Micelle-assisted bilayer formation of CTAB thin films studied with combined spectroscopic ellipsometry and quartz crystal microbalance techniques


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Our Message

- We report a novel experimental setup that combines quartz crystal microbalance (QCM-D) and spectroscopic ellipsometry (SE) techniques to monitor dynamic, in-situ thin film phenomena.
- We introduce a "virtual separation approach" that allows us to arbitrarily partition porous ultra-thin films into solvent and adsorbent layers.
- The mass ratio of solvent to total film, or mass porosity, is useful new information for understanding film structure.
- Cetyltrimethylammonium bromide (CTAB) deposited on a gold surface is used as a model system. We relate the thickness and porosity parameters to the structure of CTAB thin films and hypothesize a micelle-assisted growth mechanism.

Virtual Separation Approach

The "virtual separation approach" allows ultra-thin porous films to be segregated into adsorbent and solvent components. The "optically obtained thickness" from the SE can then be attributed to the adsorbent layer while the "mechanically obtained thickness" from the QCM-D is representative of both solvent and adsorbent layers.

In the case of ultra-thin (2nm < t < 1) porous films, these two figures are optically equivalent:

![Diagram showing virtual separation approach](image)

Results of CTAB Deposition and Manipulation of Rinsing Cycles

![Graph showing results of CTAB deposition and manipulation](image)

Phases of Micelle Film Evolution

Deposition (1):
- At first, the micelles are far apart so water between them is not mechanically coupled.

Encroachment (2):
- More micelles then adsorb (left) and encroach (right) on each other, coupling with or entrapping bordering water and forming regions of rodlike and spherelike distorted bilayer structures with disordered boundary regions.

Film Consolidation (3):
- Eventually, the substrate cannot support the expanded flat conformation, and excess CTAB molecules that cannot fit into defect zones are shed into the solution.

Rinsing (4):
- When rinsing occurs, the poorly organized defect zones are the first to be removed.

Continued Rinsing (5):
- Repairing the film at or before this point results in minimal thickness overshoot. If the remaining CTAB bilayer patches are further etched before the film is repaired, overdeposition will occur.