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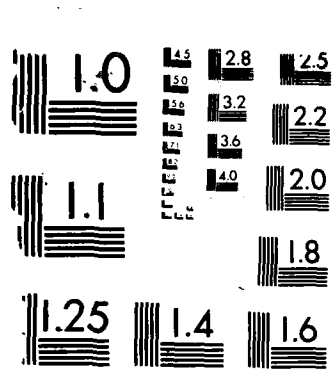

Scanning Tunneling Microscopy and Lithography of of Solid Surfaces Covered with Non-Polar Liquids

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We show that atomic resolution tunneling microscopy can be done under non-polar liquids. Two possible areas of application are explored: lithography and imaging air sensitive materials. The lithography was demonstrated by writing a 20 Å × 40 Å wide and 20 Å deep hole onto a gold surface. The imaging of air sensitive materials was demonstrated by imaging GaAs.

I. Introduction

As electrochemists have known for a long time, there are really only two ways in which a surface can be maintained clean: 1) in ultra-high vacuum and 2) under a clean liquid. Despite the importance of the liquid-solid interface in technology and biology, the vacuum-solid interface has much more attention in science. There are very good reasons for this: 1) it is simpler to understand theoretically, and 2) there are more available analytical tools. Fortunately, however, the scanning tunneling microscope,[1] which has been shown to be a powerful analytical tool,[2] will work at a liquid-solid interface. Atomic resolution images have been obtained for solids covered with liquid nitrogen,[3] liquid helium,[4,5] water[6] and conductive solutions.[7]

Here we show that atomic-resolution tunneling microscopy can be done under non-polar liquids. We demonstrate two possible areas of application: lithography and imaging air sensitive materials.

Important work has already been done in both of these areas. Lithography has been done with STMs in vacuum.[8–11] An air sensitive compound, GaAs, has been imaged not only in vacuum,[12–14] but also under a KOH solution.[15] Advantages of working under the non-polar liquids in this report rather than polar solutions include simplicity, lack of ionic conduction, and low volatility.

II. Experimental

Figure 1 shows the microscope used for this study. The springs firmly hold the scanner mount against a tripod of coarse tip-adjustment screws. Fine mechanical adjustment is achieved by a 10:1 reducing lever arrangement similar to that previously used by Demuth[16] and by Kaiser and Jacklevic.[17] The piezoelectric scanning element itself is of the single-tube design developed by Binnig and Smith.[4] The transverse calibration constant, 2.6 nm/V, was established by imaging the well-known surface structure of graphite.[18,19] The

vertical calibration constant, also 2.6 nm/V, was obtained from a simple calculation using the manufacturer's data, $d_{31} = 0.135$ nm/V, for the Channel 5400 material used for the element.[20]

Images were recorded by photographing a storage oscilloscope screen. The lines are z vs. x plots separated by Δy. Scanning was done right to left and top to bottom. The tunneling tips used were commercially available etched PtIr microelectrodes. [21]

All images were obtained with the sample at +0.1 volt with respect to the tip and 3 nA tunneling current. The tunneling current was determined by measuring the voltage drop across a $2 \times 10^6 \Omega$ shunt resistor in series with the junction. The shunt resistor limited the tunneling current, even in the case of a short, to 50 nA.

III. Results and Discussion

Figure 2 shows atomic resolution images taken under various non-polar fluids. The sample was highly oriented pyrolytic graphite.[22] Fresh surfaces were exposed by cleaving the graphite using a razor blade. Atoms were imaged under paraffin oil, silicone oil (Dow Corning 705 diffusion oil) silicone vacuum grease (Dow Corning high vacuum grease), and fluoro-carbon grease (Research Organic/Inorganic Chemical Corp. Poly-Fluor Laen grease). Graphite has previously been imaged with atomic resolution in UHV,[18] air,[23] and water.[6]

Figure 3 shows images of the GaAs (001) surface taken under various non-polar fluids. The GaAs was p type Zn doped with carrier concentrations of 1.6×10^{19} cm^{-3}. It was submerged in 1:1 NH_4OH solution and placed in an ultrasonic cleaner for $\sim$ 5 minutes. The NH_4OH dissolved the native surface oxide.[24] The sample was then dipped in methanol and immediately placed in the non-polar liquid. Some shaking was necessary to knock the methanol drops off the surface while under the non-polar liquid. These images are similar to GaAs images previously obtained in KOH.[14] In our experience, images taken in air

occasionally are as good as those under fluids, but more often they are noisy and not reproducible.

