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UNCLASSIFIED N00014-78-C-0011 F/G 7/2 NL

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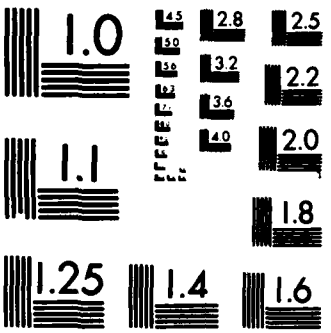

Atomic Force Microscopy of Liquid-Covered Surfaces: Atomic Resolution Images

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(Received June , 1987)

ABSTRACT: Images of graphite surfaces that are covered with oil reveal the hexagonal rings of carbon atoms. Images of a sodium chloride surface, protected from moisture by oil, exhibit a mono-atomic step. Together, these images demonstrate the potential of Atomic Force Microscopy (AFM) for studying both conducting and non-conducting surfaces - even surfaces covered with liquids. Our AFM uses a cross of double wires with an attached diamond stylus as a force sensor. The force constant is $\approx$ 40 N/m. The resonant frequency is $\approx$ 3 kHz. The lateral and vertical resolutions are 0.15 nm and 5 pm.

The Atomic Force Microscope (AFM)[1,2,3] is a new tool for investigating surfaces. The surface is scanned with a stylus. Predecessors of this instrument include profilometers[4,5,6], the topografiner[7], and Scanning Tunneling Microscopes (STM)[8,9,10]. The AFM, unlike the STM, is not restricted to conductive or semi-conductive surfaces. As for the STM, the apex of the probing tip or stylus consists ideally of a single atom. This and the smaller forces applied to the surface distinguishes the AFM from the older stylus instruments[6]. The obtainable resolution with the AFM[2] today is comparable to that achieved with STM's and much better than that of the stylus profilometers.

AFM design closely resembles that of STM's. A sample is mounted on a (x,y,z)-piezo translator and pressed against a stylus mounted on a spring with a compliance of 0.1 to 100 N/m. The deflection of the spring is monitored and kept constant by a feedback loop adjusting the position of the sample. Binnig, Quate and Gerber describe in their landmark paper[1] an AFM with a diamond stylus mounted on a gold foil. The spring deflection was monitored by tunneling from a metal tip to the foil. An insulating ceramic was imaged with lateral and vertical resolutions of 1 nm and 0.3 nm, respectively. A later improved design[2] used one edge of a slightly tilted micro-fabricated silicon oxide cantilever as spring and stylus and tunneling to monitor the deflection. AFM's of this design[2] are capable of atomic resolution on graphite, i.e. lateral resolution better than 2.5 Å. A lateral resolution of 10 nm and a vertical resolution of 1 nm were achieved with an AFM using a tungsten wire bent at its free end as a combination spring and stylus and optical interference for deflection monitoring.

Our AFM design (see Fig. 1) is an extension of an earlier STM design by our group[11]. The sample is mounted on a piezo tube which in turn is attached at its lower end to a invar base plate. The piezo tube has the necessary electrodes for generating the x-, y- and z-movement[12] (lateral and vertical sample movement). The force sensor assembly is supported by three screws with balls at their ends and can be lowered onto the sample

surface by a motor-driven screw. The force-determining spring is made of four platinum wires, each 25 μm thick. The wires cross each others in the center of a 4 mm hole in a hemispherical brass piece. Each arm of the cross consists of two parallel wires separated by 0.5 mm. The four crossing points are epoxied together with the diamond epoxied to one of them. The diamond is a fragment from a small gem that was shattered between two hardened steel plates with a hammer. It is a pyramid with a base length and height of 0.5 mm each. The spring constant of one wire, which we assume to be clamped at its ends, is[13]

$$k = \frac{3\pi E d^4}{L^3},$$

where $E = 17.0 \times 10^{10}$ Pa is Young's Modulus of platinum, $d = 25\mu$m the diameter of the wires and $L = 4$ mm the free length of the wires. Hence the force constant of four wires is $4k \approx 40$ N/m. The resonant frequency is given by

