

QUANTITATIVE AFM OF LANGMUIR-BLODGETT FILMS

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Because of their applications in the areas of non-linear optics, molecular electronics, and biosensors, Langmuir-Blodgett (LB) films have been extensively studied by a wide variety of scattering and spectroscopic techniques. The atomic force microscope¹ has emerged as an important tool for studying LB films because of its unprecedented ability to quantitatively measure films with high resolution.

The unique abilities of quantitative AFM imaging motivated us to investigate the effect of incorporating different divalent metal cations and fatty acids of different chain length into films deposited on both amorphous and ordered substrates. Once substrate effects have been accounted for, multilayer Langmuir-Blodgett films of palmitic, stearic and arachidic acid salts show that the area per molecule is primarily controlled by the detailed interactions of the counterion with the carboxylic acid group. However, the lattice dimensions and symmetry are dictated by the close packing of the alkane chains, given the constraint of area per molecule set by the counterion. Hence, AFM studies of molecular organization of fatty acid LB films may be ideal systems to check molecular dynamics calculations of alkane packing. This limiting area per molecule decreases with the degree of ionic versus covalent bonding of the metal ion with the carboxylic acid moiety, with barium arachidate (BaA) > manganese arachidate (MnA) > cadmium arachidate > lead stearate (PbSt) (Figure 1). For BaA and MnA the increased molecular area is sufficient to induce tilt in the molecular packing. The lattice parameters, symmetry, and area per molecule are independent of the length of the alkane chain of the fatty acid for all cations and substrates examined (See Table 1).

However, the choice of substrate does have a dramatic effect on the structure of monolayer and multilayer films for both PbSt and MnA. Monolayers of PbSt deposited on crystalline mica have long range order while monolayers of MnA on mica show a distinct but short-ranged order. Otherwise identical PbSt and MnA monolayers are completely disordered on amorphous oxidized silicon. Both PbSt and MnA monolayers on mica have a significantly larger lattice spacing and molecular area than do the corresponding multilayers on mica, indicating a strong coupling to the mica lattice (Table 1). For PbSt trilayers on mica, the molecular area and lattice parameters were significantly larger than those of PbSt trilayers on oxidized silicon. The monolayers of both BaA and CdA were disordered, and for CdA no structural differences were observed between multilayer films deposited on oxidized silicon or mica. In addition, the periodic height modulation changed in wavelength from a value of ~ 1.9 nm in the case of Cd to ~ 1.2 nm for Mn.² The wavelength of the height modulation is independent of the length of the alkane chain for a given cation, in contradiction to theory. No height modulation was observed for Pb. BaA films had three distinct lattice arrangements that included stacking faults and offsets by individual methylene units; however, all BaA lattice structures had the same molecular area.

Atomic force microscopy can provide the most detailed real and Fourier space information available on the structure of Langmuir-Blodgett films of fatty acid salts. Although the multilayer films of all but BaA have similar packing symmetry, the variation in the unit cell dimensions is related to the degree of covalent bonding between the metal ion and the carboxylic acid group, and to specific interactions with the substrate. The structure and extent of positional correlations of the monolayer films are dramatically affected by a change in cation and are related to substrate interactions. The period of buckling modulation is also altered by a change in cation, but not by a change in the alkane chain length.³

1. G. Binnig, C. F. Quate, and Ch. Gerber, *Phys. Rev. Lett.*, (1986)56, 930.
2. J. Garnaes, et al. *Nature*, (1992) 357, 54.
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Material	layers	substrate	a ₁ (nm)	a ₂ (nm)	mol. area (Å ²)	tilt angle	corr. len. (nm)	mod. period (nm)
PbSt	1	mica	0.447 ± 0.006	0.922 ± 0.008	20.6	0°	>40	none
PbSt	3	mica	0.514 ± 0.006	0.752 ± 0.008	19.3	0°	>40	none
PbSt	5	mica	0.497 ± 0.006	0.739 ± 0.008	18.4	0°	>40	none
PbSt	7	mica	0.493 ± 0.006	0.728 ± 0.008	17.9	0°	>40	none
PbSt	3	silicon	0.492 ± 0.006	0.728 ± 0.008	17.9	0°	>40	none
PbSt	1	silicon	none	none	?	?	?	none
CdA	1	mica	none	none	19.4	?	0	none
CdA	3	mica	0.482 ± 0.006	0.748 ± 0.008	18.0	0°	>40	1.9 ± 0.3
CdA	3	silicon	0.482 ± 0.006	0.748 ± 0.008	18.0	0°	>40	1.9 ± 0.3
MnA	1	mica	0.46 ± 0.01	0.87 ± 0.02	20.0	?	~3	none
MnA	3	mica	0.495 ± 0.006	0.791 ± 0.008	19.6	19°	>40	1.18 ± 0.08
MnA	5	mica	0.481 ± 0.01	0.812 ± 0.01	19.5	19°	>40	1.18 ± 0.08
MnA	3	silicon	0.477 ± 0.006	0.834 ± 0.008	19.9	19°	>40	1.18 ± 0.08
MnA	1	silicon	none	none	none	?	0	none
BaA	1	mica	none	none	none	?	0	none
BaA (1)	3	mica	0.44 ± 0.01	1.52 ± 0.01	20.4	26°	>40	none
BaA (2)	3	mica	0.94 ± 0.01	0.94 ± 0.01	20.2	19°	>40	none

