Scanning Tunneling Microscopy of the Local Atomic Structure of Two-Dimensional Gold and Silver Islands on Graphite

Eric Ganz, Klaus Sattler, and John Clarke

Department of Physics, University of California, Berkeley, California 94720, and Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Small, two-dimensional islands of silver and gold formed *in situ* by evaporation onto graphite cleaved in ultrahigh vacuum are imaged atom by atom with a scanning tunneling microscope. These islands contain ordered regions of roughly 50 atoms in rectangular lattices, incommensurate with the substrate lattice, that are not close packed as in the bulk fcc structure. In one series of images, the shorter lattice spacing remained constant at 2.35 ± 0.15 Å, whereas the longer decreased from 4.05 ± 0.1 to 3.5 ± 0.1 Å over a period of roughly 10 min.

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Three-dimensional crystals of Ag or Au have a close-packed structure, namely face-centered cubic. However, very little is known about the structure of these metals in two dimensions or for small particles. In the case of small clusters, the electronic structure and chemical reactivity have been extensively studied, but the morphology has remained open to debate.[1] For systems containing only a few atoms, the local environment of each atom may be unique, and it is thus desirable to study these systems on an atomic scale, since the morphology forms the basis for predictions of the behavior of these systems. We have used a scanning tunneling microscope (STM) to observe the local atomic structure of small monolayer metal islands on highly oriented pyrolytic graphite (HOPG).[2,3] In striking contrast to the bulk case, we find the lattice to be rectangular, rather than close packed.

We use HOPG as a substrate because it can be easily cleaved to provide a large (domain size $\simeq 100$ μm), flat, and chemically inert surface that is virtually free of defects. Thus, we expect the substrate to exert a minimal influence on the structure of the adatoms. Our experimental procedure has been described in detail elsewhere.[3] In essence, we cleave HOPG in a vacuum of 10^{-8} Torr, and transfer the sample to the STM in an ultrahigh-vacuum (UHV) system at 3×10^{-10} Torr. We image typically 1 μm^2 of the surface to ensure the complete absence of observable contamination before we deposit the metal. We then move the sample from the STM to another location in the UHB chamber, and evaporate roughly 0.1% of a monolayer of Ag or Au onto the graphite surface, which is at ambient temperature. Finally, we return the sample to the STM to obtain images of the deposited material. We find that most of the sample remains unadorned, with the metal adatoms distributed in small groups of flat islands.[4] In this Letter we show a few representative examples of the large number of islands we have imaged.

We operate the STM in the current-imaging mode, scanning the tip at a constant height above the surface and recording the variations in tunnel current.[5] Thus, metal adatoms are imaged as spots of enhanced current, which are displayed as lighter areas in gray-scale images. An image is obtained every 4 sec, and stored in real time on videotape. With the low coverage, we are able to image both the edge of an island and the neighboring graphite lattice simultaneously. Subsequently, we digitize the locations of the graphite-lattice spots and adsorbate atoms, and generate computer models of our data using a linear transformation to map the observed graphite lattice, which may be slightly distorted, onto a honeycomb. With the aid of this model, and the known 2.46-Å spacing of graphite,[6] we use the computer to determine the lattice spacings of the overlayer, and its orientation relative to the substrate.

Figure 1(a) is an image of a portion of a 40-Å-diam silver island, while Fig. 1(b) is the corresponding computer model. In the model, we have outlined two rectangular ordered regions. These lattices are neither commensurate with the substrate, nor close packed. A grain boundary is visible in the center of the island, and, at the top right of the image, we observe a buckling of the chains of silver atoms in the rectangular array to form a sixfold ring. By averaging measurements from four images, we find that the rectangular lattice parameters are $(2.58 \pm 0.06) \times (3.33 \pm 0.1)$ Å^2 on the left, and $(2.44 \pm 0.08) \times (3.37 \pm 0.1)$ Å^2 on the right. In subsequent images of the same island, a third ordered region was also observed with an almost square lattice, $(2.72 \pm 0.06) \times (2.79 \pm 0.08)$ Å^2.