$$f_{Res} = \frac{1}{2\pi}\sqrt{\frac{k}{m}},$$

where the mass m is the effective mass of the wire, epoxy, and diamond assembly. In our microscope, this mass was dominated by the mass of the diamond $m = 1.5 \times 10^{-7}$ kg. Thus $f_{Res} \approx 3$ kHz, which is in agreement with the performance of the microscope. The interaction between the stylus and the sample increases the effective spring constant and resonant frequency of the force sensor[14]. A cross of double wires is easy to build and is, in our experience, rigid enough laterally to not be measurably affected by the direction of scanning relative to the wires. A rough estimate of the lateral force constant can be obtained by assuming a stretching of two wires under the influence of such a force. We get for one wire [13]

$$k_{lat} = \frac{\pi d^2 E}{2L}.$$

All the variables have the same meaning as in the previous formulas. For two wires we get $k_{lat} \approx 8 \times 10^4$ N/m or 2000 times the vertical force constant. We sense the deflection of

the cross by tunneling from one of the cross wires to the edge of a triangular sensing wire. The sensing wire's cross section is a trade-off between decreased sensitivity to the local structure of the tunneling electrodes and the increased electrostatic attraction at larger tunneling areas. The sensing wire is mounted on a piezo (z') that can move it relative to the cross wires and thus set the force required to re-establish tunneling. The piezo, 2 by 2 by 10 mm, is sandwiched between two microscope cover glasses and glued to a metal plate. One side of the metal plate is attached to the holder and the other is pressed with a spring, adjustable with a screw, in a differential spring arrangement that is used for the coarse approach of the tunneling electrodes.

We used our AFM to image Highly Oriented Pyrolythic Graphite (HOPG) covered with paraffin oil[15]. We inferred the calibration of the piezo tube from atomic resolution STM images of HOPG[16]. These images also showed that the scanning directions of our piezo tube are not orthogonal. We then glued a freshly cleaved HOPG crystal to the scanning piezo and covered it immediately with a thin film of paraffin oil. The force sensor was cleaned in an acetone:ethanol 1:1 mixture in an ultrasonic cleaner prior to the experiment. We imaged graphite several times with our AFM and always used the same cross wires and diamond. Cleaning in the ultrasonic bath restored the previously lost atomic resolution most of the times. A plexiglass can on a concrete block suspended from the ceilings by rubber bungee cords isolated the microscope from sound and moving air during the experiment. All the cables running to the concrete block were attached to heavy weights on the block for vibration isolation. We first tunnel from the cross wires to the sensing wire and monitor the voltage across the z'-piezo (force adjustment piezo). After the initial drift settles, we switch the z'-voltage to the sum of the previous voltage and an offset to back the sensing wire away from the cross wires and approach the sample to the diamond stylus until a tunneling current is measured. Scan rates on the HOPG sample were between 32 ms and 2 ms per scan line (one way).

Fig. 2 shows an AFM image of HOPG covered with paraffin oil. Acquisition time for this frame consisting of 250 scan lines was 4 seconds. Black denotes depressions whereas white marks protrusions. The gray scale covers a range of 0.3 Å. The image, from which a background plane is subtracted, was captured with an Arlunya Temporal Filter and Image Storage device[17] and recorded on a VCR. Other than that, no image processing was done. The hexagonal graphite unit cell in Fig. 2 is distorted because of the non-orthogonal scanning in our microscope and is not corrected for. The measured corrugation is 0.3 Å and agrees quite well with experimental results for He scattering[18] and with theoretical calculations[19] for the contours of constant total density of charge. Note that the upper end of the stripes is brighter than the lower ones. Graphite atoms at the surface can occupy two different sites, with or without neighbors in the next lower layer. Although we were able to distinguish these two inequivalent sites with our AFM, we can not label them. The heights of the two sites differs in our measurement by less than 0.05 Å. Our microscope therefore has a lateral resolution of 1.5 Å and a vertical one of 0.05 Å.

We do not know the exact amount of force in our experiment because drift changes the deflection of the wires. We were, however, able to image the same area on the graphite surface for more than an hour. This indicates, that the force was not big enough to destroy the graphite surface.

Fig. 3 shows two images of a mono-atomic step on a cleaved sodium-chloride surface. The sample was cleaved under paraffin oil and transferred with the oil film to the AFM. The second image was taken at a faster scan speed than the first. The vibrational noise, which is in the 10 to 60 Hz range, could not be filtered out in the second image. But the overall appearance of the step and its height are preserved.

