AFM Studies of Langmuir-Blodgett Films

Jun Guo Literature Seminar April 10, 1997

Langmuir-Blodgett (LB),[1,2] was the first technique to provide the chemists with the practical capability to construct ordered molecular assemblies, and has been shown to be a powerful, convenient method for the preparation of ultrathin, uniform, and controllable films. To develop surface analysis techniques for the characterization of these films is one of the obstacles.

The Atomic Force Microscope (AFM)[3,4,5] developed in 1986 by using atomic force as the source of the image, has created new possibilities for imaging thin organic film under ambient conditions at length scales ranging from tens of microns to the sub-molecular scale. It is providing to be a valuable characterization tool for studying the surfaces of monolayer and multilayer LB films.[24,25,26] The method allows direct observation of the surface morphology of the molecular layers on the molecular scale and in real space.[6,7] AFM can be also used to provide quantitative information on the crystallographic structure of the outermost layer.

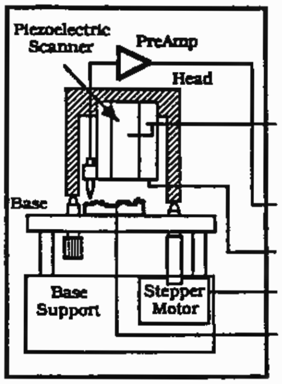

Figure 1. The microscope component of Nanoscope II AFM

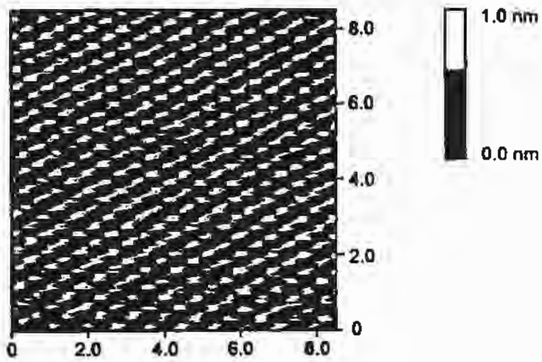

Figure 2. AFM image of an 11-layer arachidic acid/CdA_2 mixed LB film

AFM has been successfully used to image LB films of fatty acid and fatty acid salts.[11,12,13] Molecular resolution images of arachidic acid/cadmium arachidate LB films correspond to a distorted orthorhombic subcell, and some structural reorganization is evident in the transferred film, resulting in terraces of bilayer steps. substrates. The mixed arachidic acid and Cadmium arachidate (CdA_2) LB films were imaged in air, and well-defined positional and orientational ordering of the hydrocarbon chains were clearly showed. A periodic buckling superstructure along the [01] direction, as well as the boundary between two regions with different lattice orientations on CdA_2 films was observed. An overview of the time evolution of the reorganization of a three-layer CdA2 LB film submerged under the aqueous subphase was studied by AFM. The lattice structures of $PbSt_2$ and MnA_2 monolayers on mica were previously unknown and have larger lattice parameters and molecular areas than do multilayer films of the same materials, indicating that the strong interactions with the large mica lattice. Multilayer films of $PbSt_2$ CdA_2, and MnA_2 have centered rectangular "herringbone" lattices on both silicon and mica substrates. After sufficient layers, the effect of the mica substrate is eliminated and the lattice parameters and area per molecule of films deposited on mica relax to those of multilayer films on amorphous oxidized silicon. The lattice parameters, symmetry are independent of the length of the alkane chain of the fatty acid for all cations and substrates examined.[21]

Zinc metal was vacuum deposited at room temperature onto cadmium stearate LB films[14] with surfaces of either hydrophilic head groups or hydrophobic tail groups. Different growth modes on different surfaces of the LB films were observed with AFM. Fine Zn particles deposited onto the hydrophobic surface were uniform and similar in shape irrespective of the deposition rate. However on the hydrophilic surface, triangular and/or quasi-hexagonal Zn crystals were observed when the deposition rate was very slow. Chemical interaction between organic functional groups and deposited metal seems critical for the manner of growth.

