# CHAPTER IV
# RESULTS AND DISCUSSION

4.1 C_{16}TAB Adsorption on Mica

After the mica was immersed in 700 μM C_{16}TAB aqueous solution for 3 hours, patches of C_{16}TAB adsorbed on the mica surface could be imaged (Figure 4.1). The force curves were examined as the tip penetrated each of these regions, allowing a measurement of their thickness. From this, it was determined that the "darker" areas (Figure 4.2) possess a bilayer structure whereas the "lighter" areas (Figure 4.3) are monolayer, the same phenomenon, which was first observed by Ceotto *et al.* (2000). The observed thicknesses of the monolayered and bilayered patches were approximately 2.3 and 4.2 nm, respectively, again in agreement with Ceotto *et al.* (2000).
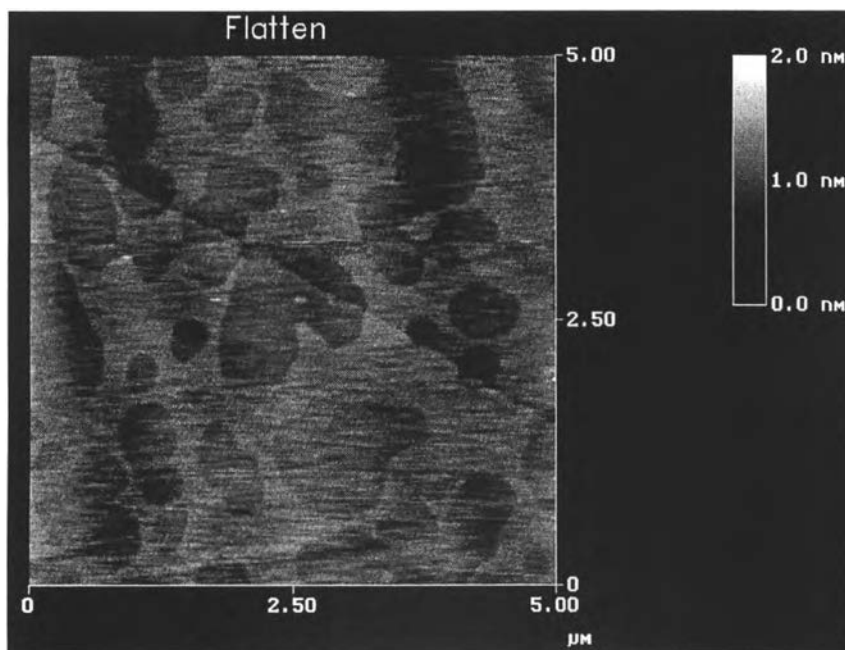
Figure 4.1 The topographic image of adsorbed C_{16}TAB on mica surface in 700μM C_{16}TAB aqueous solution.
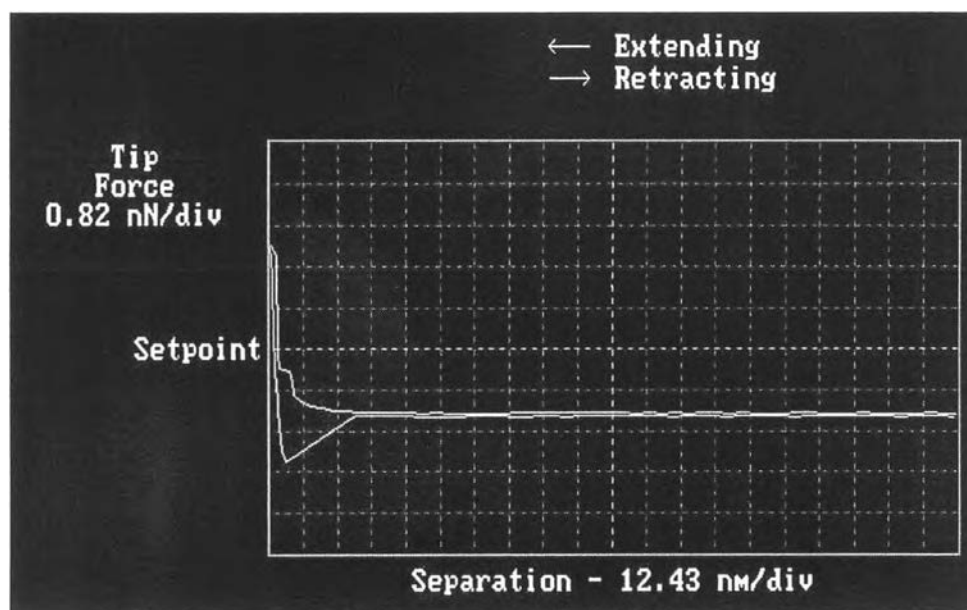
Figure 4.2 Force versus separation curve of $C_{16}TAB$ *bilayer* (darker area) on mica in 700μM $C_{16}TAB$ aqueous solution in Figure 4.1.