Figure 4 shows two images of a gold surface taken before lithography (at t = 0 sec and t = 30 sec) and two images of the same area after lithography (at t = 60 sec and t = 90 sec). These images taken before lithography are consistent with published images of gold films under oil,[3] air,[3] and aqueous solutions[6,19] that have appeared previously. Specifically the present images are higher magnification views of the top of a "rolling hill" similar to those in the earlier images.

The lithography was done under fluoro-carbon grease (Research Organic/Inorganic Chemical Corp. Poly-Fluor Laen grease). The lithography method was similar to that used by Becker *et al.* to write on Germanium.[10] First two images of a gold surface with a characteristic feature were taken to determine drift rate. In this case, from the small mound in the lower left corner the drift rate could be seen to be $\approx 1/2$ Å/sec. Next the tip was positioned in the center of the scan area and scanning stopped. The bias voltage was increased from the 0.1 volt used for imaging until the feedback voltage, which was applied to the z-piezo to keep the tunneling current constant, jumped suddenly. This usually occured at $\lesssim 3$ volts with the sample positive with respect to the tip. After this lithography, which took about 20 sec, the bias voltage was reduced back to 0.1 volt and the same area was imaged twice more. We were able to produce similar holes in five out of five trials.

Using a non-polar imaging fluid was the key to doing lithography out of a vacuum chamber. Our previous trials under air, water, and aqueous solutions were unsuccessful in producing nanometer scale features. In these trials we were unable to turn the bias voltage above 2 volts. At these low bias voltages the tunneling electrons do not have enough energy to break chemical bonds.

Images obtained under different fluids are of varying quality. In an attempt to determine if images are effected by the fluid used, we imaged both a thin gold film on a glass substrate and a GaAs sample five times under each fluid. These results indicated that most, if not all, of the variation between images is due to variations in tunneling tips and differences between different regions on the sample. We did not observe any systematic variation in images obtained with different oils and greases.

IV. Conclusions

In summary, a STM operated with its sample and tip covered with non-polar fluids can:

1. Achieve atomic resolution.
2. Provide images of air sensitive materials.
3. Be operated with a high enough tip to sample voltage to do lithography.

V. Acknowledgements

We thank R. Sonnenfeld for providing and helping us prepare the GaAs surfaces, B. Drake for helping design and build our STM, R. Becker, J. Golovchenko, and B. Swartzentruber for their inspiration on lithography, and W. Kaska for suggesting and supplying the fluorocarbon grease. This work was supported by the National Science Foundation Solid State Physics Division under grant No. DMR 86-13486. The STM imaging system was built, in part, with support from the Office of Naval Research.

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FIGURE CAPTIONS

1. The construction of this STM was simplified by the use of a single-tube scanner /17/. The largest area which can be imaged is 1 μ × 1 μ.

2. Images of atoms on a graphite surface that was covered with different oils and greases. To ensure that there was no residual film on the tip or sample, we used a new tunneling tip and a freshly cleaved graphite surface for each fluid. Note that the spacing of the atoms is comparable in all images suggesting that viscous drag is a negligible factor–even for grease.

3. Images of the surface of GaAs taken under different oils and greases. To ensure that there was no residual film on the tip or sample we used a new tunneling tip and a different GaAs sample (cut from the same wafer) for each fluid. GaAs is difficult to image in air because of the formation of a surface oxide. The small features visible under the silicone oil indicate a vertical resolution of better than 10 Å.

4. Images of the same area of a gold surface covered with fluorocarbon grease taken before (at t = 0 sec and t = 30 sec) and after (at t = 60 sec and t = 90 sec) positioning the tip in the center of the frame and raising the bias voltage up to ≈3 V. The hole produced in this way is approximately 20 Å× 40 Åwide and 20 Ådeep.