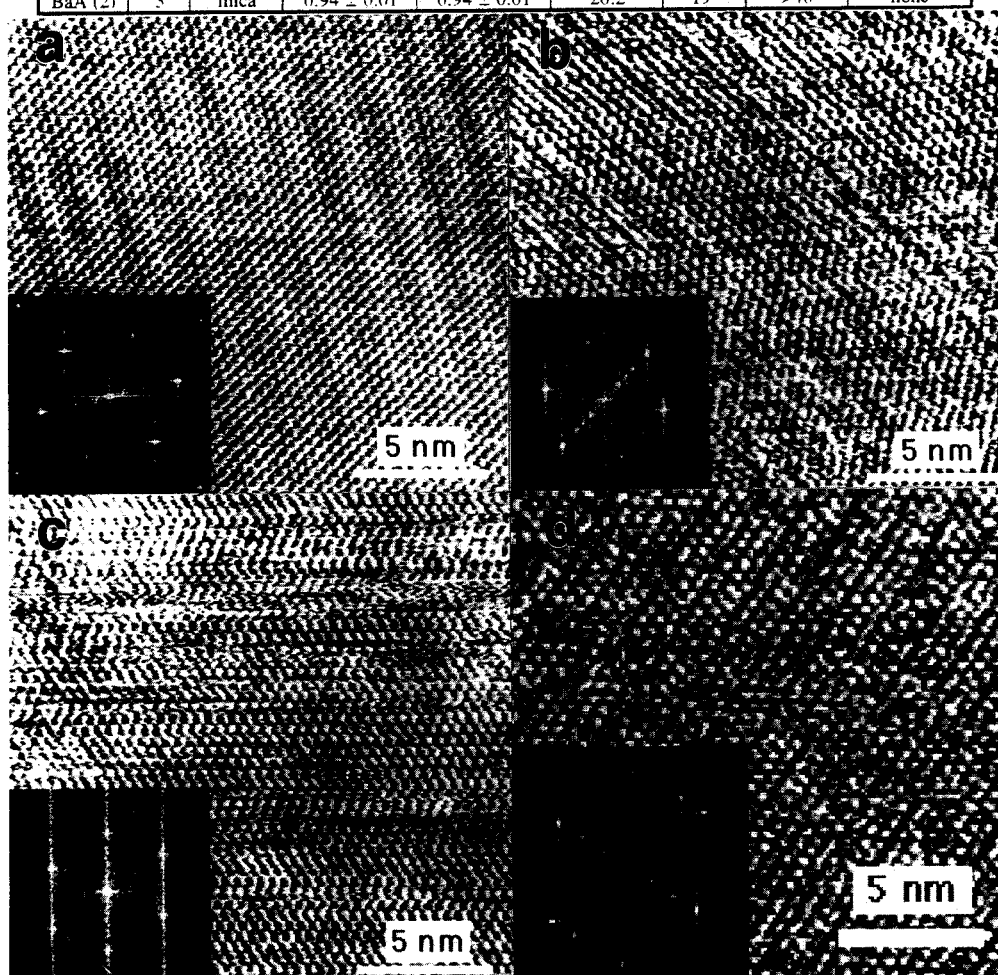


FIG. 1. AFM images of trilayer films of a) CdA; b) MnA; c) PbSt; and d) BaA with the Fourier transforms of the images inset. From the FT's we can quantitatively determine the lattice parameters and symmetry of the films, and by correlating with the images, we can determine the real space packing.