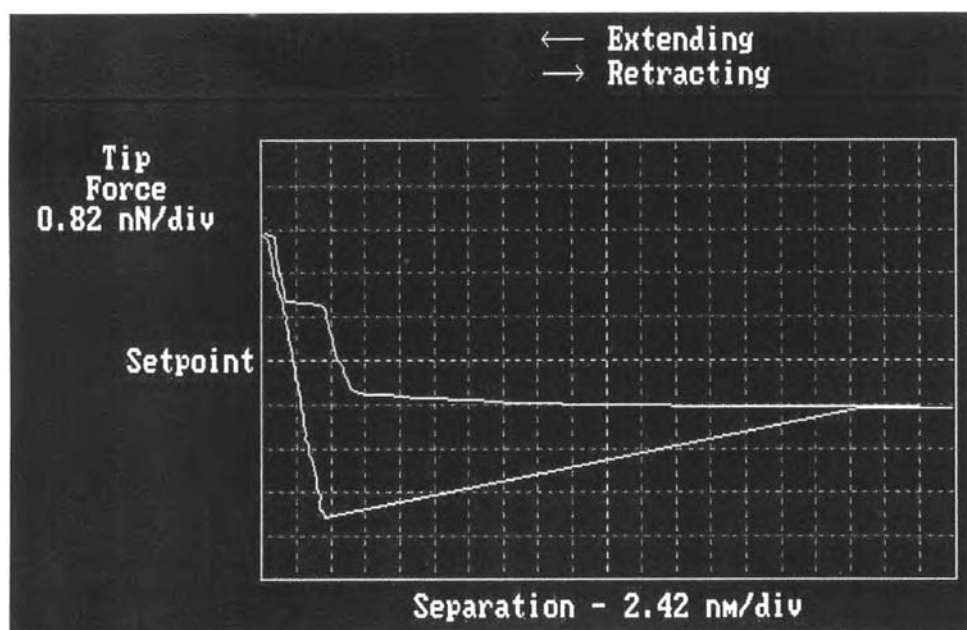
Figure 4.3 Force versus separation curve of $C_{16}TAB$ *monolayer* (lighter area) on mica in 700μM $C_{16}TAB$ aqueous solution in Figure 4.1.

4.2 Effect of TBOS Concentration on Adsorbed C_{16}TAB Aggregates on Mica in TBOS-C_{16}TAB Aqueous Solution

The adsorption of TBOS and silica formation on mica in the absence of C_{16}TAB was imaged in 295 μM TBOS aqueous solution. At eighteen minutes reaction time, the TBOS tends to adsorb and form small cylindrical aggregates scattered around the surface (Figure 4.4(a)). As the reaction proceeds larger TBOS clusters form as shown in Figure 4.4(b). Upon completion of the reaction the surface was covered by scattered small clusters (Figure 4.4(c)).

Figure 4.5(a) shows the fibrous texture formed on the mica surface when the feed solution contained 30 μM TBOS-700 μM C_{16}TAB. The fibers were approximately 100 nm in diameter, much larger than a typical C_{16}TAB cylindrical micelle. Scattered droplet-shaped aggregates (Figure 4.5(b)) and flat layers with some aggregates on top (Figure 4.5(c)) were observed at TBOS concentrations of 295 and 1476 μM, respectively. The fibers (at 30 μM TBOS) and discrete aggregates (295 μM TBOS) are easily removed by replacement of the TBOS-C_{16}TAB solution with water and methanol at initial reaction time, whereas, the flat layer is hard to remove and thus assumed to be a solid, three-dimensional structure at initial reaction time.

As mentioned, the fibrous texture was easily removed from the surface by replacement of the modifying solution in fluid cell at reaction time of 1 hour. We assumed that TBOS molecules are encapsulated within the fibers. And the encapsulation retards the polymerization of TBOS by surfactant template blocking. This blocking phenomenon is similar to alkoxysilane emulsion stabilized by surfactant adsorption at emulsion-water interface as reported by Fisher (2000). The same reason should be applied to the case of discrete droplet formation except the mechanism of formation. For droplet formation, it was suggested that TBOS might be encapsulated within C_{16}TAB bilayer until it forms continuous ultra thin liquid film within the bilayer. Then, since C_{16}TAB in solution reduces interfacial tension at surface aggregates-water interface, thus, this effect always decreases thin film surface area and thereby surface energy (Majumdar and Mezeic, 1998). Combined

with van der Waals force with positive Hamaker constant, which always plays an important role to destabilize thin liquid film under liquid (Thiele and Velade, 2001). These destabilizing factors have more dominant effect to liquid film stability than liquid film stabilizing factor (electrostatic, hydration, and van der Waals with negative Hamaker constant). Therefore, flat liquid film ruptures to form discrete droplets instead of flat layer. To summarize, the fibrous texture appears to be due to the effects of TBOS adsolubilization, whereas, the discrete droplet formation is possibly due to both TBOS adsolubilization and the phase separation of TBOS within the bilayer. As a result the TBOS liquid phase separates within the $C_{16}TAB$ bilayer. Solid structures grown from the bottom of the droplets was observed as shown in Figure 4.6, which was obtained after the droplets were swept by the AFM tip. The flat layer at higher TBOS concentrations is due to the rapid polymerization of TBOS or silicate anion molecules (which form rapidly in bulk solution at high TBOS concentrations) solubilizing at the admicelle-water interface.