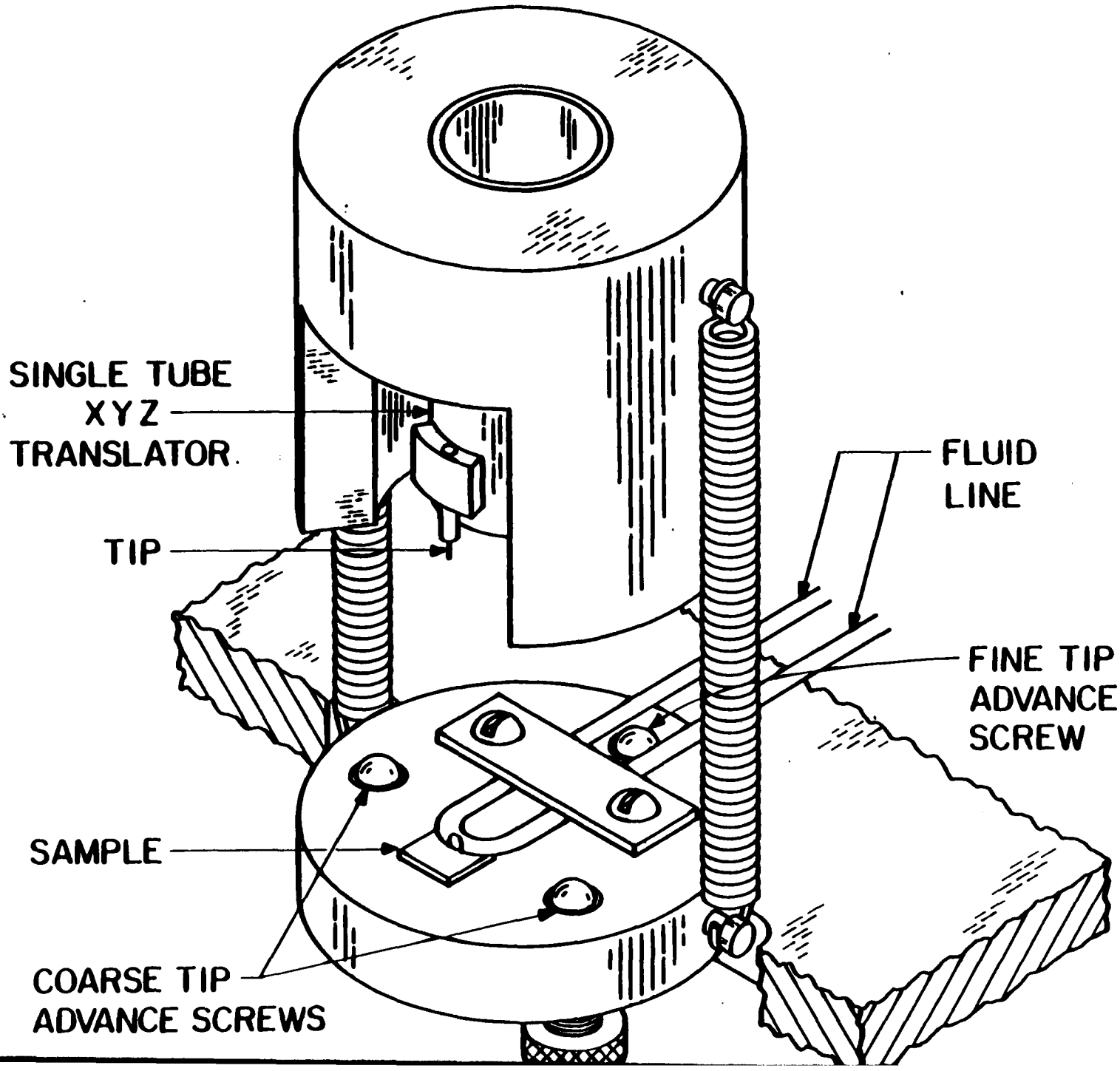

Fig. 1

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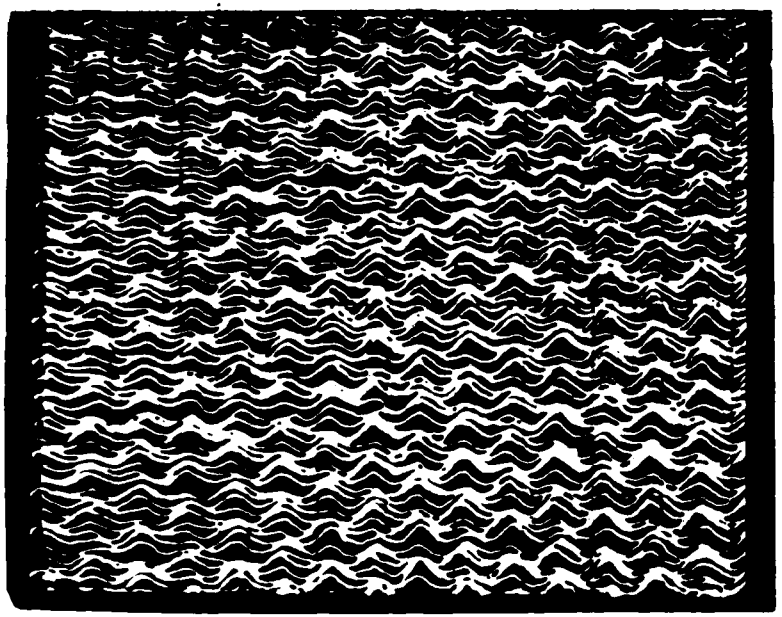
