

# Combining SE with QCM-D Measurements

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Both spectroscopic ellipsometry (SE) and Quartz Crystal Microbalance with Dissipation (QCM-D) can detect sub-monolayer changes in thickness of nanometer scale films. However, the two techniques measure quite different things: QCM-D measures the mass and associated mechanical properties of the film, while SE measures volume (via thickness) and associated optical properties.

Combining these two complimentary techniques gives us new information that cannot be determined from either technique alone. For example, swelling or collapse can be differentiated from adsorption or desorption (mass change). In the example below, we determine solvent fractions of a film less than 2nm thick – essentially overcoming the index thickness correlation problem for films less than 10nm thick.

Simultaneous measurements in the same chamber guarantee both instruments measure the same film and process conditions at all times. This is critical for many self-assembled and biological films, because their properties can vary significantly from one run to the next, even under nominally identical starting conditions.

## The QCM-D technique<sup>1</sup>

Quartz is piezoelectric and vibrates at a resonant frequency when a voltage is applied. Any change in mass of material attached to the crystal – a change in either film thickness or density – changes its resonant frequency. The Quartz Crystal Microbalance (QCM) technique relates the frequency shift to changes in a film mass (and thickness) via the Sauerbrey<sup>1</sup> equation. This equation works well for rigid films which suffer minimal energy loss as the crystal vibrates.

Quartz Crystal Microbalance with Dissipation (QCM-D) measures both shift in resonant frequency and the crystal oscillation decay rate when the driving voltage is removed. The decay rate is a measure of dissipation – the ratio of energy lost to energy stored ( $D = E_{\text{lost}} / 2\pi E_{\text{stored}}$ ). Dissipation is proportional to film elasticity and viscosity. Viscoelastic or “soft” films induce significant energy dissipation and frequency (overtone)-dependent response. The Voigt viscoelastic model<sup>1</sup> accounts for the dissipation, and allows QCM-D data analysis using fitting techniques (similar to ellipsometric data analysis by regression).

## Combined QCM-D/SE Cell

Figure 1 shows an M-2000<sup>®</sup> ellipsometer integrated with Q-Sense QCM-D E-series including an E1 chamber and ellipsometry module. Cell temperature can be varied from 18° to 45°C ( $\pm 0.02^\circ\text{C}$ ).

Figure 2 illustrates the combined cell. Two gold electrodes provide electrical contacts for the quartz crystal. The top gold surface is also the substrate onto which films can be deposited. Liquid is injected via ports located on top of the cell. Light enters and exits the cell through small windows on each side at a 65° angle of incidence.

During the experiment, data are simultaneously acquired using the Q-Sense software and CompleteEASE<sup>®</sup> ellipsometry software.

## Analysis Example: CTAB layer on gold<sup>2</sup>

Cetyltrimethylammonium Bromide (CTAB) is a cationic surfactant with a hydrophilic tertiary amine “head” and hydrophobic hydrocarbon “tail.” It forms micelle spheres



Figure 1. Q-Sense QCM-D E-series (with an E1 chamber), mounted on an M-2000 spectroscopic ellipsometer.

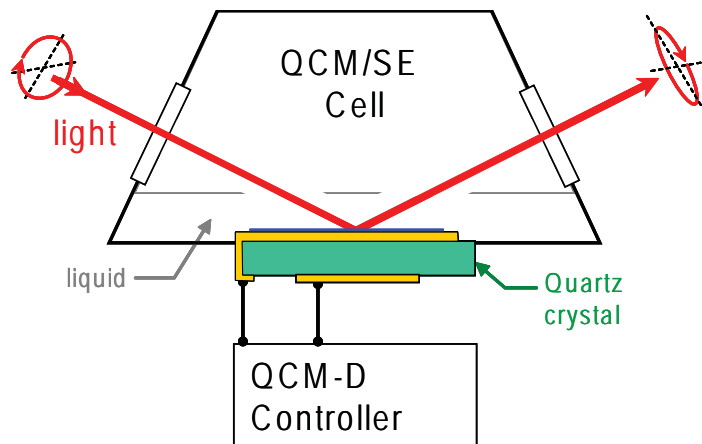


Figure 2. Schematic of QCM-D/SE liquid cell.

in water at concentrations above ~1 mM. On gold, it forms a layer with water trapped between CTAB molecules. Depending upon concentration, pH, and other factors, molecules adjust conformation as they adsorb on the surface – sometimes standing straight-up with the hydrophilic head facing water, or sometimes in spherical micelle structures.

Figure 3 shows raw data for a CTAB 2.5mM solution flush-rinse cycle. Clearly both QCM-D and SE are sensitive to the film properties. The question is: how do we analyze the data?

**QCM-D is sensitive to the total mass** coupled to the surface, including adsorbed molecules and any trapped water. From QCM-D data, a thickness,  $d_{QCM-D}$ , is calculated using the Sauerbrey equation (the dissipation is small, indicating a rigid film<sup>2</sup>) as shown in the red curve in Figures 4 and 5.

**SE is sensitive to the thickness and index** of the near-surface region, where adsorbed CTAB molecules differentiate the index from the surrounding water ambient. However, because the film is less than 2nm, thickness and index correlate. Therefore the film was modeled as two layers<sup>2</sup>: a fully dense CTAB layer ( $n_{CTAB} = 1.5$ ) next to the gold; and a water layer indistinguishable from the ambient. The resulting thickness,  $d_{SE}$  (green curve in Figures 4 and 5), represents only the adsorbed CTAB.