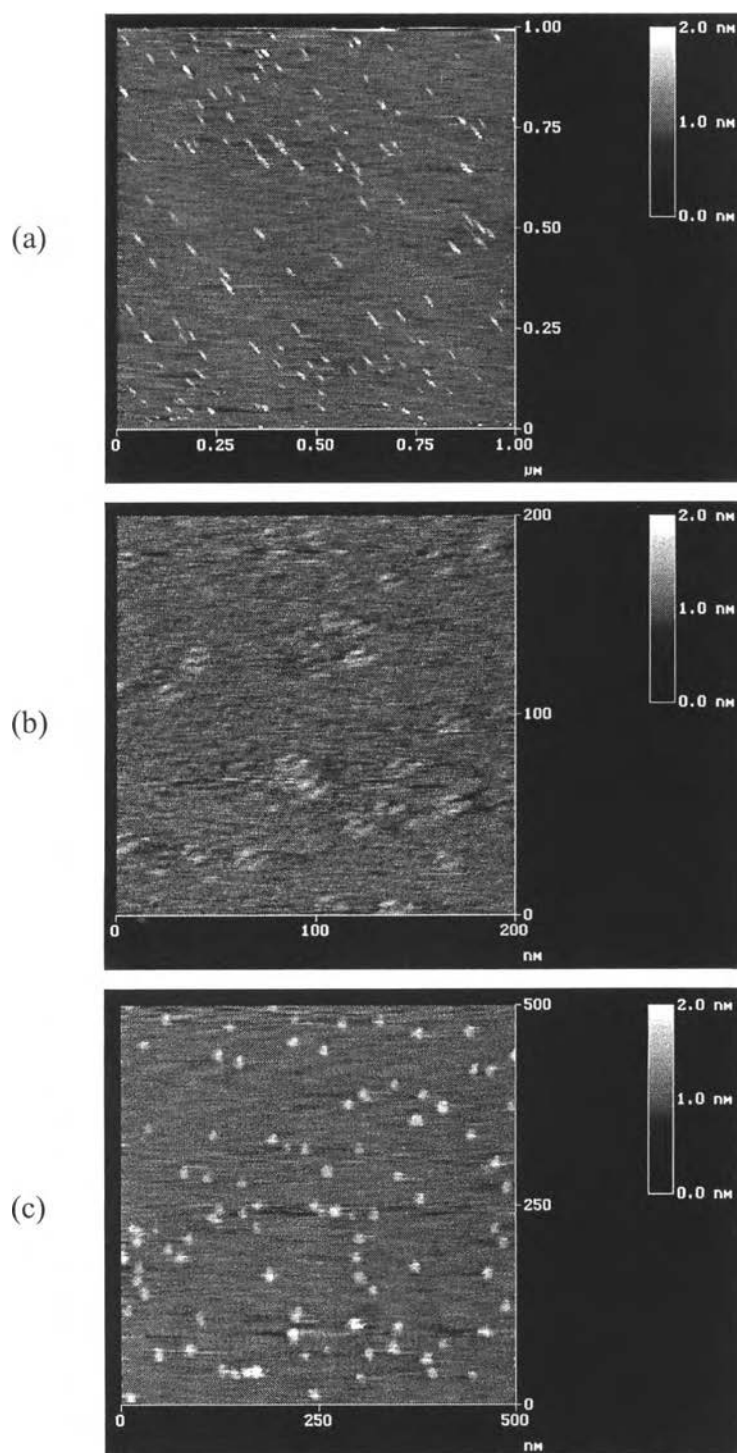
Figure 4.4 The topographic image of silica film growth on mica in 295 μM TBOS aqueous solution at reaction time of (a) 18 minutes (b) 60 minutes and (c) 90 minutes.
