CHAPTER III
EXPERIMENTAL

3.1 Materials

Cetyltrimethylammonium bromide (C_{16}TAB), a cationic surfactant with 99% purity, was purchased from Sigma Chemical (St. Louis, MO). Tetra-n-butoxysilane (TBOS), 95% purity, was purchased from Gelest (Tullytown, PA). Mica discs with 9.9 mm diameter were obtained from Ted Pella (Redding, CA). All materials were used as received. De-ionized water was obtained by a Barnstead E-pure water system with a resistivity of 18.3 M .cm.

3.2 Experimental Methods

The atomic force microscope, a MultiMode™ scanning probe microscope (SPM), purchased from Digital Instruments, Inc. (Santa Barbara, CA), was equipped with a AS-130V ("J" vertical) scanner with maximum lateral and vertical scan ranges of 125μm × 125μm and 5.0μm respectively. The NanoScope IIIa software was used to capture and analyze images. Mica discs were mounted on metal discs with adhesive tape before imaging. The images were obtained through TappingMode and contact mode imaging in air and in liquid, respectively.

3.2.1 Tapping Mode AFM

Tapping mode was used to image surface aggregates on dried silica samples under ambient conditions. The temperature was approximately 22±1 °C for all experiments. Tapping Mode Etched Silicon Probes (TESP), purchased from Digital Instruments (Santa Barbara, CA), were used. TESP possess spring constants of 20-100 N/m, a nominal tip radius of curvature of 5-10 nm, and a resonance frequency of 200-400 kHz. The operating relative humidity, which was monitored by a humidity probe obtained from Cole-Parmer Instrument (Vernon Hill, IL), was not controlled

but ranged between 10 and 30%. Topographic and phase images were captured simultaneously.

3.2.2 Contact Mode AFM

Contact mode AFM was used to capture the images of surface aggregates in TBOS-C_{16}TAB aqueous solutions on mica surfaces using the fluid cell obtained from Digital Instruments (Santa Barbara, CA) and silicon nitride probes (Model NP). The NP probes have a 200μm length and a nominal tip radius of curvature from 20-60 nm. The operating temperature was kept at approximately 22±1°C. The topographic and cantilever deflection images were captured simultaneously in aqueous solution.

3.3 Ultra Thin Silica Film Growth Studies

3.3.1 Dried Film Studies

A mica disc was peeled in air and immersed in 0.7 mM C_{16}TAB aqueous solution for 3 hours to obtain a C_{16}TAB bilayer structure on the surface in which to solubilized TBOS, even though the layer is not fully developed at this time (Chen *et al.*, 1993). The disc was then transferred to a solution consisting of TBOS, C_{16}TAB, and DI-water as shown in Table 3.1. The reaction took place in 20-ml glass vials sealed with a screw cap. The temperature was maintained at 22±1 °C. After the desired reaction time was reached, the mica disc was removed from the solution and rinsed with DI-water (5 minutes) and methanol (5 minutes), respectively. The rinsed disc was then transferred to a dessicator for 1 day at 22±1 °C before imaging.

3.2.2 In-Situ Film Studies

A freshly cleaved mica disc was mounted on top of the piezoelectric scanner. The fluid cell with O-ring and silicon nitride cantilever was assembled on the scanner, surrounding the mica disc. C_{16}TAB aqueous solution was injected into the fluid cell and allowed to equilibrate for 3 hours. The C_{16}TAB solution was then drawn off by syringe and replaced by the solutions described in Table 3.1. The surface was then imaged over time by contact mode AFM.

Table 3.1 Concentrations of solutes in modifying aqueous solutions .

Sample no.	Concentrations of solutes in surface modifying aqueous solutions	
	TBOS (μM)	C_{16}TAB (μM)
1	0	700
2	295	0
3	30	700
4	295	700
5	1476	700