G. W. Bailey and C. L. Rieder, Eds., Proc. 51st Annual Meeting of the Microscopy Society of America

STM OF FREEZE-FRACTURE REPLICAS: PROBLEMS AND PROMISES

J. T. Woodward and J. A. N. Zasadzinski

Departments of Physics and Chemical Engineering, University of California, Santa Barbara, CA 93106

The Scanning Tunneling Microscope (STM) offers exciting new ways of imaging surfaces of biological or organic materials with resolution to the sub-molecular scale. Rigid, conductive surfaces can readily be imaged with the STM with atomic resolution. Unfortunately, organic surfaces are neither sufficiently conductive or rigid enough to be examined directly with the STM. At present, non-conductive surfaces can be examined in two ways: 1) Using the AFM, which measures the deflection of a weak spring as it is dragged across the surface, or 2) coating or replicating non-conductive surfaces with metal layers so as to make them conductive, then imaging with the STM. However, we have found that the conventional freeze-fracture technique, while extremely useful for imaging bulk organic materials with STM, must be modified considerably for optimal use in the STM.

In principle, the STM operates by measuring the tunneling current between a conductive tip and a conductive sample across a vacuum gap. However, unless the measurement is carried out in high vacuum environments, there is a liquid film of contamination that physically connects the STM tip with the sample. This mechanical coupling can lead to STM images with exaggerated height measurements. Simple modifications to TEM freeze-fracture replicas including a 0.1 micron backing layer of silver and mounting the replicas on a fine-mesh silver filters eliminate much of the height amplification.[1] If we then image the sample in a controlled environment, we can obtain reliable measures of feature heights.

STM imaging was done using a Nanoscope II STM enclosed in a sealed belljar. The belljar was evacuated with a rotary pump and a cold trap to approximately .1 torr before backfilling with dry nitrogen. To test whether eliminating the condensed contamination layer would also eliminate surface amplifications we examined Langmuir-Blodgett films of cadmium arachidate (CdA) with well-known step heights. The majority of the islands are a bilayer different in height from the surrounding area. The height of the bilayer is known from X-ray and AFM measurements to be 5.5 nm.[2] Platinum carbon replicas of the reorganized surfaces of CdA were made as described previously.[1] Ten images taken with three different tips gave 28 bilayer height measurements. The mean bilayer height was 5.1 ± 0.4 nm, in good agreement with the expected bilayer thickness (See Fig. 1a). Seventy percent of the measurements fell within eight percent of the mean, which is similar to the errors in measuring the films directly with the AFM.[2] There was no difference in heights measured with different tips. The chamber was then opened to air and several more images were taken. We then began flushing the system with dry nitrogen while taking more images. Fig. 1b shows the effect of just four minutes exposure to air. The height difference between the background and the bilayer 'hole' increased by 17% and several of the small features on the background show a significant increase in apparent height. The difference between the highest and lowest points (z-range) in the image has increased from 18.6 nm in Fig. 1a to 40.0 nm in Fig. 1b. Fig. 1c was taken after a few minutes of flushing the belljar with nitrogen. The step height has lowered to only 8.5% greater than its original value and the z-range was 26.4 nm. After about 30 minutes of flushing with dry nitrogen, the image heights returned to their original values.

This revised STM-replica technique provides us with simple, repeatable measures of surface feature heights, providing that precautions are taken to avoid feature distortions due to contamination. The cadmium arachidate multilayers provide a well characterized calibration for the 5 nm range that will be useful for our continuing investigations of bilayer structure and topology.[3]

1. J. T. Woodward, J. A. Zasadzinski, and P. K. Hansma, *J. Vac. Sci. Technol. B*, **9**, 1231 (1991)
2. D.K. Schwartz, R. Viswanathan, and J.A.N. Zasadzinski, *J. Phys. Chem.*, **96**, 10444 (1992).
3. This work was supported by ONR grant #N00014-90-J-1551 and NSF grant #CTS-9212790.