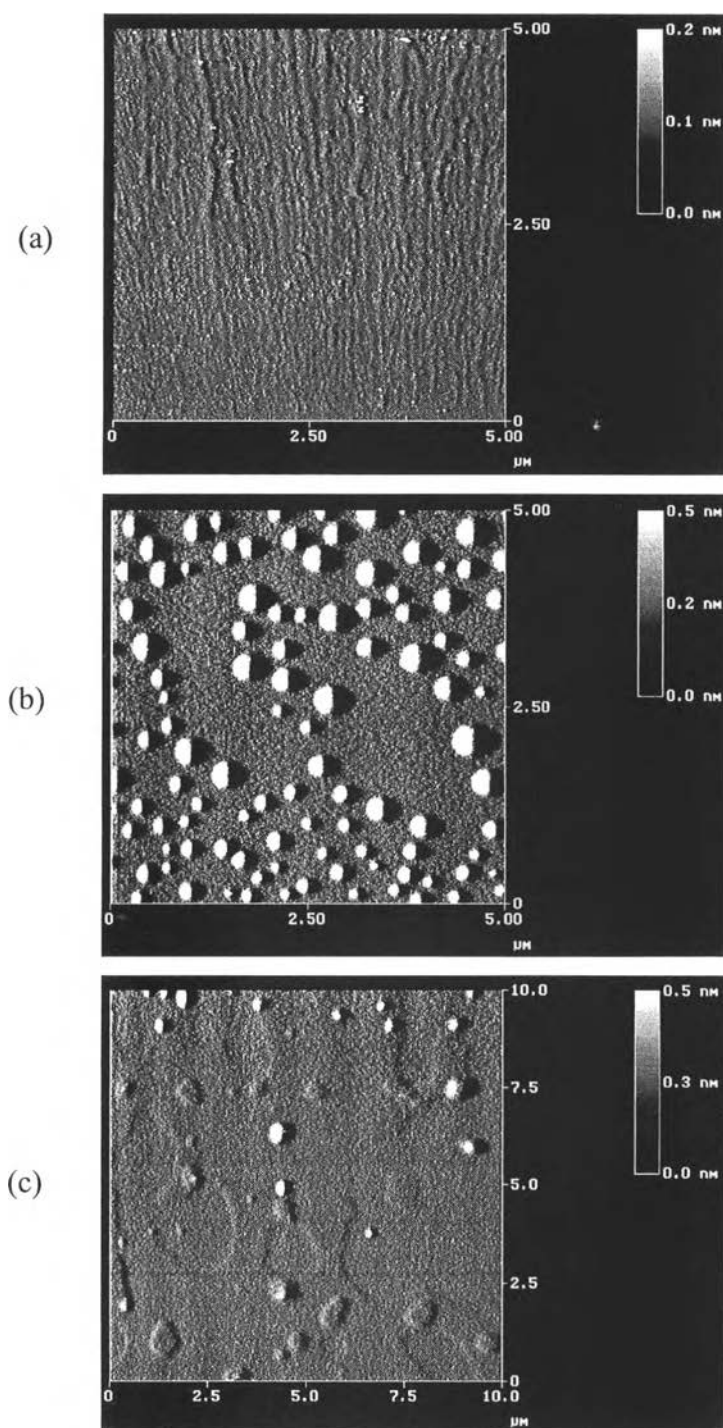
Figure 4.5 The deflection images of surface aggregates on mica surface imaged in TBOS-700 μM C_{16}TAB aqueous solution at TBOS concentration of (a) 30 μM (b) 295 μM and (c) 1476 μM at reaction time of 1 hour.
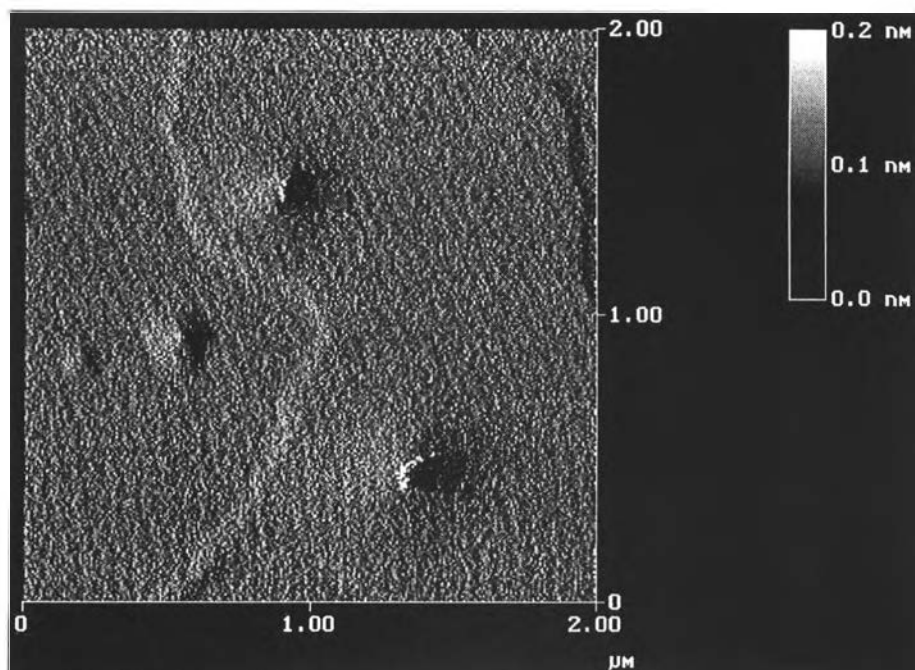
Figure 4.6 The deflection image of residual droplets after swept with AFM tip on mica in 295 μM TBOS-700 μM C_{16}TAB aqueous solution at reaction time of 2 hours.

