Monitoring Organic Thin Film Growth *in-situ* with Combined Quartz Crystal Microbalance and Spectroscopic Ellipsometry

AS-TuP20

UNIVERSITY OF NEBRASKA-LINCOLN

K. B. Rodenhausen[1]*, M. Guericke[2], T. Hofmann[1], M. Schubert[1], T. E.Tiwald[3], M. Solinsky[4], and M. Wagner[4]

[1]Department of Electrical Engineering and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, U.S.A.
[2]University of Heidelberg, Germany *[3]J.A.Woollam Co., Lincoln, NE, U.S.A.* *[4]Procter & Gamble, Cincinnati, OH, U.S.A.*

*kbrod@cox.net http://ellipsometry.unl.edu

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.**
- **Cetyltrimethylammonium bromide (CTAB) deposited on a gold surface is used as a model system.**
- **QCM-D measures total mass including water trapped in the thin organic film whereas SE excludes water from the measurement. The combination of the two instruments allows the determination of a lower bound of the thin film's optical constants and the thin film's porosity.**

Studying Organic Solvent-Rich Thin Films

Assumptions and Considerations

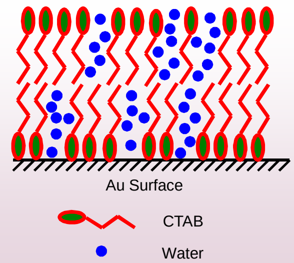
- The film density and index of refraction over all wavelengths are assumed values (1 gm/mL and 1.5, respectively, for CTAB).
- The product of the index of refraction and the film thickness is proportional to the change of the optical parameter, delta. For very thin films, this n * d product is difficult to separate because the other optical parameter, psi, is not sensitive at these thicknesses.
- Similarly, the index of refraction and the film thickness are inversely proportional.

How the SE Complements the QCM-D

- Though the QCM-D is accurate in measuring the total attached mass, the amount of non-solvent material that forms a fraction of this total is still unknown.

How the QCM-D Complements the SE

- The thickness reported by the QCM-D should always be greater than or equal to that reported by the SE. The lower bound of the index of refraction is the value that raises the SE thickness to the QCM-D thickness (over a time duration of constant porosity).

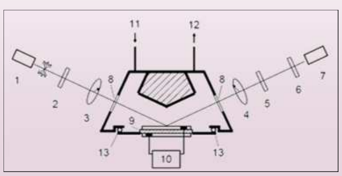


Experimental Setup and Chemistry

Instrumentation

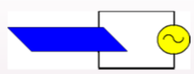
SE/QCM-D Liquid Cell

- Specially designed cell allows for simultaneous measurement of mass uptake by SE and QCM-D.
- SE beam proceeds through the optical ports. Window and aqueous medium effects are taken into account in the model.

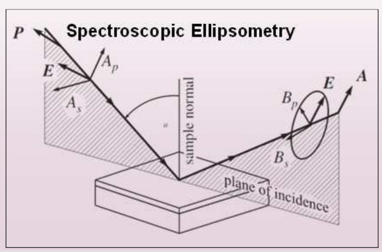


Quartz Crystal Microbalance

Piezoelectric material, e.g. quartz

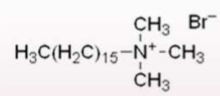


Oscillatory circuit



Model System

Cetyltrimethylammonium Bromide (CTAB)

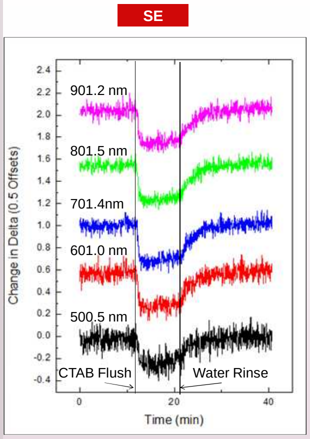


- Cationic surfactant with a hydrophilic tertiary amine "head" and hydrophobic hydrocarbon "tail."
- Forms micelle spheres at approximately 1 mM to shield tails from water.
- Molecules arrange themselves as a bi-layer on gold similar to lipids around cells.
- Used in detergents and as a capping agent for nanoparticle synthesis.

Measured Data and Analysis

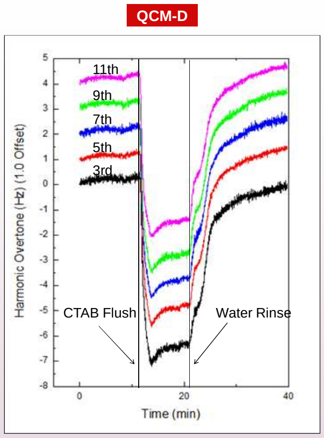
SE and QCM-D Raw Data

SE



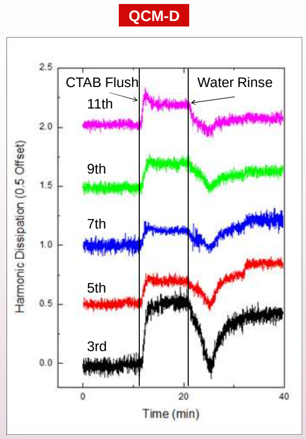
Delta parameter from SE for five selected wavelengths plotted against time. At each time slice, the average delta value for all 265 wavelengths was used to model the thickness from the SE side.

QCM-D



Frequency shift normalized by harmonic number.

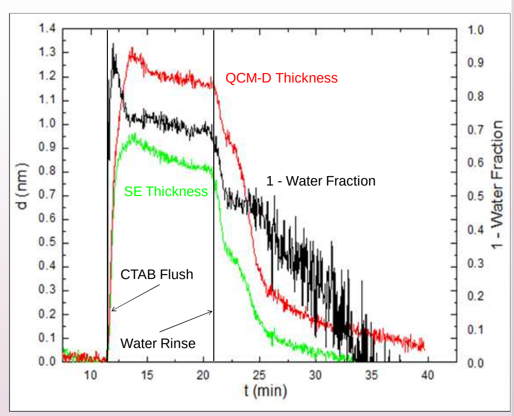
QCM-D



Dissipation of each harmonic number

$$f_w = \frac{\rho_w * (d_{QCM} - d_{SE})}{\rho_w * (d_{QCM} - d_{SE}) + \rho_f * d_{SE}}$$

Determination of Thickness and Porosity



SE and QCM-D thicknesses on the left y-axis and the void fraction (calculated by the displayed equation) on the right y-axis. Note that the void fraction temporarily levels out when the top CTAB layer is likely removed by the water at approximately 23 minutes..

Special acknowledgement: T. Vijtalla, KSV Instruments LTD., Helsinki, Finland
AVS 56th International Symposium, San Jose, Nov. 8-11, 2009

We acknowledge financial support from Procter & Gamble, J. A. Woollam Co., Inc., and NSF-EPSCoR