

Atomic-Resolution Imaging of Close-Packed Metal Surfaces by Scanning Tunneling Microscopy

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The resolution of individual atoms in scanning-tunneling-microscopy (STM) images of Al(111) is demonstrated. From results of gap-width and energy-dependent measurements the corrugation observed in the STM images cannot reflect the electronic structure of the Al surface near E_F , as usually assumed for such images, but must be due to tip-surface interactions. On the basis of an investigation of the process of tip preparation, an elastic deformation of the frontmost end of the tip mediated by adhesive tip-surface interactions is proposed as the predominant factor for atomic-resolution STM imaging of such metal surfaces.

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The resolution of individual atoms or bonds by scanning tunneling microscopy (STM) is related to local variations in the probing tunnel current. These are commonly attributed to the presence of localized electronic states on the surface around E_F , which contribute to the tunnel current.¹ Because of the delocalized valence electrons of metals the atomic corrugation on metal surfaces is expected to be much weaker than that of, e.g., semiconductor surfaces and the resolution of individual atoms on a close-packed metal surface has been reported so far only once.² In this Letter we present results of a systematic STM study on the resolution of individual atoms on the close-packed (111) surface of the nearly free electron metal aluminum. This leads us to propose an elastic deformation of the tip end mediated by adhesive tip-sample interactions as the main mechanism responsible for the resolution of atomic corrugation on these kinds of metal surfaces.

The experiments were performed under ultrahigh vacuum conditions ($p < 1 \times 10^{-10}$ torr) with use of an STM with a mechanically driven tip-sample approach. Standard techniques for sample preparation and characterization such as ion sputtering, low-energy electron diffraction (LEED), and Auger-electron spectroscopy (AES) were *in situ* accessible via a sample transfer system. Following a procedure of mechanical and electrochemical polishing the Al(111) sample was prepared in an ultrahigh vacuum by cycles of Ar^+ sputtering at 300 K and annealing to 800 K. Surface contaminations were reduced to below 1% of a monolayer as judged from AES, and the surface exhibited a LEED pattern with round and sharp spots on a negligible background, indicative of a well ordered surface. This was in accordance with our STM images, which revealed that large fractions of the surface consisted of terraces of several hundred angstroms width. STM tips were prepared by elec-

trochemical etching of a 0.7-mm-diam tungsten wire. Prior to each experiment the tips were cleaned by field desorption in front of a gold foil. This procedure of tip preparation always resulted in stable but relatively blunt tips leading to STM images of monoatomic step edges of ~ 50 -Å width.

Extremely high lateral resolution was reproducibly achieved by briefly raising the sample potential to < -6 V while the surface was scanned in tunneling mode. After such a treatment the STM images revealed an additional surface corrugation reflecting the hexagonal lattice of the close-packed fcc(111) surface. A grey scale representation of an image obtained at a bias voltage of -50 mV and a tunnel current of 6 nA after such a treatment is displayed in Fig. 1. The distortion at the

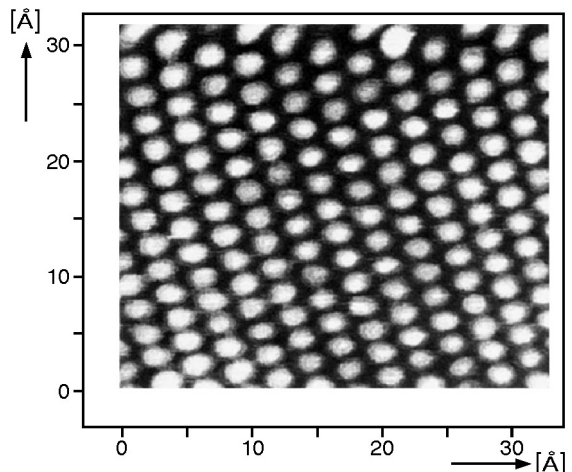


FIG. 1. Grey scale representation of an STM image of the clean Al(111) surface ($34 \times 34 \text{ \AA}^2$, corrugation amplitude 0.3 \AA , $V_t = -50 \text{ mV}$, $I_t = 6 \text{ nA}$).

