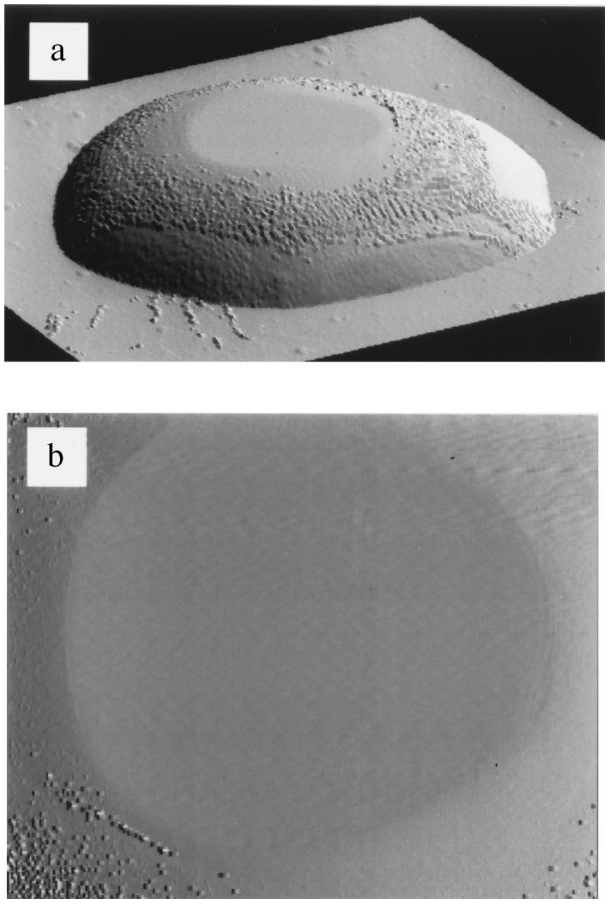

FIG. 1. STM images of Pb particle on Cu(111) equilibrated at 430 K. (a) Three-dimensional view of entire particle with a (111) facet; $2518\times2518\ \mathrm{nm}^2$. (b) Detailed on-top view of facet region; $886\times730\ \mathrm{nm}^2$.

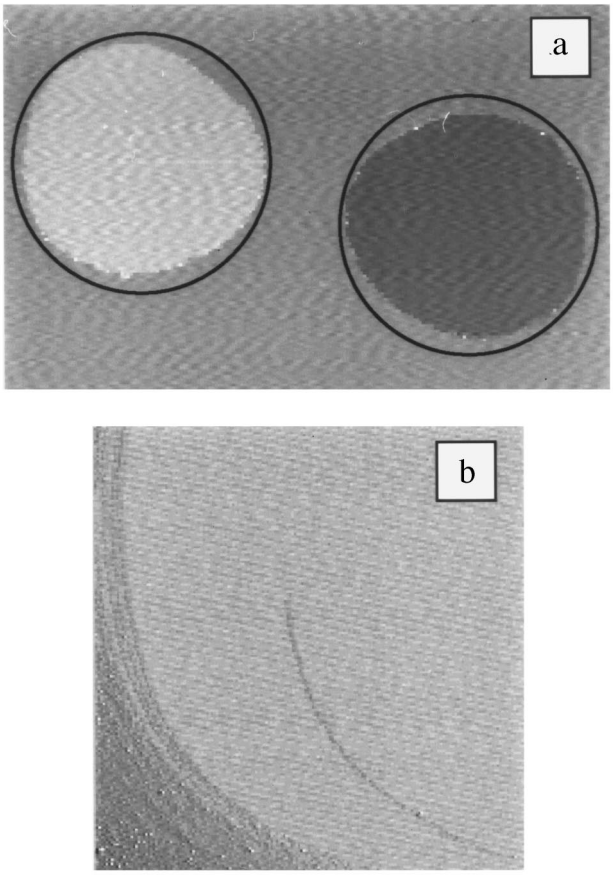

FIG. 2. STM images of Pb(111) facet sections. (a) A particle annealed at 520 K exhibits adatom (left) and vacancy (right) islands of threefold symmetry. Circles are added to aid the judgment of the island shape: $393\times251\ \mathrm{nm}^2$. (b) A single step emerging from a facet, indicative of a dislocation intercepting the surface. Note also the steps bounding the facet: $684\times770\ \mathrm{nm}^2$.

and 700 nm/s for most images, such that larger slopes could be measured reliably. First observation of the crystallites showed that the (111) facets are parallel to the (111) Cu substrate.