Most of the atoms in Fig. 1 are imaged as single spots. The observed shape of each atoms is unique and reproducible from image to image, leading us to believe that the electronic structure, which presumably depends on the local environment, varies from atom to atom. It is also possible that vibration of a Ag atom about its equilibrium position produces an asymmetric shape.[7] The position of each atom was observed to be stable over

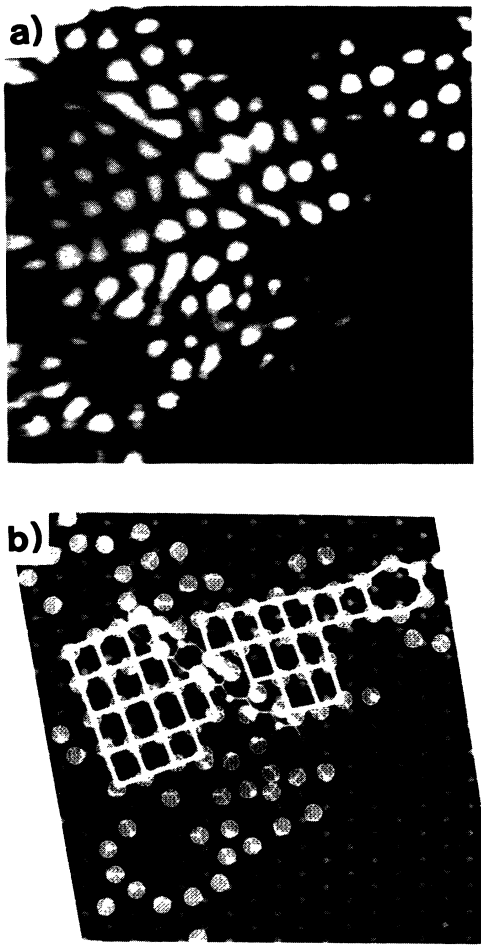

FIG. 1. (a) 35×35-Å^2 STM current image of part of a monolayer Ag island on graphite. The graphite honeycomb lattice is visible at the lower right. (b) Computer model showing the positions of the adatoms (filled circles) on the graphite honeycomb lattice (small dots at β sites). Lines have been drawn to guide the eye.

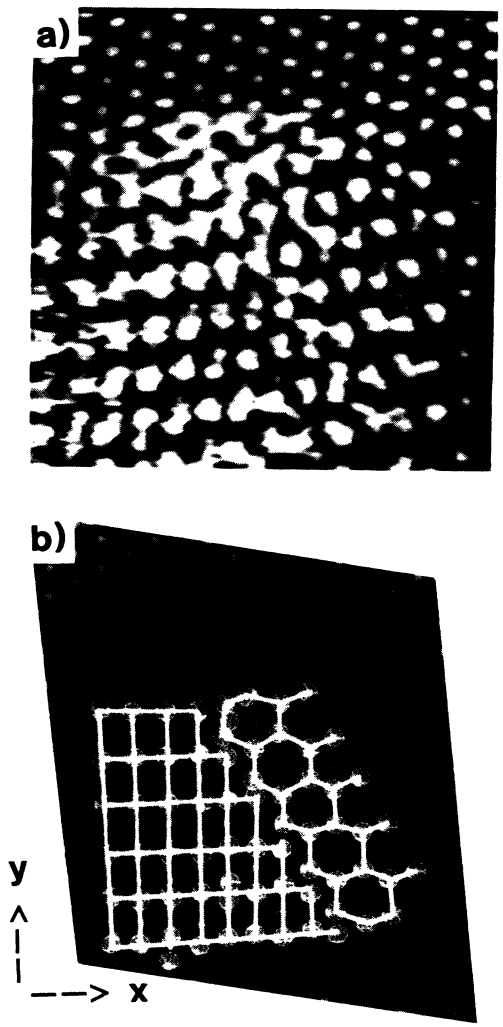

FIG. 2. (a) 35×35-Å^2 image of region A of a monolayer Au island on graphite. The graphite is imaged as dots at the top. (b) Computer model showing a rectangular lattice on the left and a honeycomb lattice on the right.