upper part is due to hysteresis in the piezoelectric drive. The nearest-neighbor distance between two protrusions of 3 Å is in good agreement with the crystallographic interatomic distance of 2.86 Å in aluminum. The corrugation amplitude, determined to be 0.3 Å in this image, mostly lies in the range of 0.1–0.4 Å, depending on tunnel conditions. Following the above tip preparation similar images were routinely obtained at positive and negative bias voltages and at tunnel currents between 1 and 100 nA. It should be noted that this state of high resolution is rather unstable: The tunnel current often exhibits brief instabilities and the resolution of the tip can change abruptly without any apparent reason.

These results are in striking contrast to any predictions based on a first-order approximation for metal surfaces, in which the STM image was directly linked to the contour lines of the total charge density at the center of the (spherical) tip.³ As expected for an almost free electron metal a slab calculation of an Al(111) film revealed no measurable corrugation in the total charge density already at 3 Å above the topmost layer,⁴ which is certainly less than normal electrode distances in STM. Likewise the He scattering potential, which is directly associated with the total charge density at the turnaround point of the scattered atoms,⁵ exhibited a corrugation amplitude of <0.02 Å for Al(111).⁶ Even for an ideal, monoatomic tip at a given distance away from the surface the observed corrugation cannot exceed the corrugation in the total charge density at that distance as long as there are no additional effects invalidating this model. This means an atomic corrugation of the observed amplitude should not have been resolved on Al(111) by STM even at very close distances.

For a better understanding of the physical basis of the

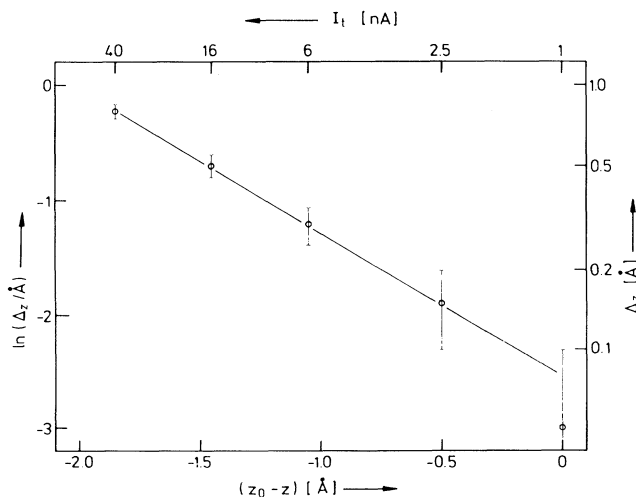


FIG. 2. Atomic corrugation amplitude Δz as a function of the relative tip sample distance $(z_0 - z)$. $V_t = -50$ mV, I_t as indicated.

strong enhancement in lateral resolution the correlation between corrugation amplitude and tunneling parameters (tunnel current, tunnel voltage, tip size) was investigated in more detail. Figure 2 reproduces results of an experiment on the correlation between corrugation amplitude and gap width, in which a set of STM images was recorded at different tunnel currents. The resulting changes in corrugation amplitude are plotted as a function of the relative vertical displacement of the tip ($z - z_0$) for currents between 40 and 1 nA (bias voltage -50 mV). In view of the instabilities at high-resolution conditions only data from one experiment (with constant tip shape) can be used for the quantitative evaluation. The data demonstrated that the corrugation amplitude not only can reach rather large absolute values—0.8 Å at 40 nA—but also that the corrugation can be detected over a range of gap widths of at least 2 Å. So even if the gap width at 40 nA correspond to 3 Å, the corrugation would still have been detected at 5-Å tunnel distance, which is far outside the turnaround point for He scattering. The tunnel barrier calculated from these data amounts to ~ 3.5 eV.