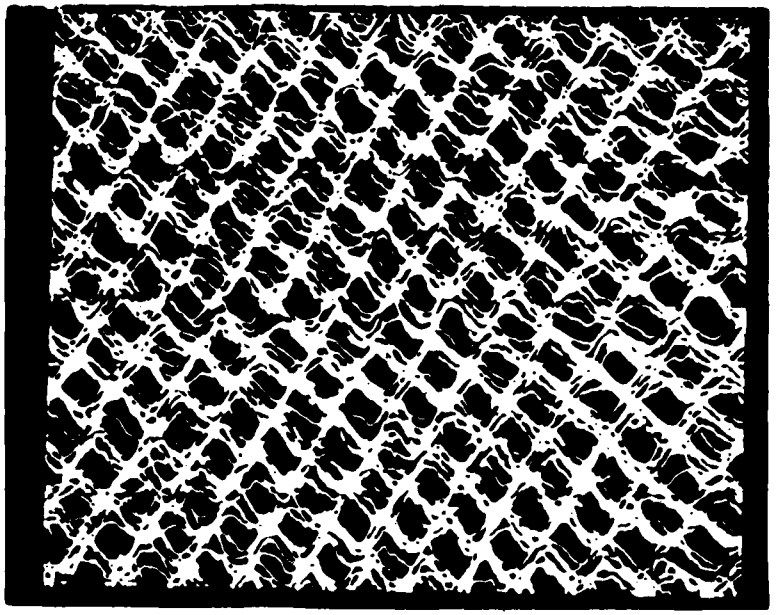


PARAFFIN OIL



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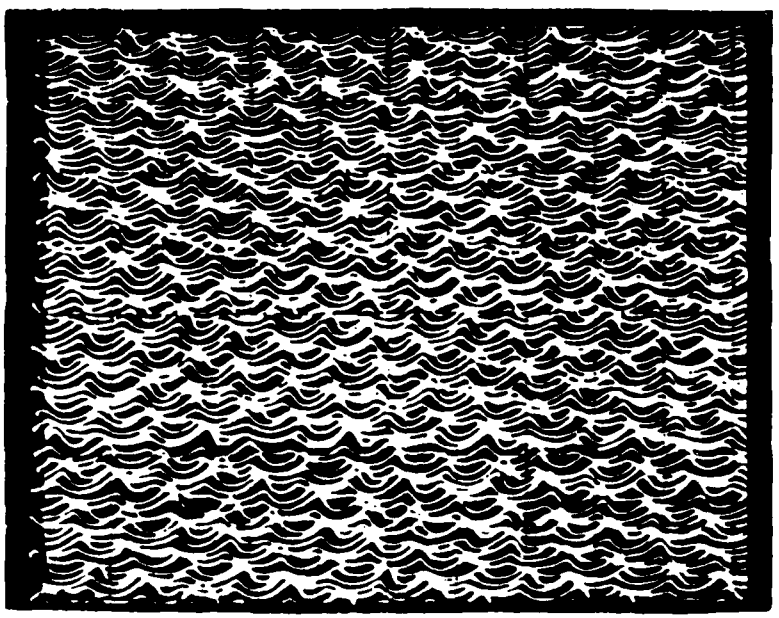