**We extract new information by combining these results** to calculate  $f_{CTAB}$ , the ratio of adsorbate mass (CTAB) to total mass (CTAB + water).  $f_{CTAB}$  is the black curve in Figures 4 and 5. (Equation adapted from ref 2.)

$$f_{CTAB} = \frac{\rho_{CTAB} d_{SE}}{\rho_{CTAB} d_{SE} + \rho_{H2O} (d_{QCM-D} - d_{SE})}$$

Comparing the 2.5mM CTAB solution (Figure 4), to a 0.1mM solution (Figure 5), we can see quite different behaviors.

**The 2.5mM solution (above micelle-formation limit):**

Most of the CTAB is adsorbed within 30 sec after injection ( $d_{SE} \sim 85\%$  max at 30 sec). During initial CTAB adsorption, very little water is trapped ( $f_{CTAB}$  peaks at ~0.9).  $f_{CTAB}$  then falls to ~0.7 as water infiltrates the adsorbed CTAB. Then  $f_{CTAB}$ ,  $d_{QCM-D}$  and  $d_{SE}$  all drop slightly over time, as some of the weakly-bound CTAB returns to solution.

The first 30 sec of rinsing removes weakly bound CTAB.  $f_{CTAB}$  plateaus at 0.5, indicating 50% of the remaining layer is water. After ~4.5 min of rinsing, the most tightly bound CTAB begins to leave the surface and  $f_{CTAB}$ ,  $d_{QCM-D}$  and  $d_{SE}$  all drop to zero.

**The 0.1mM solution (below micelle formation limit):** CTAB is slowly adsorbed, then rinsed away in a monotonic fashion.  $f_{CTAB}$  indicates that the amount of trapped water remains nearly constant throughout the injection/rinse cycle. This monotonic behavior occurs because the 0.1mM film forms by adsorption of individual CTAB molecules. In contrast, the 2.5mM film forms mainly from adsorbed micelles, which change conformation in complex ways during injection and rinse<sup>2</sup>.

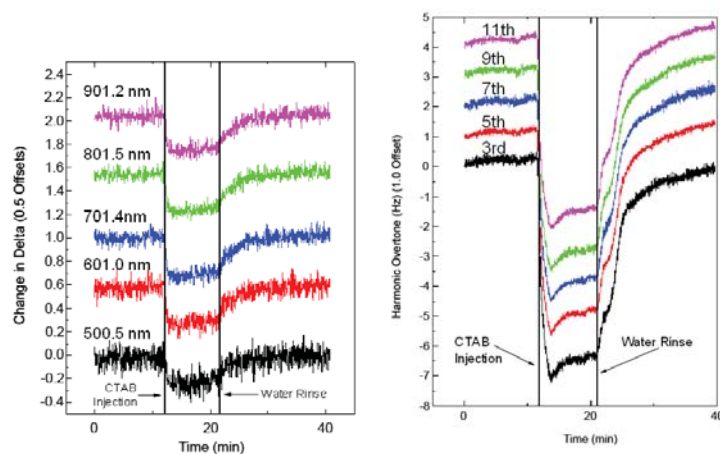


Figure 3. Raw data for 2.5mM CTAB experiment. Left: Ellipsometric  $\Delta$  (5 of 512 wavelengths). Right: QCM-D frequency-shifts for 3rd – 11th harmonics.

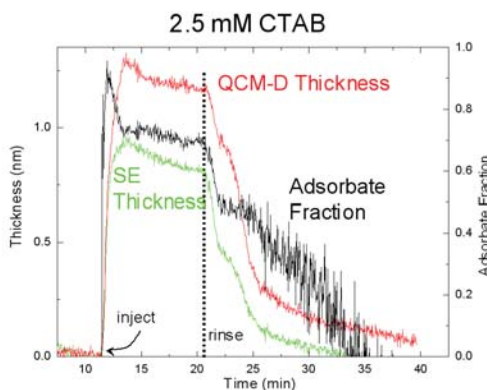


Figure 4. 2.5mM CTAB injection/rinse cycle results.

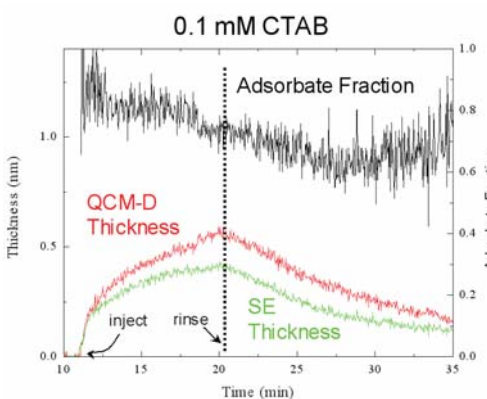


Figure 5. 0.1mM CTAB injection/rinse cycle results.

References:

- Hook et al, *Langmuir* **14** 729 (1998). Also G. Sauerbrey, *Zeitschrift für Physik A Hadrons and Nuclei* **155**, 206 (1959). Also Voinova, M. V.; et al. *Phys. Scr.* **1999**, 59, 391-396.
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