For Au(111) the authors postulate an electronic enhancement comparable to that predicted for graphite surfaces, where tunneling is limited to one specific state and strongly localized.⁷ The corrugation in the STM scans over Au(111) was associated with a surface state at the Γ point of the Brillouin zone.² For Al(111) a surface state in a partial band gap of the projected band structure at \bar{K} close to E_F was calculated and experimentally verified by angular-resolved photoemission as a pronounced feature at ~ 0.5 eV.⁸

The electronic structure of the metal surfaces discussed here is, however, distinctly different from that of a graphite surface since in the former case there exist other states in the energy region of the band gap just below E_F . The assignment of the observed corrugation solely to an electronic state effect would thus demand that tunneling via the surface state dominates the total tunnel current, although various other (bulk) states are available.

Experiments on the tunnel voltage dependence revealed that the atomic corrugation could be resolved in the bias range of -1 V $< V_t < +1$ V, and exhibit a constant amplitude, provided that the average distance was maintained. This not only rules out any dominant contribution of the surface state at 0.5 eV mentioned above, but also rules out effects due to a distortion in the electron distribution induced by the electric field between tip and surface as recently discussed by Inglesfield.⁹

The most significant single parameter for the observed corrugation apparently relates to the specific procedure of tip preparation. Likewise other studies on Au surfaces^{2,10} not only quote a similar treatment for getting high-resolution images but also describe comparable effects on the stability of the tunnel conditions. To ob-

tain more information on the actual processes during this procedure a series of STM images of the same area were taken before and after tip preparation and while the potential was switched to a high value. A selection of these images, is reproduced in Fig. 3. The undermost image recorded at $V_t = -500$ mV and $I_t = 1$ nA [Fig. 3(a)] is characteristic of imaging conditions using blunt tips as obtained by field desorption. Two monoatomic steps at the left- and right- hand sides of the image, respectively, extend over ~ 40 Å, indicating the low lateral resolution. In Fig. 3(b) the first lines on the left-hand side were still taken at the same low bias potential, while subsequently this was raised suddenly to -7.5 V and left at this voltage for approximately four scan lines. The tip responds to this potential jump by a sudden withdrawal by ~ 30 Å. This is much more than the 2–4 Å that could be expected from the constant current condition. While the bias is kept at -7.5 V the scan lines are strongly disturbed. Subsequently the bias potential was reduced to its initial value of -500 mV again. Now the tip does not return to its former z position but remains displaced from that by about 25 Å. From this sequence it is deduced that the tip actually gets longer by ~ 25 Å. The results of this treatment are obvious from Fig. 3(c). A

small trace of highly defective surface at the left-hand side of the image marks the area where the bias voltage had been raised. This treatment thus has destroyed the formerly smooth surface over the entire area of high bias conditions.

The lateral resolution was improved dramatically by this procedure which is demonstrated by the extension of the step edges in Figs. 3(b) and 3(c). They are reduced now to < 8 Å as compared to ~ 40 Å in Fig. 3(a). This procedure turned out to be completely reproducible and in most cases resulted in tips getting atomic resolution. The tip in this state is, however, rather unstable and often undergoes irreversible changes. Since in the foregoing discussion an ideal, monoatomic tip was already assumed, a "sharpening" of the tip alone cannot account for the increase in resolved corrugation within that picture.

The observed deformation of the Al surface and the lengthening of the tip, either by restructuring of the tip itself or by material transfer from sample to tip, indicate strong interactions between tip and sample at least during high bias conditions. Interactions of any kind, however, are not included in the "transfer Hamiltonian" formalism used by Tersoff and Hamann.³ Such interactions were recently found to contribute significantly to the STM images of graphite, where at small gap widths, repulsive interactions together with the elasticity of graphite normal to the carbon planes led to a pronounced amplification of the electronic corrugation.¹¹ For STM measurements on metal surfaces it was found that even at normal tunnel conditions (tunnel resistance 10^6 – 10^9 Ω) sizable adhesion forces are acting, which decay exponentially into vacuum.¹² We propose tip-surface interactions also to be responsible for the enhancement in corrugation observed in STM images of these close-packed metal surfaces.