4.3 Effect of Reaction Time on Film Persistence

The reaction time needed to obtain a persistent solid film structure was studied. Two blanks were studied, mica in C_{16}TAB aqueous solution and in TBOS aqueous solution. In the former case, small C_{16}TAB clusters were found scattered across the mica surface after the modified surface was washed with water and methanol and dried at ambient temperature (Figure 4.7). In the latter case, a surface pattern of short cylindrical nucleates (Figure 4.8(a)) was observed on the surface at a reaction time of 15 minutes. The "cap-like" structure (Figure 4.8(b)) was observed at 2 hours reaction time. Surprisingly, a fibrous texture (Figure 4.8(c)) was observed at 24 hours reaction time. It was explained that in the presence of the growth of randomly oriented nuclei, only those grains will survive in which the direction of maximum rate growth approximately coincides with the normal to the crystallization front and might be caused by high surface mobility of adatoms during deposition.

In the case of systems modified within TBOS-C_{16}TAB aqueous solution, a surface pattern similar to that of residual C_{16}TAB on mica was observed at short reaction times (Figure 4.9(a) and Figure 4.9(b)). As a two-dimensional silica film had not formed yet the surface aggregates are easily removed from the surface during washing. At TBOS concentrations of 30 µM a fibrous texture (Figure 4.9(c)) was obtained at 24 hours reaction time which is similar in structure to those seen in the absence of C_{16}TAB. These fibers were approximately 40 nm in diameter, which is much more than that observed from the film modified without C_{16}TAB at the same TBOS concentration. Discrete droplets and a buckled structure were observed at the higher TBOS concentration (295 µM) and 24 hours reaction time (Figure 4.10(c)). Though these are most likely formed by adsolubilized TBOS, the surface structure is still