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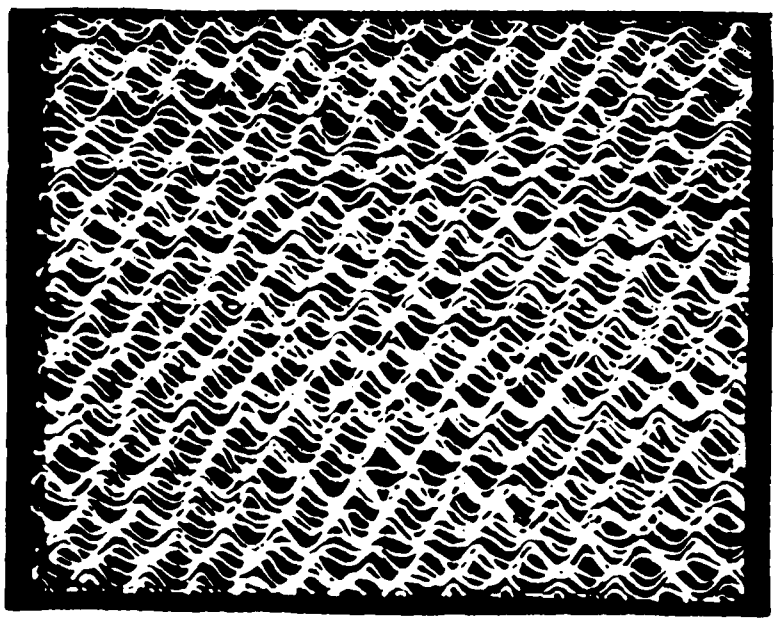

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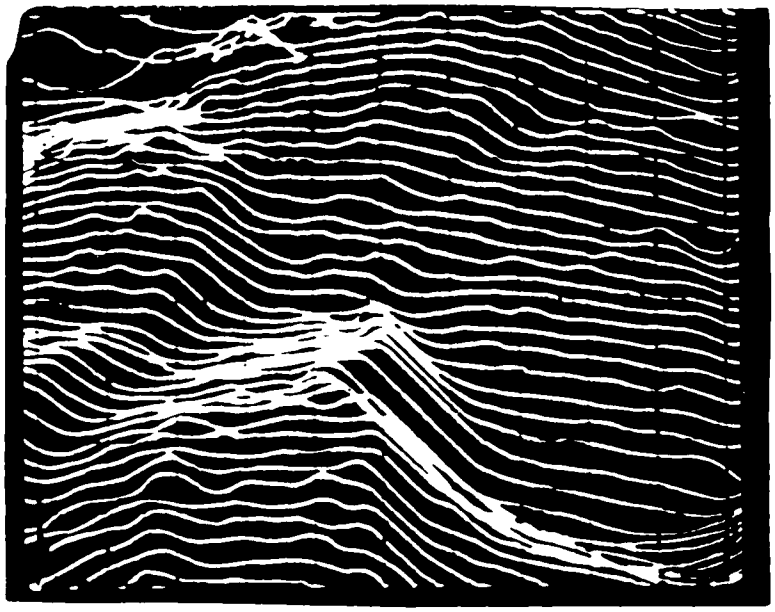
Fig. 2