Phenyl group containing compounds can be also used to form LB films.[22] The structure and surface morphology of an azobenzene containing LB film were investigated by using AFM. [16] Molecular resolved AFM images revealed a slightly distorted monoclinic crystal structure. Using polarized UV excitation of the azobenzene containing LB film, selective trans-to-cis photoisomerization was obtained and was characterized by the polarized UV-visible spectra. Clear morphological differences between films subjected to unpolarized vs polarized UV illumination were observed with in-situ AFM. Domains on the order of 10 nm in diameter or less are thought to be associated with the photoisomerization process. The annealing effects on LB films of octadecyl TCNQ (2-octadecyl-7,7,8,8-tetracyanoquinodimethane) have been investigated by AFM[17] and other spectroscopies. An AFM image of a one-layer LB film of octadecyl TCNQ scanned at room temperature shows that the film consists of numerous platelike microcrystal domains. A periodic structure of octadecyl-TCNQ molecules with a period of 0.85 nm can be observed inside these domains. After the annealing, some of these domains lie on top of one another, keeping their original morphology. The rest seem to melt into a globular bulk sample. In the case of an 11-layer film, it can be seen from its AFM images that a number of domains with smaller size cover the substrate and that they completely melt after the annealing cycle.

In order to model biological membrane, DPPE (1,2-dihexadecanoyl-*sn*-glycero-3-phosphoethanolamine) LB films were characterized by AFM[18,19] to determine the topography and to monitor the stability of the deposited films in air and under water at varying experimental parameters. Nanometric resolution was achieved on DPPE crystal and LB films and allowed the determination of the corresponding lattice constants. The reorganization of DPPE bilayer when going from the water to the air was directly observed to form monolayer and trilayer domains.

The combination of LB film and AFM or STM can be useful for storage devices with huge capacity.[20] Bits of 10 nm in diameter had been written in polyimide LB films using the AFM combined with STM for simultaneous operation. Clear spots were observed in the current image at the points where voltage pulses are applied, while no specific features such as protrusions or holes were observed in the AFM image. These results show that the bits can be attributed to the change in conductance of the LB film.

References

1. (a) Roberts, G. G., *Langmuir-Blodgett Films*, Plenum, New York, **1990**. (b) Ulman, A., *An introduction of Ultrathin Organic Films*, Academic Press, San Diego, CA, **1991**.

2. (a) Swalen, J. D. et al. "Molecular Monolayers and Films", *Langmuir* **1987**, 3, 932. (b) Whitesides, G. M., Mathias, J. P. and Seto, C. T. "Molecular Self-Assembly and Nanochemistry, " *Science* **1991**, *254*, 1312.

3. Binnig, G., Quate, C. F. and Gerber, Ch. "Atomic Force Microscope," *Phys. Rev. Lett.* **1986**, *56*, 930.

4. Drake, B., Prater, C. B., Weisenhorn, A. L. and Quate, C. F. "Imaging Crystals, Polymers and Processes in Water with the AFM," *Science* **1989**, *243*, 1586

5. Rugar, D. and Hansma, P., "Atomic Force Microscopy," *Phys. Today* **1990**, October, 23.

6 Marti, O., Ribi, H., Drake, B., Albrecht, T., Quate, C. and Hansma, P. "Atomic Force Microscopy of an Organic Monolayer, "*Science* **1988**, *239*, 51.

7. Gould, S. A. C., Marti, O., Drake, B., Stucky, G. D. "Molecular Resolution Images of Amino Acid Crystals with the AFM," *Nature* **1988**, *332*, 332.

8. Meyer, E., Howald, L., Roth, S. "Molecular Resolution Images of Langmuir-Blodgett Films using AFM, " *Nature* **1991**, *349*, 398.

9. Zasadzinski, J. A. N., Helm, C. A., Hansma, P.K. "Molecular Ordering in LB Bilayers of DMPE Imaged Under Water," *Biophys. J.* **1991**, *59*, 755.

10. Bourdieu, L., Silberzan and Chatenay, D. "Langmuir-Blodgett Films: From microns t o angstroms," *Phys. Rev. Lett.* **1991**, *67*, 2029.

11. Zasadzinski, J. A., Viswanathan, R., Schwartz, D. K., Garnaes, J., Madsen, L., Chiruvolu, S., Woodward, J. T., Longo, M. L. "Applications of Atomic Force Microscopy to Structural Characterization of Organic Thin Films," *Colliods and Surfaces* **1994**, *93*, 305-333.