The forces resulting from the interaction of all electrons rather than those close to E_F can contribute to the corrugation observed in an STM image in two different ways. They can, similar to effects in chemisorption, modify the spatial and energetical distribution of states, including those which contribute to the tunnel current. In addition, they can affect the equilibrium position of the surface atoms and the topmost tip atoms. While tip-induced distortions of the metal lattice can be neglected to first order—the interlayer distances of close-packed metal surfaces are also rather insensitive to the presence of adsorbates—the effects upon the distribution of states may be larger. For a rough guidance this can be compared to the corrugation of the potential felt by a migrating Al atom, since both the tunnel current and the chemisorption bond are related to the overlap. For the surface diffusion of hard-sphere atoms the corrugation would amount to 0.39 Å, but due to the delocalized sp electrons the real quantity will be significantly smaller.

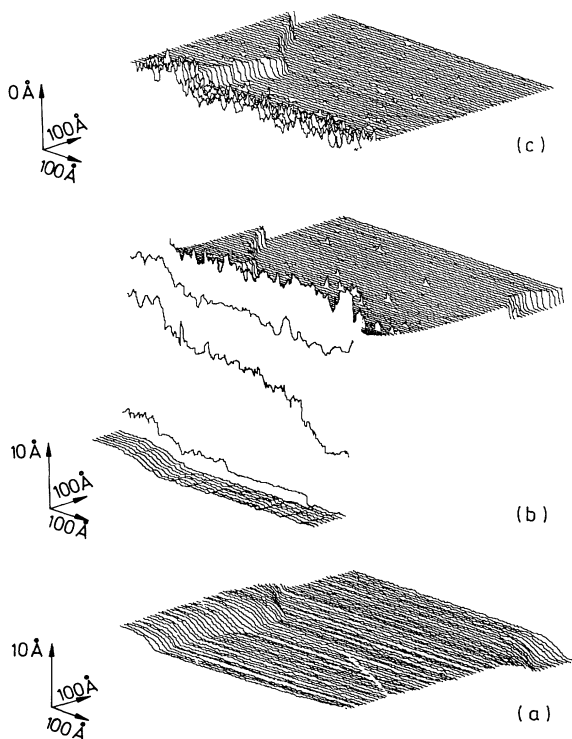


FIG. 3. Sequence of STM images of the same area recorded (a) before, (b) during, and (c) after tip preparation by briefly raising the tip voltage during four lines in (b) (tip lengthening) from -500 mV to -7.5 V ($I_t = 1$ nA).

There remain the effects upon the probing tip itself, the apex of which was shown to be formed by a metal cluster. Independent of whether this cluster consists of Al transferred from the sample or of W atoms, "adsorbed" clusters of that size are known to be rather unstable and to frequently change their shape.¹³ This can well account for the instabilities in tunneling conditions observed experimentally. In addition such clusters may also be distorted elastically. In combination with a corrugation in the contours of constant force and thus with spatial differences in the forces encountered by the tip during an STM scan this effect can account for a large fraction of the observed corrugation, as long as the contours of constant tunnel current (without interaction) are different from the contours of constant force. Also, this effect should decay exponentially with distance, as it is observed experimentally. This latter mechanism we make largely responsible for the resolution of atomic corrugation in the STM images of the close-packed surfaces Al(111) reported here and of Au(111), for which the process of tip preparation as well as the instability of the "high-resolution" tip were reported to be very similar to the present findings.²

In summary we have shown that even for an almost free electron metal such as aluminum the individual atoms of the close-packed (111) surface can be resolved by STM. From the measurements of the energy and gap-width dependence of the atomic corrugation a predominantly electronic origin of this phenomenon can be ruled out. It is directly demonstrated that by the ap-

plied procedure of tip preparation a metal cluster is formed on an otherwise blunt tip. An elastic deformation of this cluster, caused by adhesion forces between tip and sample, is proposed as an amplification mechanism for the existing electronic corrugation, which is made responsible for the resolution of individual atoms on this and other close-packed metal surfaces.

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