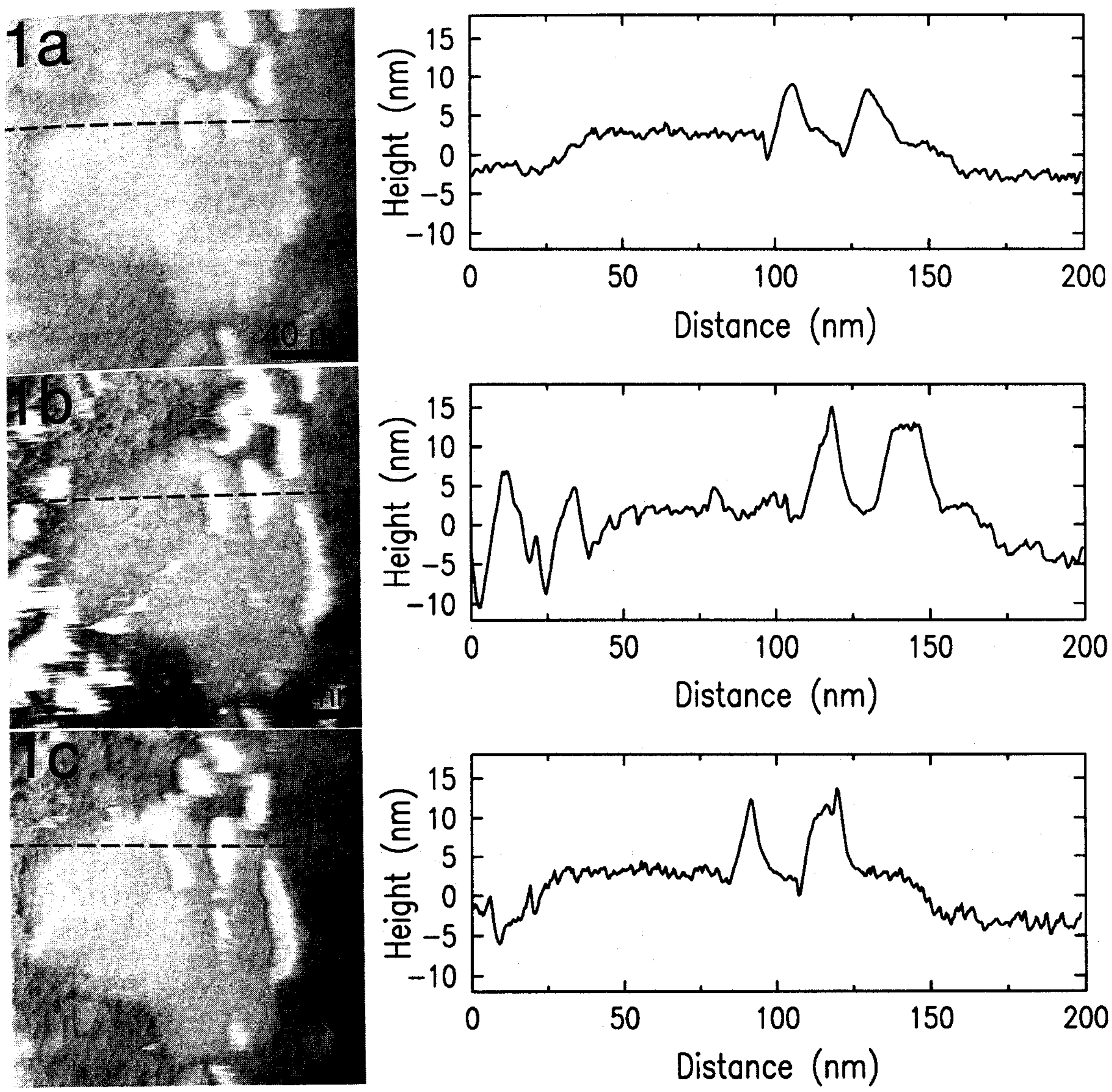

FIG. 1a. STM image of freeze-fracture replica of reorganized cadmium arachidate (CdA) multilayer film.[2] The film consists of discrete bilayer islands with a well defined bilayer steps between layers. This replica was imaged after the belljar surrounding the STM was evacuated to 0.1 torr for 1 hour and backfilled with dry nitrogen. The measured step heights were 5.1 ± 0.4 nm, in good agreement with AFM and X-ray results and the step heights were independent of tip and stable for hours.
Fig. 1b. STM image of same area as Fig. 1a except that the belljar was open to lab air for 4 minutes before imaging. The surface feature heights are amplified and several "new" features have appeared.
Fig. 1c. STM image of the same area as Figs. 1a and 1b, after the belljar was flushed with dry nitrogen for 30 minutes. The feature heights and general sample topography have returned to those in Fig. 1a.