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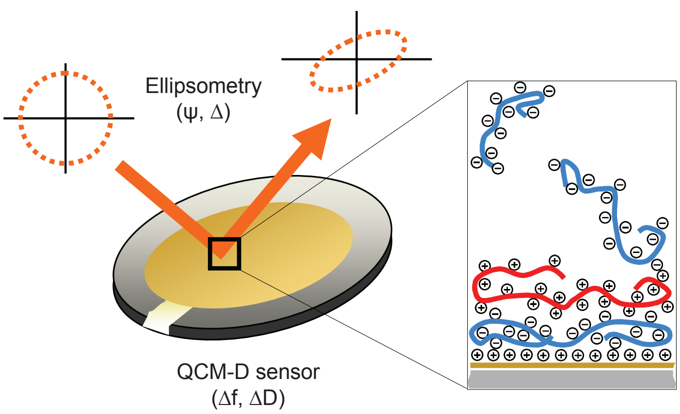
Q-Sense | [Technology Note] 3

In-situ combination of QCM-D and ellipsometry

Thorough and unambiguous analysis of surface phenomena requires characterization by several techniques, where merging them into the same setup is a very promising approach. Q-Sense Ellipsometry Module combines two real-time surface-sensitive characterization techniques, Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) and ellipsometry into one setup. This allows for data to be recorded simultaneously with both techniques on the same sensor surface. Information that can be derived from such a measurement include mass, thickness, solvent content, viscoelastic properties and the refractive index of thin molecular films.

Principle

QCM-D is an acoustic surface-sensitive technique, which provides simultaneous, real-time information about the mass and structure of thin films. The mass of an adsorbed layer is sensed as a change in the resonance frequency of the sensor movement (frequency). Viscoelastic or structural properties are deduced from the dissipation (or the damping of the oscillation). Ellipsometry is an optical surface sensitive technique, which measures changes in the ellipsometric angles, Psi (ψ) and Delta (Δ). From the measurement of these angles, the mass, thickness as well as optical properties of adsorbed layers can be obtained. A remarkable difference between both techniques is that trapped solvent contributes to the mass measured by QCM-D, while it does not for ellipsometry. A combination of both techniques can thus provide insight into the solvent content in the adsorbed films.



[Figure 1]: Sketch of the combined QCM-D / ellipsometry setup. Changes in the polarization state of light upon reflection at the QCM-D sensor surface are monitored simultaneously to measuring changes in the vibrational behavior of the QCM-D sensor. The build up of a polyelectrolyte multilayer is used as measurement example.

Figure 1 illustrates the combined setup: the change in the polarization state of light upon reflection on the QCM-D sensor surface is monitored by the ellipsometer; the shifts in frequency and dissipation are measured simultaneously by QCM-D. The Q-Sense Ellipsometry Module, designed for parallel measurements by QCM-D and ellipsometry, can be used with the Q-Sense E-Series systems (E4 or E1) together with an ellipsometer. Here, a spectroscopic ellipsometer (M-2000V from J.A. Woollam) was used.