periods of minutes, with the edges of the island rough and disordered. This surface roughness[8] suggests that the atoms are pinned to the substrate; otherwise we would expect surface self-diffusion to produce a smooth surface.[4] By contrast, atoms in the interior of the islands form ordered, incommensurate structures suggesting that when the atoms have more nearest neighbors, the Ag-Ag interaction is dominant. Furthermore, as the Ag atoms bind to other Ag atoms, the interaction with the substrate is reduced because of rebonding effects.[9]

A portion of a gold island (region A) is shown in Fig. 2. In the interior of the island, there are two domains, each with its own ordered structure: On the left we observe a rectangular lattice with spacings of $(2.47 \pm 0.06) \times (3.9 \pm 0.1)$ Å^2, and on the right a honeycomb lattice. The whole island is rotated by $3.4° \pm 1.4°$ relative to the substrate. We have analyzed thirteen images of this region taken over a period of 90 sec. We find that the short axis α of the rectangular structure remained roughly constant at 2.35 ± 0.15 Å, while the long axis β shrank from 4.05 ± 0.1 Å for the first frames to 3.80 ± 0.1 Å for the last frames of the series. We then moved the STM tip to a different region (B) of the same island, where we made a series of 22 images over a period of 10 min. Figure 3 shows three images near the end of this series. We observe that while the value of α remains constant at 2.35 ± 0.1 Å, β decreases from 3.8 ± 0.1 Å for the first images to a final value of 3.50 ± 0.1 Å which remains relatively constant. We plot the values of α and β for all 35 images in Fig. 4.

The nearest-neighbor spacings observed along the chains of Figs. 2 and 3(a) (2.35 ± 0.1 and 2.47 ± 0.06 Å) are surprisingly small. Now, one would certainly expect these values to be smaller than in the bulk: As the