In summary, atomic-resolution imaging is possible even with a relatively crude AFM fabricated on a screw with fine wires, epoxy, and a small fragment from a shattered diamond. We hope that future, more sophisticated AFM's will allow routine atomic-resolution

imaging of insulators, adsorbed molecules, monolayer assemblies, and perhaps even biological systems.

We thank the Physics Machine Shop and especially Mat Wilson, Rudi Stuber and K n Voelker for helping to build and debug the microscope. We also appreciated the help of the Physics Electronic Shop and Eloise Martzen and Anna Dietler, our secretaries. We had useful discussions with G. Binnig, C. F. Quate, D. Smith, T. Albrecht, J. Schneir, R. Sonnenfeld, and S. Alexander. V. Elings helped us to improve our electronics.

This work was supported in part by the Office of Naval Research and by a grant from the Schweizerischer Nationalfonds zur Förderung der Wissenschaften, Switzerland (O. Marti).

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FIGURE CAPTIONS

1. Schematic Drawing of our AFM. The right side shows the screw holder with the differential spring adjusting screw, the sample and the x,y,z-scanner. At the left side are closeups of the differential spring adjusting mechanism on top and of the cross wires with the diamond tip and the sensing wire below.

2. AFM image of HOPG that is covered with paraffin oil. The height varies by 0.3 Å between the lowest (dark) and the highest (white) spots. Non-orthogonal scanning directions cause the distortion of the image.

3. a) Line scan display of an AFM image of NaCl that is covered with paraffin oil. The scanning area is 45 by 45 Å. The measured height of the step is $\approx$ 3 Å compared to the 2.82 Å derived from the crystal structure. b) The same step at a higher scanning speed. At this scanning speed, the vibrational noise had about the same frequency as the step and could not be filtered out.