Pb is a difficult material to study by STM. Kuipers and Frenken[10] previously reported that the Pb(110) surface is somewhat unstable under (presumably van der Waals) attractive forces imposed on the Pb surface by the imaging tip of the STM. Because of the high atomic mobility over Pb surfaces, even at room temperature, atoms can well up from the surface toward the tip to create surface irregularities. Such effects can be minimized by maintaining the sample at as low a temperature as possible. In the present experiments, the lowest temperature achievable was room temperature. In addition, faster scanning rates and tunneling at lower voltages and currents seemed to minimize the problem.

Figure 1(a) shows a Pb particle on Cu(111) after equilibration at 430 K for 72 h. One can note the presence of small bumps on the curved Pb surfaces, which are attributed to the tip-surface interaction phenomenon described above.[10] Note that the (111) facet of the crystallite in the figure is free of such surface irregularities. This is also confirmed in Fig. 1(b), which shows a higher-resolution scan over the facet and near-facet regions of the same crystallite. Surface bumps due to tip-surface interactions were almost never observed on (111) facets. This result is consistent with previous STM studies of atomically resolved step structures on the Pb(111) surface,[11] in which no such interactions were reported.

Most (111) facets imaged at high resolution did not display any evidence of steps or other defects. However, certain types of defects were occasionally observed: adatom and vacancy islands, and steps which originated at the points where screw dislocations intercept the facet surface. For example, Fig. 2(a) is an image over part of a facet which displays both a vacancy and an adatom island. Note the noncircular shape of these islands. Figure 2(b) shows a section of particle image near the facet edge, with a single step originating on the facet at a dislocation emergence point. The same image also displays well-resolved monatomic steps at the facet edge. Thus the facet edge can be localized with atomic resolution in such STM images.

Figure 3 shows line profiles taken across different crystallite images shown in Figs. 1 and 2. The profile in Fig. 3(a) illustrates the z sensitivity of the STM by showing a line scan across the two islands of Fig. 2(a). The z jumps in this scan are about 0.3 nm, proving that the islands are adatom and vacancy islands of monatomic height [a monatomic step on Pb(111) is 0.287 nm high]. It clearly demonstrates that the vertical resolution of the STM is sufficient to identify the presence of monatomic surface steps unambiguously. A similar scan across the image in Fig. 2(b) also showed steps to be of monatomic height.

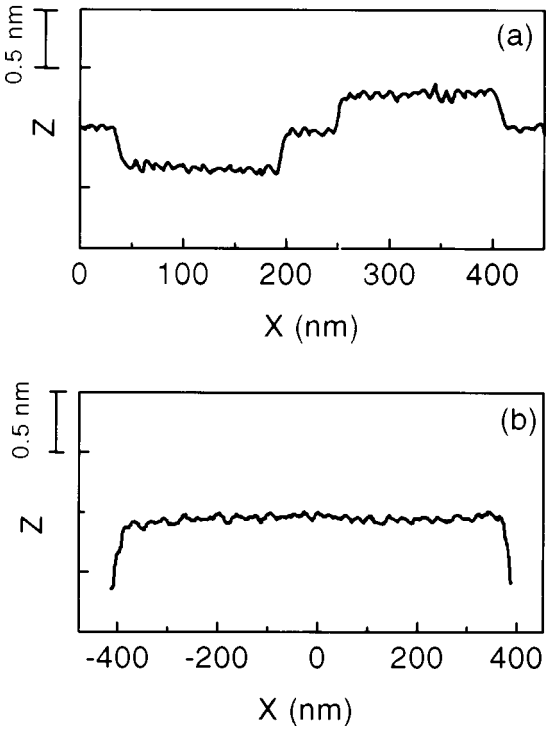

FIG. 3. Line profiles across STM images. (a) Line profile of Fig. 2(a) showing islands to be of monatomic height. (b) Line profile across the entire (111) facet of the particle shown in Fig. 1(b). This line profile does not exhibit evidence of any steps.

Although the grey scale images of the (111) facet in Fig. 1 did not show any evidence of steps, a more quantitative demonstration of the absence of steps was obtained by inspecting line scans across the facet in several azimuthal directions. All of these line scans were flat except for some electronic noise. As an example there is the line profile in Fig. 3(b) which was obtained from the image of the facet displayed in Fig. 1(b). The z resolution of this profile is the same as in Fig. 3(a), and thus sufficient to resolve steps, if they were present; however, no evidence of a vertical offset of a scale commensurate with a step is to be seen. Therefore this particular facet is step free over the entire cross section of about 700 nm.