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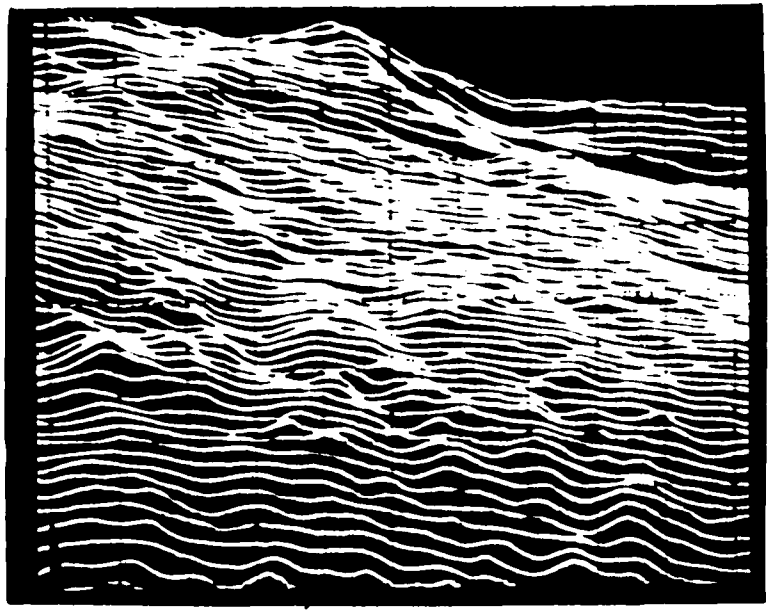

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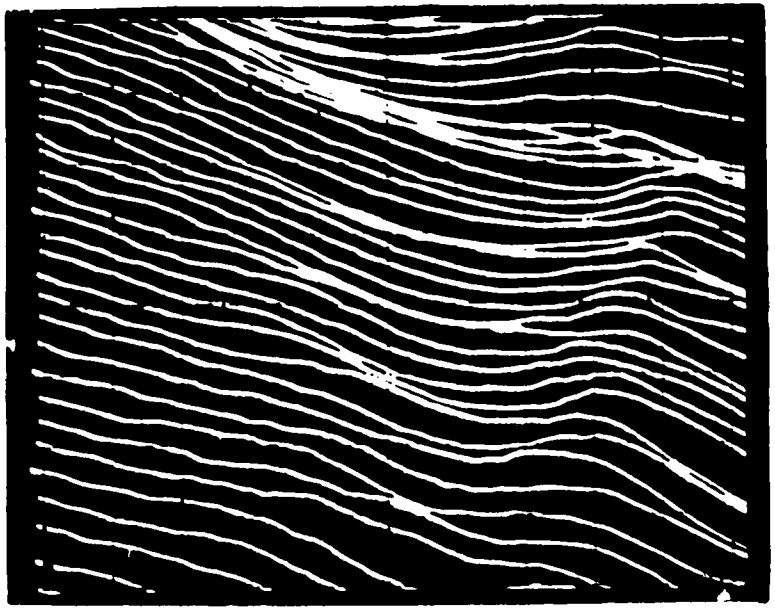

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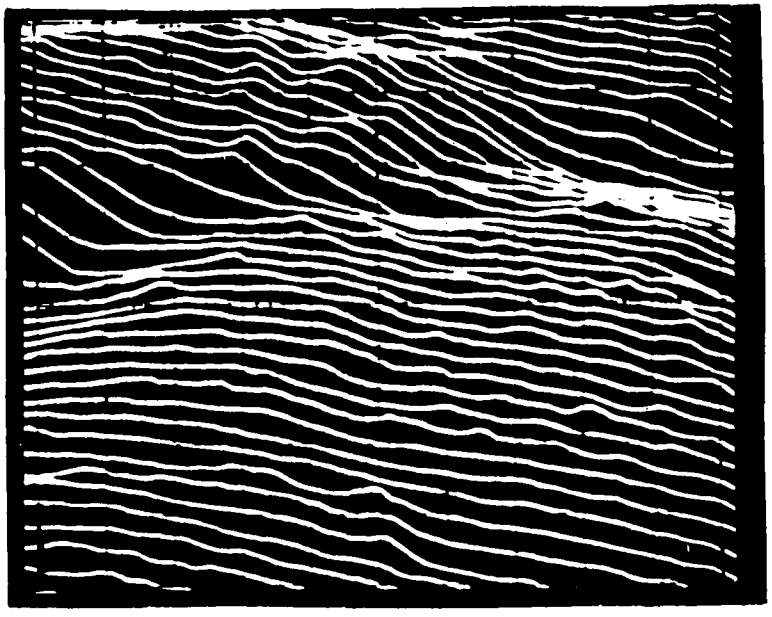