similar to C_{16}TAB residue. Moreover, it was believed that the solid film is unstable due to the elastic energy competing with the surface energy, inhibiting increases in surface roughening (Chopra, 1979). At high TBOS concentration (*i.e.*, 1476 µM) mounded aggregates scattered widely across the surface were observed at long reaction times (Figure 4.11). It was assumed that the disappearance of flat layer and surface aggregates seen in in-situ imaging is due to the destruction of the surface film by capillary forces during washing and drying.
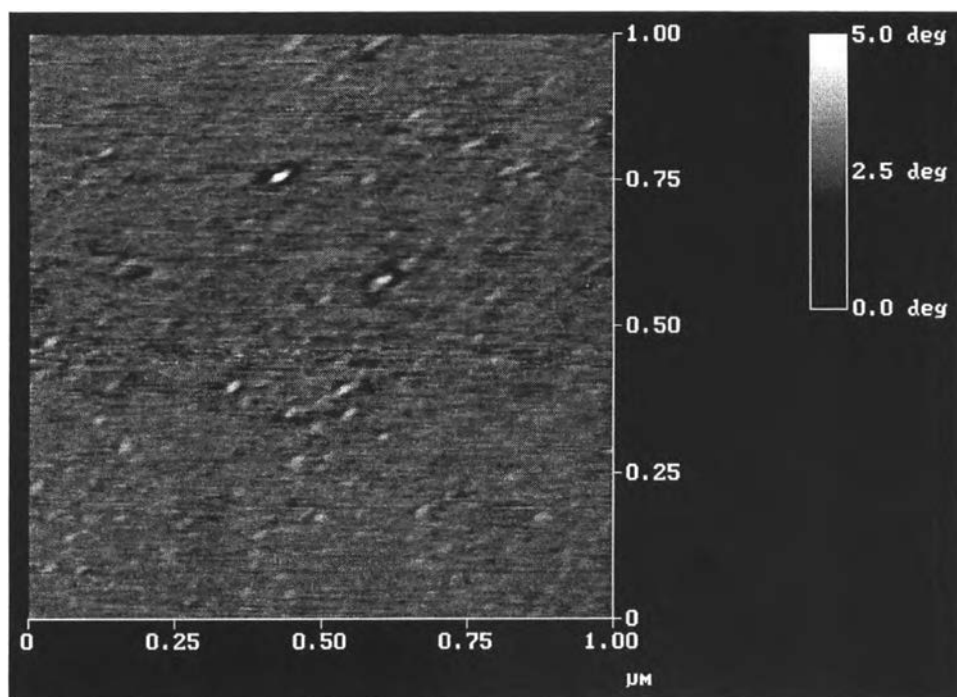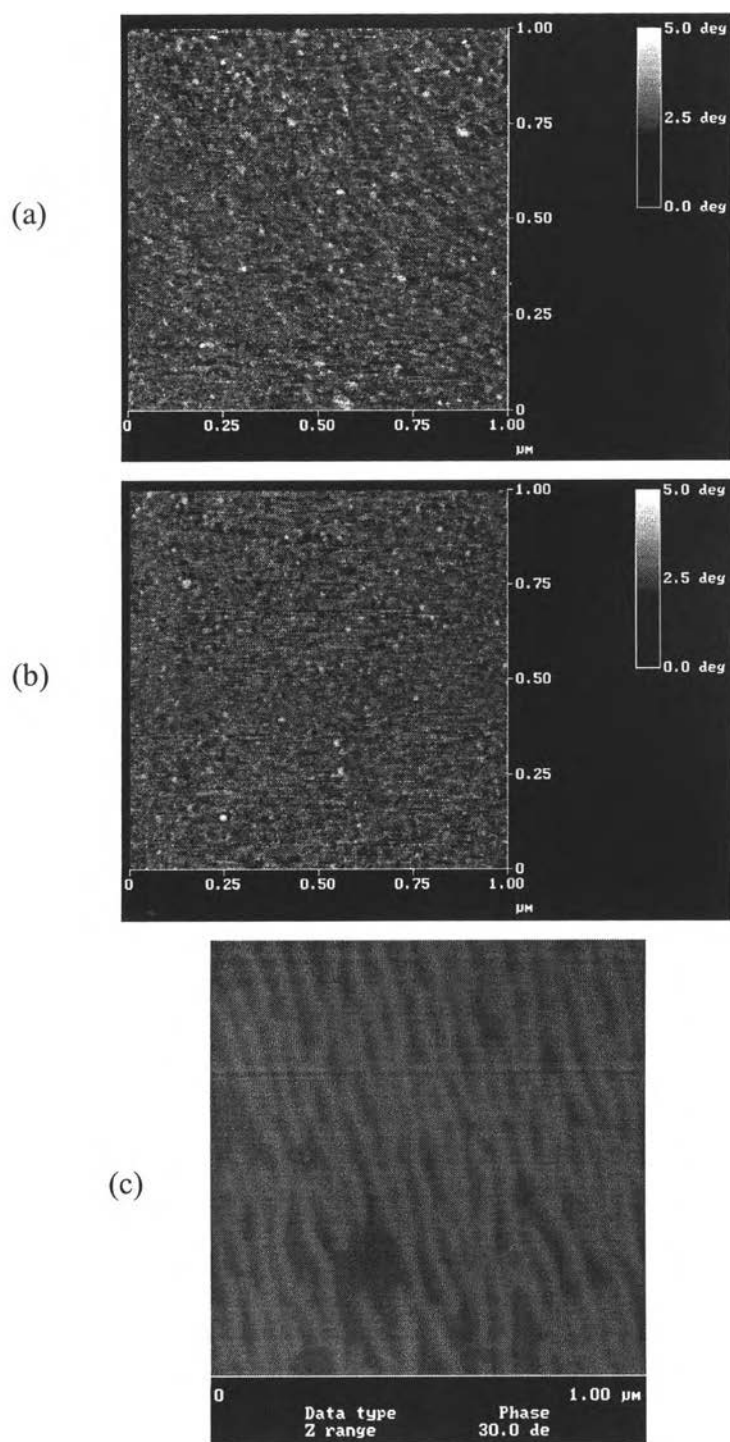
Figure 4.7 Phase image of dried residual $C_{16}TAB$ on mica surface after washing and drying.
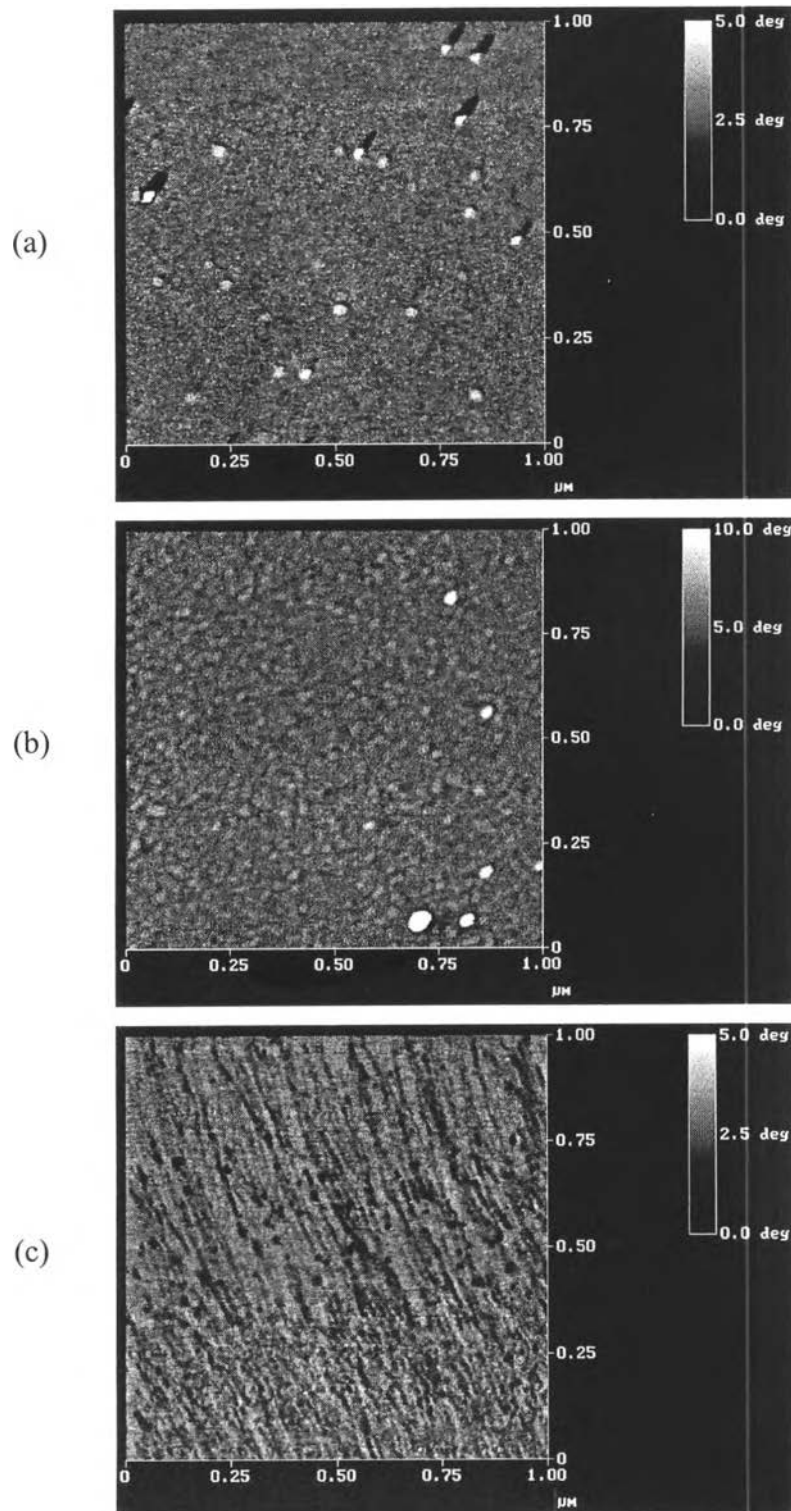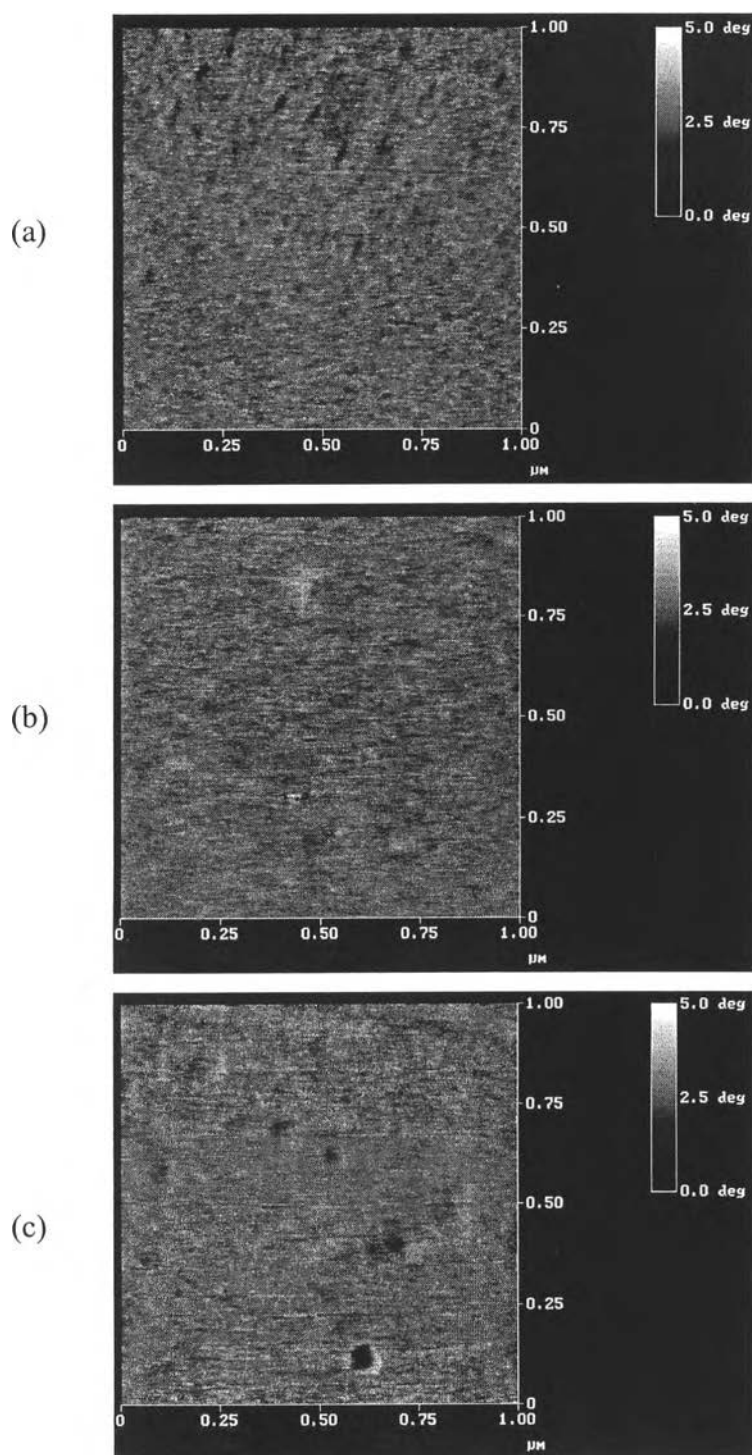
Figure 4.8 Phase images of dried silica film deposited on mica surface in 295 µM
TBOS aqueous solution at reaction time of (a) 15 minutes (b) 2 hours and (c) 24
hours.