When line profiles across the entire particle, such as in Fig. 1(a), were taken and examined at the same magnification as in Fig. 3, the (111) facet appeared distorted in a concave dishlike fashion. The depth of the dish was about 1 nm but there were no jumps in the trace, such as expected for steps. We believe that the distortion is due to piezorelaxation.[12] After the tip and z piezo have traversed the rising portion corresponding to the entire height of the particle, the piezo is in a nonequilibrium state. Arriving at the flat facet, the piezo relaxes causing an apparent gradual height change. The relaxation time was found to be of the order of 0.2 s. This effect may occur whenever objects with a large aspect ratio *and* large dimensions are imaged by STM.

Our STM results indicate that many of the (111) facets examined in detail show no atomic steps, except for the descending steps at their edges, where they connect smoothly to the curved surfaces of the crystallite. One example of the step structure at the facet edge was shown in Fig. 2(b); another one with better resolution is presented in Fig. 4. Although the latter facet shows also two adatom islands, it is flat right to the edge which is indicated by an increasing density of descending steps. The frequently observed perfect flatness of the facets is in accord with the theoretical prediction of ideal flat facets corresponding to sharp cusps in the plot of surface free-energy anisotropy, mentioned at the beginning of this paper. The result is nevertheless surprising, given that the facets examined range from several hundreds of nanometers to about 1 μm in size. Such mesoscopic-sized facets could very well have achieved average flatness by having an equal number of steps of opposite signs, but that is not the case. Thus our data show that facets on equilibrated crystals are atomically flat, as long as point defects such as adatoms and vacancies (which were not resolvable in this study) are ignored. Deviations from flatness arise occasionally whenever dislocations with a screw component intercept the (111) facet. Taking an average dislocation density of 10^{10} m/m^3, typical of well-annealed metals, we estimate that one in 50 of the particles examined (average diameter 2 μm) would contain an appropriate dislocation.

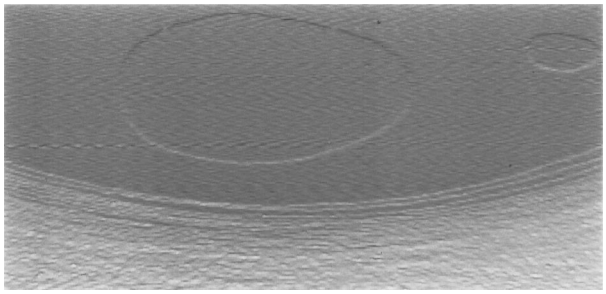

FIG. 4. Partial STM image of a particle annealed at 480 K, and the (111) facet illustrating the step structure next to the facet; 775 $\times$ 527 nm^2. Note also the two islands on the facet. All steps are monatomic.

Another issue worthy of note is the shape of (111) facets and islands. In previous studies of equilibrated Pb crystals, no particular mention has been made of the shape of (111) facets. As can be seen in Fig. 1(b), the facets imaged by STM deviate from circular shape and display the threefold symmetry characteristic of $\langle 111 \rangle$ directions in cubic crystals. This same symmetry is also obvious in the image of the adatom and vacancy islands shown in Fig. 2(a). These deviations from circular shape reflect the anisotropy of the step free energy[13–16] which is expected on fcc (111) surfaces due to differences in the structure of the step edges. A step edge lying along a $\langle 110 \rangle$ direction on a (111) surface can be terminated either by a two-row (100) facet (type-A step) or a two-row (111) facet (type-B step), thus leading to an anisotropy of step energy. In the case of small monatomic islands observed on Pt(111) surfaces after annealing at 625 K, this anisotropy leads to hexagonal shapes which are bounded by three short (type A) and three long (type B) steps.[13] The corners of the hexagons on Pt(111) are not perfectly sharp, due to the step roughening expected at any nonzero temperature.[17] The islands shown in Fig. 2(a) display much more significant rounding of the corners than those observed on Pt(111). This is to be expected, since the present islands have been equilibrated at a much higher temperature (relative

to the melting point T_m) than those on Pt. The ratio of the step free energies of Pb was evaluated from the ratio of distances from the midpoint of the islands to the nearest and farthest edges, respectively. This ratio has a value of 0.91 ± 0.02 (at 520 K) which is in close agreement with the value 0.87 (at 473 K) derived previously from the anisotropy of the surface free energy for Pb.[18] These numbers also agree with ratios of 0.87 determined for Pt(111),[13] and 0.93 reported recently for Ir(111) at 1000 K.[16] The narrow range of the step energy ratios observed for several fcc metals at different relative temperatures T/T_m indicates that it reflects the basic structural difference of the two steps on the (111) surface. Finally, it is interesting to note that the shapes of adatom and vacancy islands are related by mirror symmetry. This is consistent with the reversal in the location of the type-A and -B steps of these two types of island.