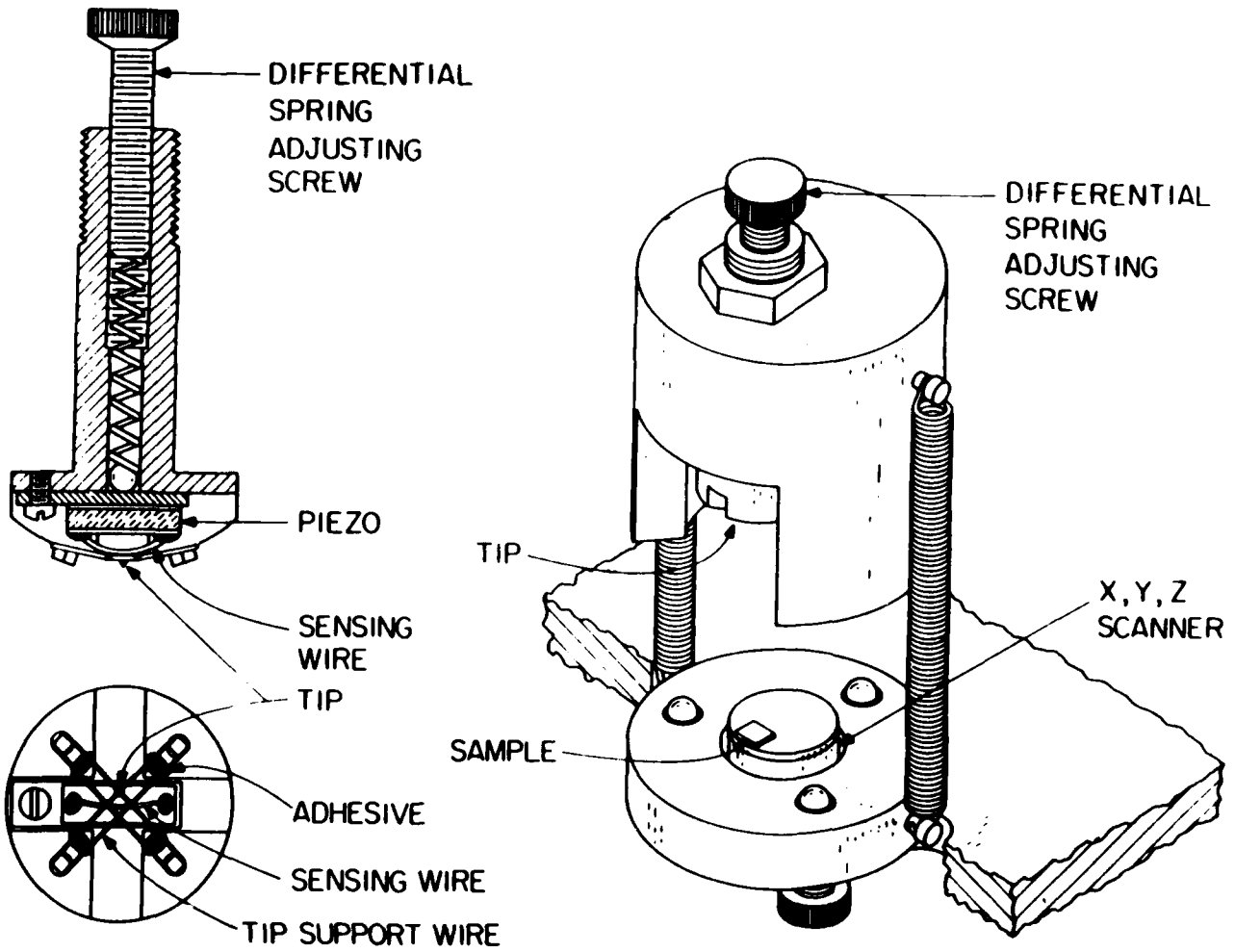

Figure 1
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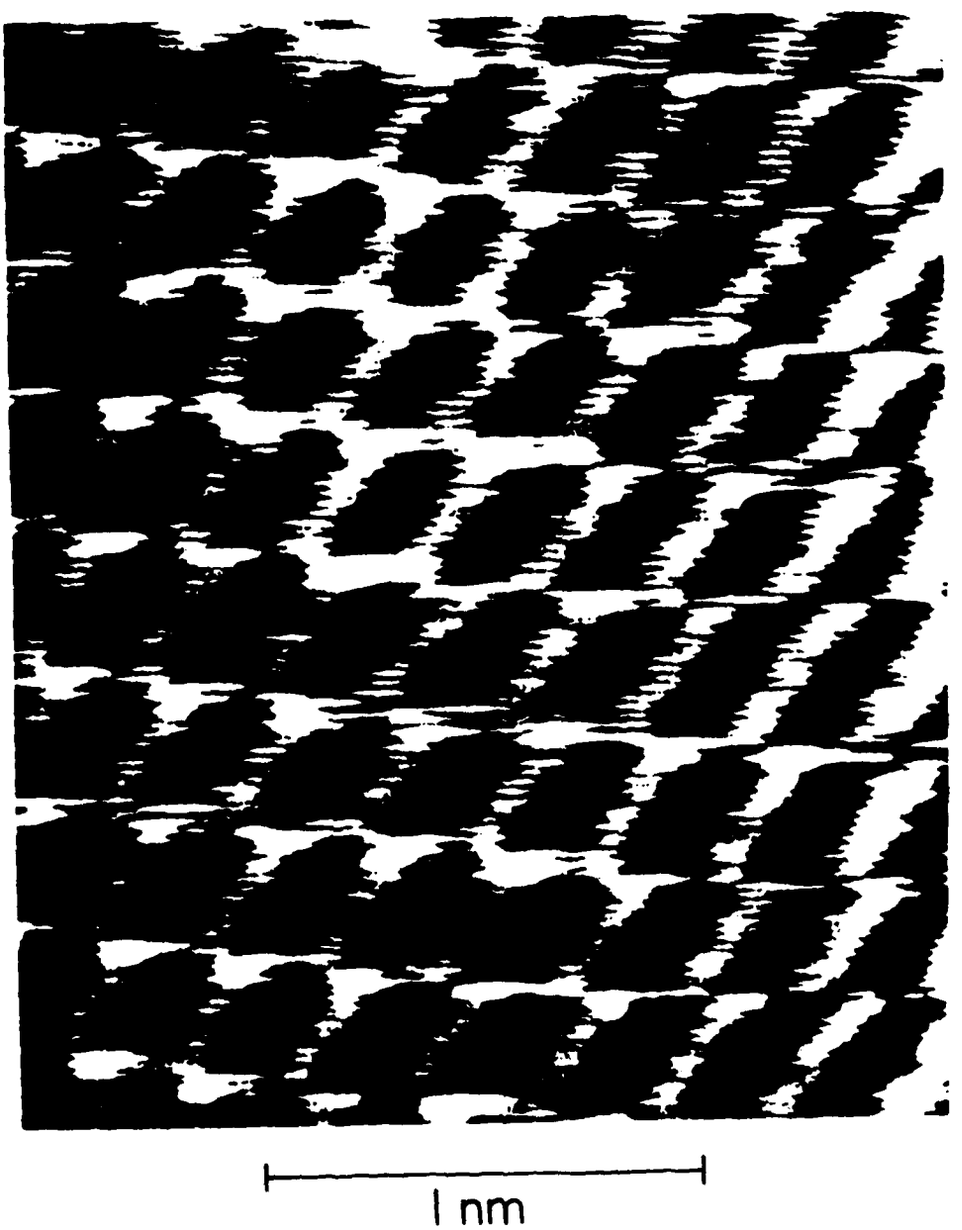