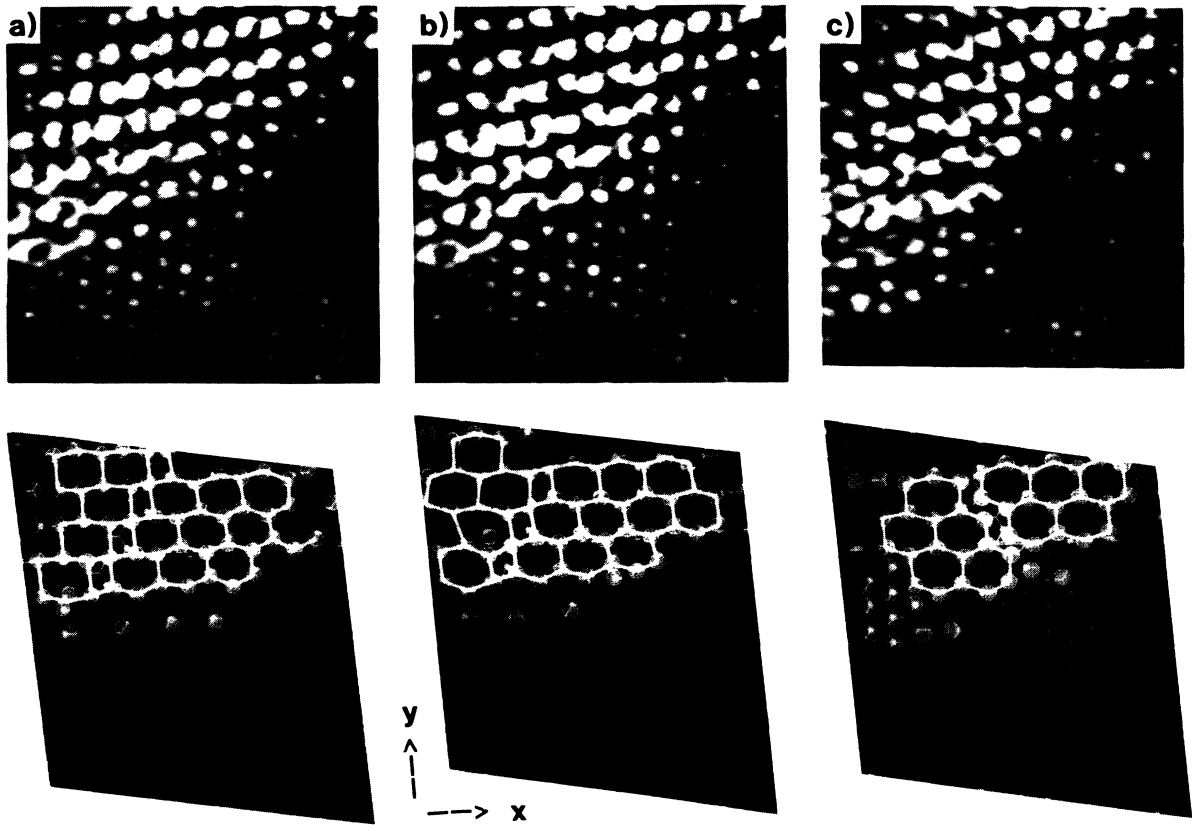

FIG. 3. (a) 35×35-Å^2 image of another region, B, of the same Au island as in Fig. 2 with an image taken (b) 4 sec later, and (c) another image from the same series. In (a), we observe chains of atoms on the left-hand side. We have extended the chains with a horizontal dashed line. We see that on the right-hand side, the chains are buckled up from the line. In (b) and (c), both sides are buckled, down on the left and up on the right, and the two different structures are separated by a domain wall (shaded). Excess spots visible in the interior of the island are presumably β sites of the graphite substrate.

dimensionality of a crystal structure is reduced from 3D to 2D to 1D, the bond length is decreased as the number of nearest neighbors is reduced,[10] for example, from 2.88 Å for bulk Au to 2.47 Å for a dimer.[11] With appropriate parameters, the model of Tomanek, Mukherjee, and Bennemann[10] gives rough estimates of 2.55 Å for a 1D chain, with two nearest neighbors, and 2.75 Å for a close-packed 2D layer with six nearest neighbors. However, the observed bond lengths in the chains are equal to or somewhat smaller than the dimer length, definitely less than the prediction of a 1D chain. This reduction in bond length may arise from the interaction with the substrate.

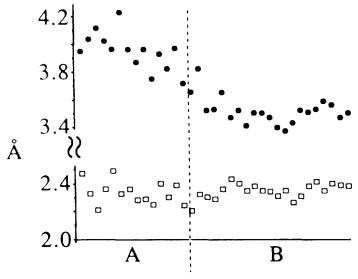

FIG. 4. Plot of the short-axis, α (squares), and long-axis, β (circles), lattice spacings for the 35 images of regions A and B of the Au island. The images were obtained over a period of 1.5 min for region A and 10 min for region B.

Neither the Ag nor Au islands exhibit the close-packed structure observed in larger and thicker films.[4] We would expect the ground state of an infinite, 2D film to be close packed in the absence of any interaction with the substrate. Possibly, the observed rectangular structures represent thermal excitations from this ground state. Alternatively, since the islands are rather small in extent, the effects of surface tension may be important. Yet another possibility is that the rectangular structures arise from the interaction between the adatoms and the substrate, which, while weak, is nonzero: Drechsler, Metois, and Heyraud estimate 0.26 eV per Au atom.[4] Our images confirm that the interaction is small since the island structures are neither commensurate with nor aligned with the substrate lattice. The fact that the β axis of the Au lattice was observed to decrease smoothly

with time also suggests that the Au-graphic coupling is weak, and that there is a shallow minimum in the potential energy as β is varied. One can hope to resolve these issues only with a detailed model calculation.

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[1]*Metal Clusters*, edited by F. Trager and G. zu Putlitz (Springer-Verlag, New York, 1986).

[2]D. W. Abraham, K. Sattler, E. Ganz, H. J. Mamin, R. E. Thomson, and J. Clarke, Appl. Phys. Lett. **49**, 853 (1986).