The present STM technique for imaging the ECS of small particles opens up a number of potentially interesting lines of research.[18] There have been several attempts to check the value of universal exponents which describe the shape of curved surfaces in the vicinity of facets.[19–21] This previous work has been based on SEM images of crystallites, in which it is quite difficult to precisely identify the edge of the facet. The uncertainty in the specification of the facet edge is problematic, because significant changes in the calculated exponents can result from small changes in the location assigned to the facet edge. We believe that a solution to this problem has been demonstrated by the present work, in which the position of the facet edge is clearly identified by the first step surrounding the facet.[18] In addition, future work should make it possible to determine not only the precise location of the facet edge, but also allow very precise shapes of the near-facet curved surfaces to be obtained with a resolution at the scale of atomic steps. Finally, it should be possible to study the manner in which the curved part of the ECS varies with azimuthal orientation around the facet.

The authors wish to acknowledge support for this collaborative research from NATO (No. CRG970120). S.S. and P.W. also wish to acknowledge support for their visits to the Forschungszentrum Juelich from the Alexander von Humboldt Foundation. Finally, P.W. acknowledges support of his research by the National Science Foundation, under Grant No. DMR 9530 469.

[1] J. W. Gibbs, *Collected Works I* (Longmans, Green, New York, 1928).
[2] C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C. S. Smith (University of Chicago Press, Chicago, 1952), p. 5.
[3] J. C. Heyraud and J. J. Métois, J. Cryst. Growth **50**, 571 (1980).
[4] J. C. Heyraud and J. J. Métois, Surf. Sci. **128**, 334 (1983).
[5] A. Pavlovska, K. Faulian, and E. Bauer, Surf. Sci. **221**, 233 (1989).
[6] W. C. Cheng and P. Wynblatt, Surf. Sci. **364**, 417 (1996); J. Cryst. Growth **173**, 513 (1997).
[7] J. C. Heyraud, J. J. Métois, and J. M. Bermond, J. Cryst. Growth **98**, 355 (1989).
[8] K. Besocke, Surf. Sci. **181**, 145 (1987).
[9] G. Rao, D. B. Zhang, and P. Wynblatt, Acta Metall. Mater. **41**, 3331 (1993).
[10] L. Kuipers and J. W. M. Frenken, Phys. Rev. Lett. **70**, 3907 (1993).
[11] L. Kuipers, M. S. Hoogeman, J. W. M. Frenken, and H. van Beijeren, Phys. Rev. B **52**, 11 387 (1995).
[12] R. W. Basedow and T. D. Cocks, J. Phys. E **13**, 840 (1980); S. Vieira, IBM J. Res. Dev. **30**, 553 (1986).
[13] T. Michely and G. Comsa, Surf. Sci. **256**, 217 (1991).
[14] R. Stumpf and M. Scheffler, Phys. Rev. Lett. **72**, 254 (1994).
[15] J. Jacobsen, K. W. Jacobsen, and J. K. Norskov, Surf. Sci. **359**, 37 (1996).
[16] M. Rost, T. Michely, and G. Comsa, Phys. Rev. B (to be published).
[17] C. Jayaprakash, W. F. Saam, and S. Teitel, Phys. Rev. Lett. **50**, 2017 (1983).
[18] H. P. Bonzel and S. Surnev, in *Dynamics of Crystal Surfaces and Interfaces*, edited by P. M. Duxbury and T. Pence (Plenum, New York, 1997).
[19] C. Rottman, M. Wortis, J. C. Heyraud, and J. J. Métois, Phys. Rev. Lett. **52**, 1009 (1984).
[20] J. J. Sáenz and N. Garcia, Surf. Sci. **155**, 24 (1985).
[21] J. J. Métois and J. C. Heyraud, Surf. Sci. **180**, 647 (1987).