12. Evenson, S. A., Badyal, J. S., Pearson, C., Petty, M. C. "Skeletonization of Mixed Arachidic Acid/Cadmium Arachidate LB Films: A study Using AFM", *Advanced Materials* **1997**, *9*, 58-61.

13 Kurnaz, M.L. and Schwartz, D.K. "Morphology of Microphase Separation in Arachidic Acid/Cadmium Arachidate Langmuir-Blodgett Multilayers," *J. Phys. Chem.* **1996**, *100*, 1113-1119.

14. Lin, H., Ando, H., Seon, W., Kuwabara, K., Koumoto, K. "Two-Dimensionally Oriented Organic Molecules as a Substrate for Vapor Growth of Zinc Thin Films," *Thin Solid Films* **1996**, 281-282, 521-524.

15. Namba, M., Sugawara, M., Buhlmann, P., Umezawa, Y. "Molecular Resolution Images of a Calix[6]arene from AFM," *Langmuir* **1995**, *11*, 635-638.

16. Wang, R., Jiang, L., Iyoda, T., Tryk, D. A., Hashimoto, K., Fujishima, A. "Investigation of the Surface Morphology and Photoisomerization of an Azobenzene-Containing Ultrathin Film," *Langmuir* **1996**, *12*, 2052-2057.

17. Wang, Y., Nichogi, K., Iriyama, K., Ozaki, Y. "Dependence of Thermal Behaviors on the Number of Layers in Langmuir-Blodgett Films of 2-Octadecyl-7,7,8,8-tetracyanoquinodimethane," *J. Phys. Chem.* **1996**, *100*, 374-380.

18. Solletti, J.M., Botreau, M., Sommer, F., Brunat, W.L., Kasas, S., Duc, T.M., Celio, M. R. "Elaboration and Characterization of Phospholipid Langmuir-Blodgett Films", *Langmuir* **1996**, *12*, 5379-5386.

19. Berzina, T.S., Troitsky, V., I., Petrigliano, A., Alliata, D., Yu, A., Nicolini, C. "Langmuir-Blodgett Films Composed of monolayers of amphiphilic molecules and adsorbed soluble proteins, "*Thin Solid Films* **1996**, 284-285, 757-761.

20. Yano, K., Kuroda, R., Shimada, Y., Shido, S., Kyogaku, M., Matsuda, H., Takimoto, K., Eguchi, K., Nakagiri, T. "Information Storage using Conductance Change of Langmuir-Blodgett Film and AFM/STM," *J. Vac. Sci. Technol.* **1996**, B14(2), 1353-1355.

21. Gyorvary, E., Peltonen, J., and Rosenholm, J. B. "Reorganization of Metal Stearate LB Films Studied by AFM and Contact Angle Measurements," *Thin Solid Films* **1996**, 284-285, 368-372.

22. Qian, X., Tai, Z., Sun, X., Xiao, S., Wu, H., Lu, Z., Wei, Y. "Molecular packing in LB films of a new porphyrin investigated by AFM, "*Thin Solid Films* **1996**, 284-285, 432-435.

23. Hansma, H. G., Gould, S. A. C., Hansma, P. K., Gaub, H. E., Longo, M. L., Zasadzinski, J. A. N. "Imaging Nanometer Scale Defects in Langmuir-Blodgett Films with the AFM," *Langmuir* **1991**, *7*, 1051.

24. Viswanathan, R., Schwartz, D.K., Garnaes, J. and Zasadzinski, J. A. N. "AFM Imaging of Substrate and pH Effects on Langmuir-Blodgett Monolayers," *Langmuir* **1992**, *8*, 1603.

25. Schwartz, D. K, Viswanathan. R. and Zasadzinzki, J. A. N. "Reorganization and Crystallite Formation in Langmuir-Blodgett Films, " *J. Phys. Chem.* **1992**, *96*, 10444.

26. Alves, C. A., Smith, E. L. and Porter, M. D. "Atomic Scale Imaging of Alkanethiolate Monolayer at Gold Surfaces with AFM, " *J. Am. Chem. Soc.* **1992**, *114*, 1222.