[3]E. Ganz, K. Sattler, and J. Clarke, J. Vac. Sci. Technol. A (to be published).

[4]M. Drechsler, J. J. Metois, and J. C. Heyraud, Surf. Sci. **108**, 549 (1981).

[5]A. Bryant, D. P. E. Smith, and C. F. Quate, Appl. Phys. Lett. **48**, 832 (1986).

[6]P. Trucano and R. Chen, Nature (London) **258**, 137 (1975).

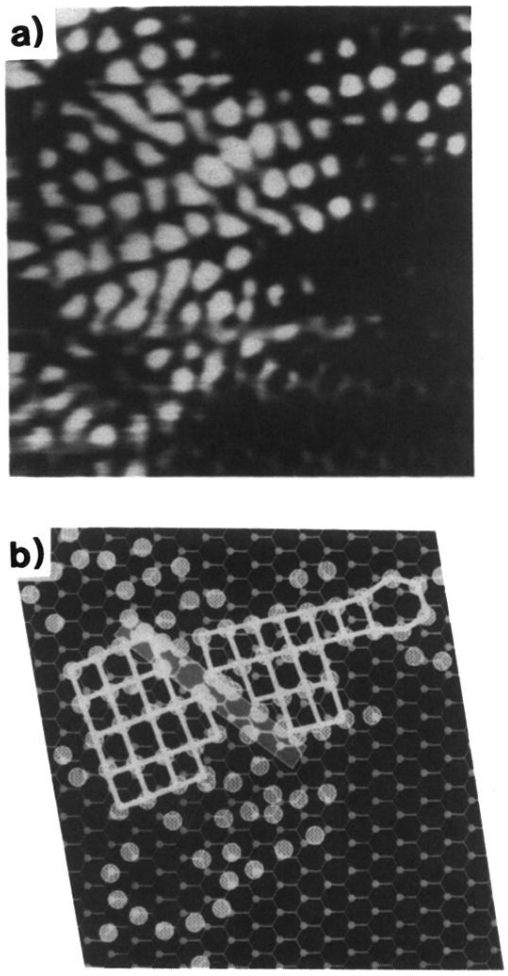
[7]M. de Crescenzi, P. Picozzi, S. Santucci, C. Battistoni, and G. Mattogno, Surf. Sci. **156**, 352 (1985).

[8]J. Kolaczkiewicz and E. Bauer, Phys. Rev. Lett. **54**, 574 (1985).

[9]P. J. Feibelman, Phys. Rev. Lett. **58**, 2766 (1987).

[10]D. Tománek, S. Mukherjee, and K. H. Bennemann, Phys. Rev. B **28**, 665 (1983).

[11]K. S. Krasnow *et al.*, *Handbook of Molecular Constants of Inorganic Compounds* (Israel Program for Scientific Translations, Jerusalem, 1970).



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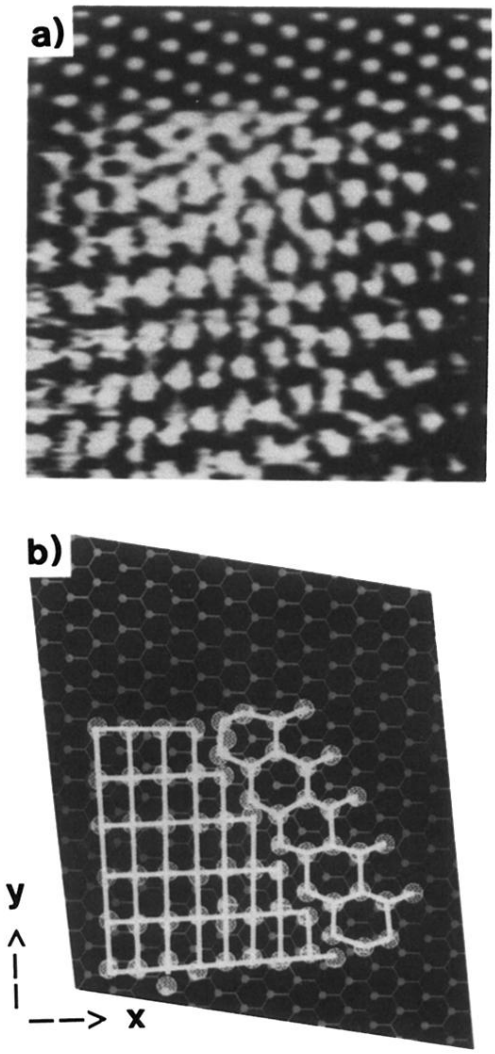