MICROSCOPE IMMERSION OIL

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Fig. 3

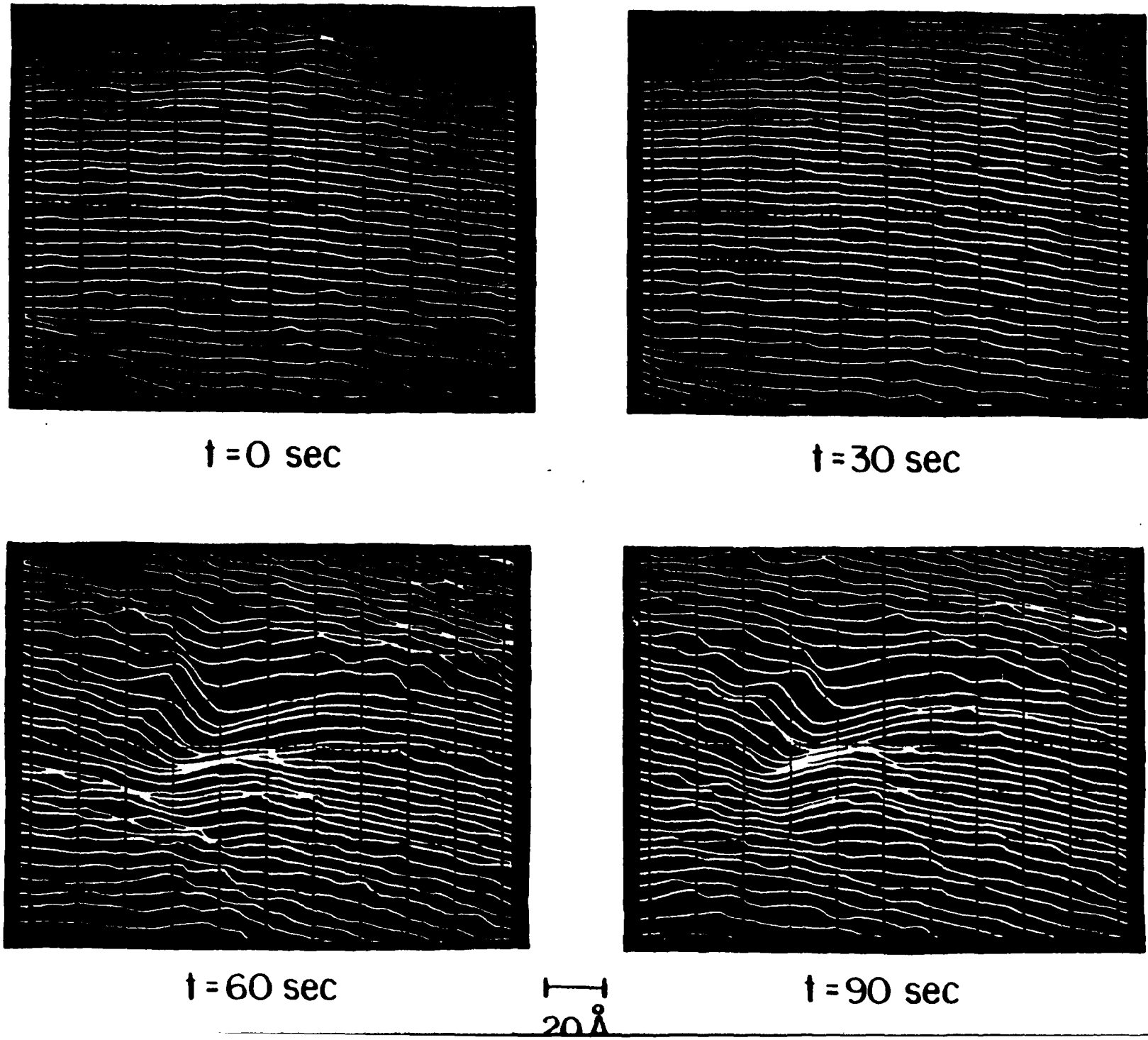

Fig. 4 Schneir et

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We show that atomic resolution tunneling microscopy can be done under non-polar liquids. Two possible areas of application are explored: lithography and imaging air sensitive materials. The lithography was demonstrated by wirting a 20 Å x 40 Å wide and 20 Å deep hole onto a gold surface. The imaging of air sensitive materials was demonstrated by imaging GaAs.

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