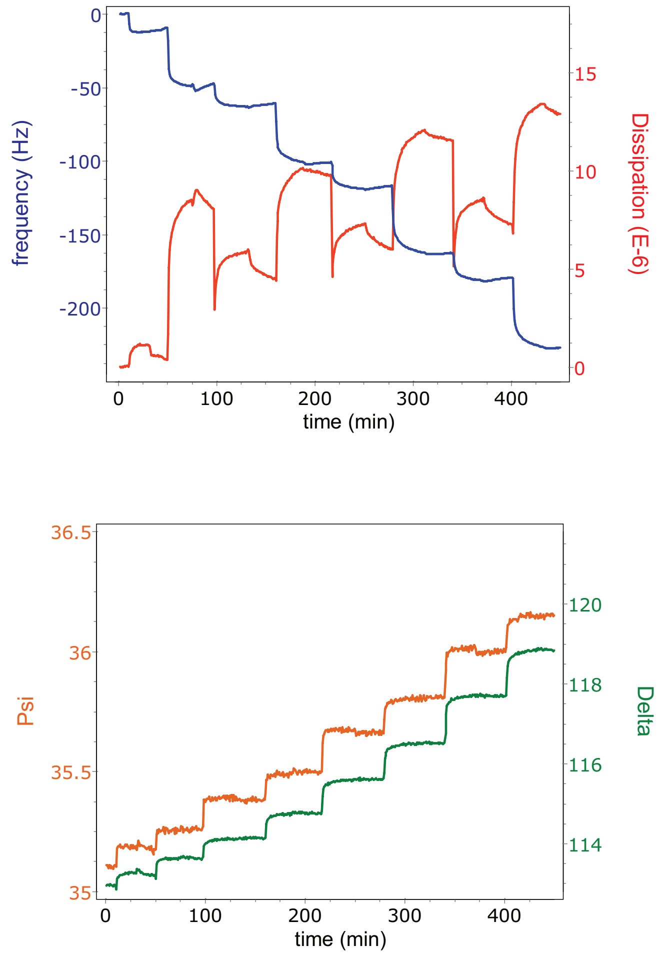
Analysis

Figure 2 shows the raw data from a combined experiment, where a build-up of a polyelectrolyte multilayer was monitored. The signal-to-noise ratios and the signal stability are similar to those typically observed in standard measurements by each technique individually.

The multilayer mass, measured by QCM-D can be derived from modeling the data in QTools*. From the ellipsometric response, the thickness, d, and the refractive index, n, of the film can be obtained by modeling the data. Here a block-model was used to fit the data. In the simplest approximation, the total deposited biomolecular mass can then be derived by:

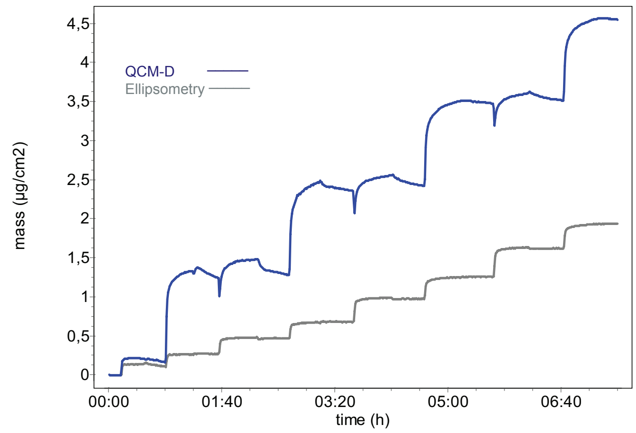
$$m_{opt} = \frac{d \times (n - n_{solvent})}{dn/dc}$$

with dn/dc being the refractive index increment that characterizes the dependence of the solution’s refractive index on the molecular concentration of the solute.



[Figure 2]: Raw data for binding of polyethylenimine followed by formation of a polyelectrolyte multilayer of three alginate-chitosan double layers and alginate addition as the last step. (A) Shifts in frequency and dissipation, as measured by QCM-D (5th overtone). (B) Ellipsometric angles, Δ and ψ, at a wavelength of 697.7 nm.

The evolution of the mass for the multilayer build-up, as sensed by QCM-D and ellipsometry, is shown in Figure 3. Values from QCM-D are generally higher than those measured by ellipsometry. The difference reflects solvent trapped in the multilayer film. Starting directly from the first alginate-chitosan double layer, the film growth is linear, as expected for this polyelectrolyte system. Measured by QCM-D, the mass increments for alginate deposition are typically much higher than those for chitosan. Interestingly, the opposite trend can be observed for the optical mass: here, the mass increase is slightly higher for chitosan than for alginate. This behavior reflects differences in the solvent content of both layers: upon addition of alginate less polymeric material adsorbs but much more water is coupled into the film than upon addition of chitosan layers.



[Figure 3]: Adsorbed mass, as determined from the ellipsometric (grey) and QCM-D (blue) data in Figure 2.

Summary

Both QCM-D and ellipsometry allow for time-resolved characterization of adsorption processes and changes in the properties of thin films on surfaces. The two techniques are complementary, and their combination provides information about mechanical and optical properties simultaneously.
Potential applications include:

i. Measurement of time-resolved changes in the hydration of thin biomolecular films.

ii. Monitoring the build-up of polymer films, e.g., polyelectrolyte multilayers or polymer brushes, and their reaction to external cues. Swelling/collapse of the films can be easily distinguished from adsorption/desorption events.

iii. Refined analysis of adsorption processes that involve morphological changes in the adsorbed layers, e.g., the formation of supported lipid bilayers.

References:

This work was performed by S. Stahl, J. Iturri Ramos, J. Zhou, S. Moya and R. Richter (CIC biomaGUNE, San Sebastian, Spain), in collaboration with Q-Sense AB.

* QTools is an analysis software included in the Q-Sense QCM-D systems. QTools includes the Voigt viscoelastic model and the Sauerbrey relation model. Since dissipation is low for this interaction, mass from QCM-D can be derived from the frequency change Δf by using the Sauerbrey relation: mQCM-D = -C × Δf.

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