Figure 2
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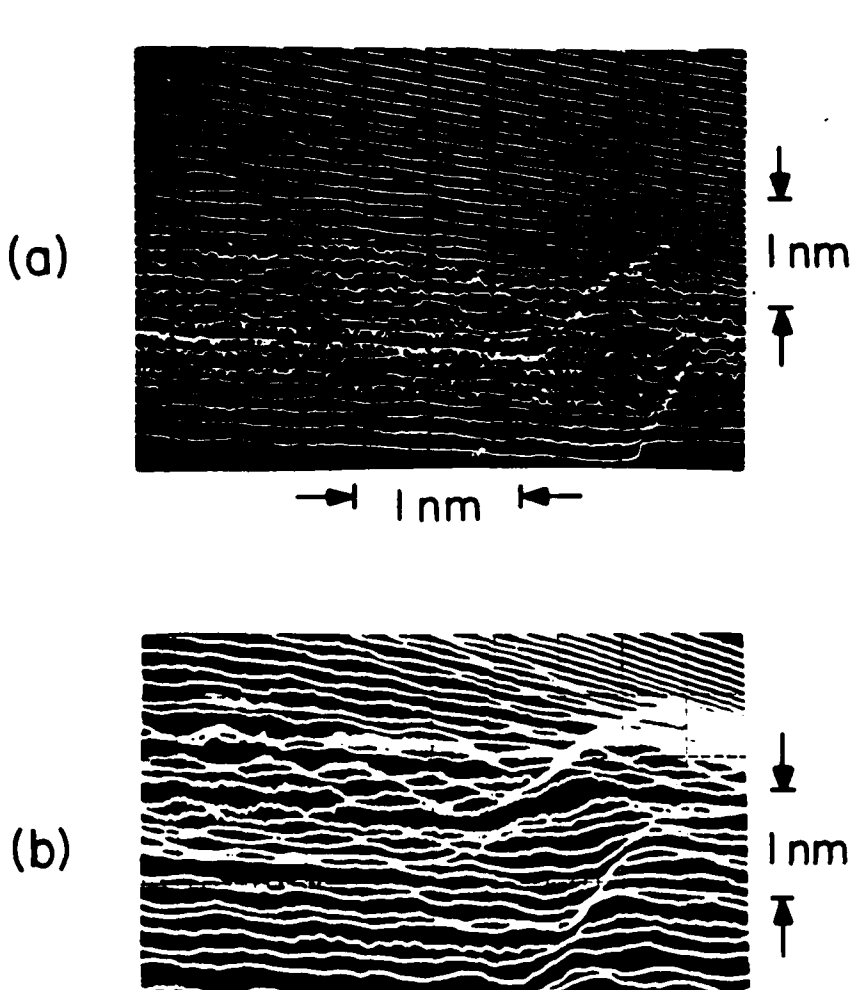

Figure 3
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Contract N00014-78-C-0011

Task No. 056-673/112384 (410)

Technical Report No. 26

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by

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prepared for publication in:

Applied Physics Letters

University of Californiaa
Department of Physics
Santa Barbara, CA 93106

A-1

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 26	2. GOVT ACCESSION NO. ADA182482	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Atomic Force Microscopy of Liquid-Covered Surfaces: Atomic Resolution Images		5. TYPE OF REPORT & PERIOD COVERED Technical 2/1/85-1/31/87
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) O. Marti, B. Drake and P.K. Hansma		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C0011
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics University of California Santa Barbara, CA 93106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR056-673/11-23-84 (410)
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE June 19, 1987
		13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Office of Naval Research Department of the Navy Arlington, VA 22217		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

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