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.

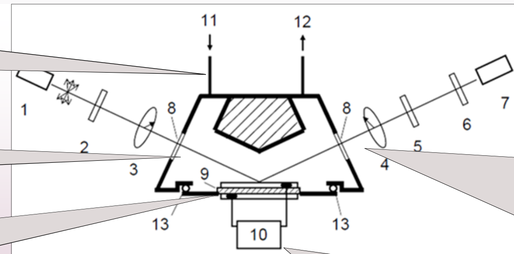
• Cetyltrimethylammonium bromide (CTAB) deposited on a gold surface is used as a model system. We relate the thickness and porosity parameters to the structure of CTAB thin films and hypothesize a micelle-assisted growth mechanism.

Instrumentation

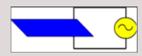
Liquid cell allows fluids to be introduced and exchanged during measurements.

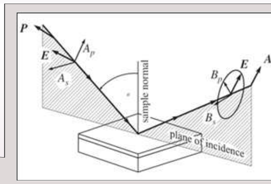
Cell windows and liquid ambient compensated by optical model.

QCM-D sensor with gold overlayer measures mass attachment from changes in vibration frequency and dissipation.



QCM-D signal stems from an oscillatory circuit that includes a piezoelectric material such as quartz.



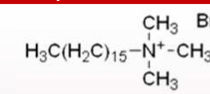


Beam channel allows polarized light to proceed from source to detector. The change of polarization state is a material property.

Höök et al. *Anal. Chem.* **2001**, *73*, 5796-5804.
Azzam and Bashara. *Ellipsometry and Polarized Light*. North-Holland Publ. Co.: Amsterdam, 1984.

Chemistry of Model System

Cetyltrimethylammonium Bromide (CTAB)



• Cationic surfactant with a hydrophilic tertiary ammonium salt "head" and hydrophobic hydrocarbon "tail."

• Forms micelle spheres at approximately 1 mM to shield tails from water.

• Molecules arrange themselves as a bilayer on gold similarly in some ways to lipids around cells.

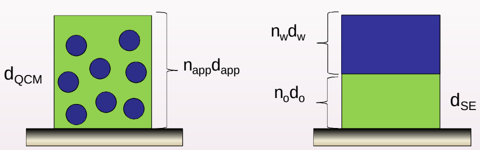
• Used in detergents and as a capping agent for nanoparticle synthesis.

Wei et al. *Appl. Surf. Sci.* **2005**, *252*, 1189-1196.

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 ($2\pi nd/\lambda \ll 1$) porous films, these two figures are optically equivalent:



$$c * \delta\Delta = n_{app} d_{app} = n_o d_o = n_o d_{SE}$$

•This approach requires assumption of n_o and ρ_o. In this work, we assume n_o = 1.5 for all λ and ρ_o = 1 g/cm³.

•For rigid thin films, the Sauerbrey relation models the QCM-D data. **However, this general approach can apply for viscoelastic thin films as well!**

$$\delta v_N = \frac{-2v_0^2}{N\sqrt{\rho_q \mu_q}} \frac{m}{A}$$

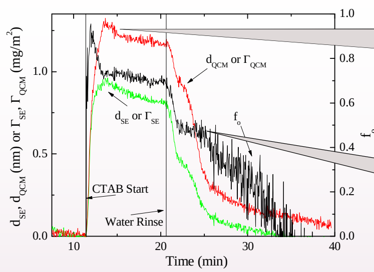
• A "mass porosity" parameter can be found by starting from the mass fraction ratio of the adsorbed mass to the total film mass (including attached solvent).

$$f_o = \frac{\rho_o * d_{SE}}{\rho_w * (d_{QCM} - d_{SE}) + \rho_o * d_{SE}}$$

Rodenhausen et al. *Langmuir* **2010**, *In submission*.

Results of CTAB Deposition and Manipulation of Rinsing Cycles

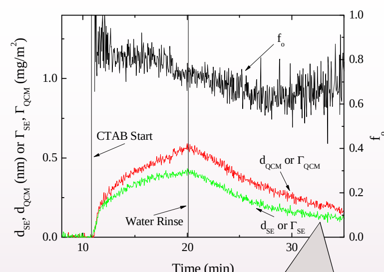
2.5 mM CTAB



Overdeposition and shedding behavior only present from solutions over the critical micelle concentration (CMC).

Interruption in removal may be due to inhomogeneous film structure.

0.1 mM CTAB

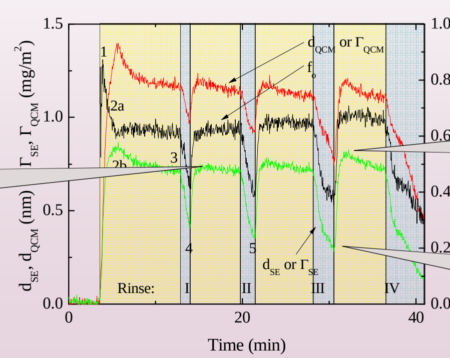


Smooth deposition and relatively constant adsorbent fraction imply uniform film.

2.5 mM CTAB

This graph demonstrates what happens when the rinse cycle is manipulated. Film deposition occurs in orange regimes and rinsing happens over blue regimes.

Before a critical point of film rinsing is reached, subsequent depositions do not exhibit overdeposition behavior.



Overdeposition behavior returns after a critical amount of film is rinsed off.

The critical point of where overdeposition behavior may return is when film removal of the previous cycle continues past its pause.

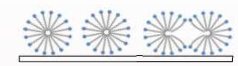
Rodenhausen et al. *Langmuir* **2010**, *In submission*.

Phases of Micelle Film Evolution

Deposition (1):

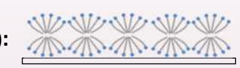
• At first, the micelles are far apart so water between them is not mechanically coupled .

Encroachment (2):



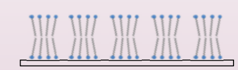
• More micelles then adsorb (**left**) and encroach (**right**) on each other, coupling with or entrapping bordering water and forming regions of rodlike and spherelike distorted bilayer structures with disordered boundary regions.

Film Consolidation (3):



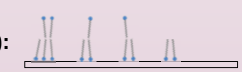
• Eventually, the substrate cannot support the expanded flat conformation, and excess CTAB molecules that cannot fit into defect zones are shed into the solution .

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.

Macakova, Blomberg, and Claesson. *Langmuir* **2007**, *23*, 12436-12444

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