Figure 4.9 Phase images of dried silica film deposited on mica surface in 30 μM TBOS-700 μM C$_{16}$TAB aqueous solution at reaction time of (a) 15 minutes (b) 2 hours and (c) 24 hours.
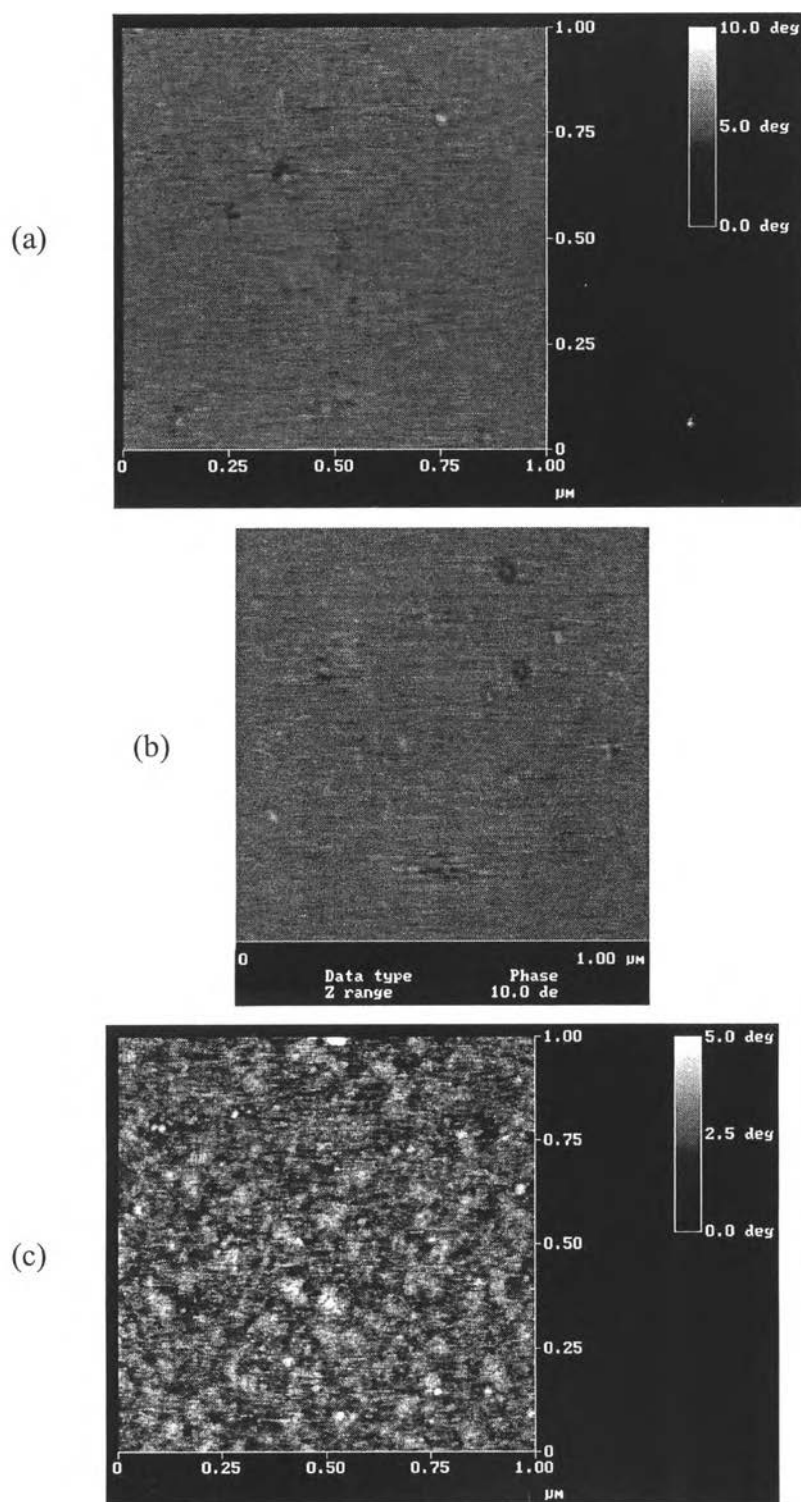
Figure 4.10 Phase images of dried silica film deposited on mica surface in 295 µM TBOS-700 µM C_{16}TAB aqueous solution at reaction time of (a) 15 minutes (b) 2 hours and (c) 24 hours.

Figure 4.11 Phase images of dried silica film deposited on mica surface in 1476 μM TBOS-700 μM C_{16}TAB aqueous solution at reaction time of (a) 15 minutes (b) 2 hours and (c) 24 hours.