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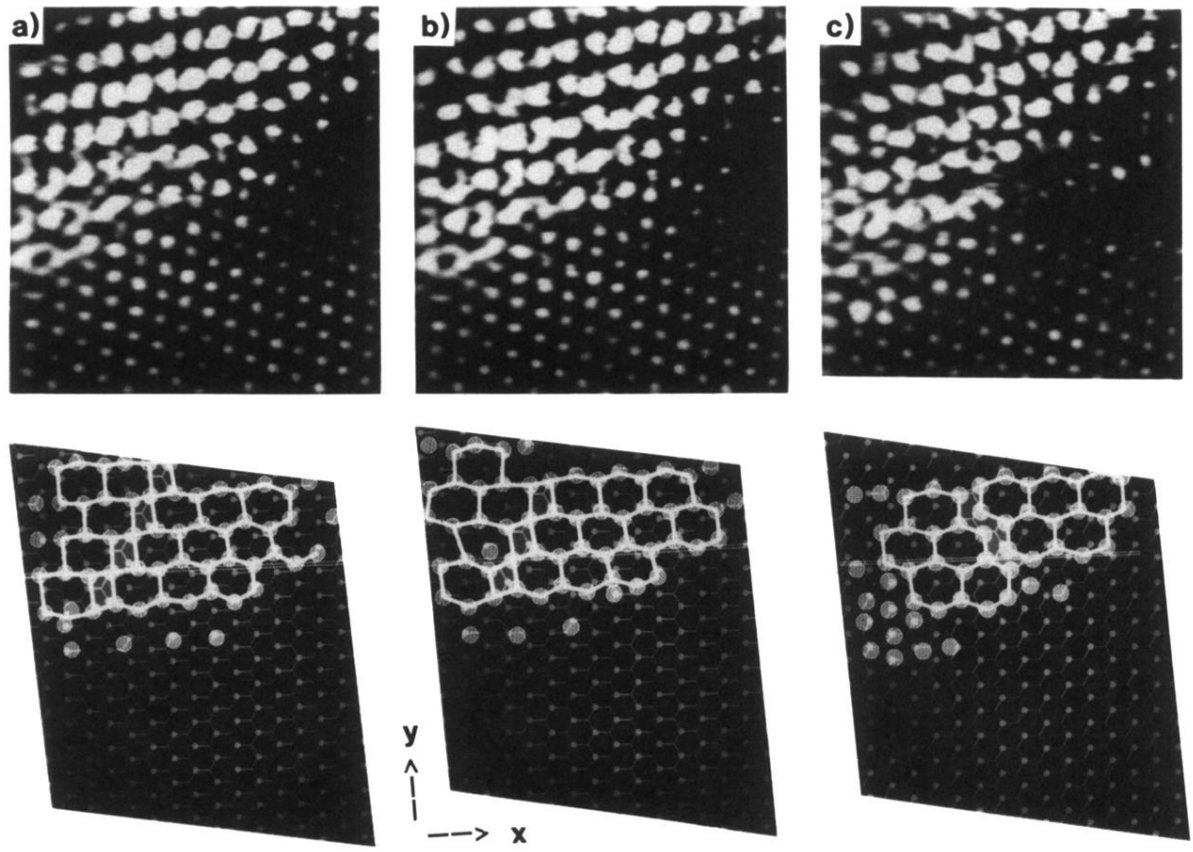

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