Monitoring Organic Thin Film Growth and its Water Content With Combined Quartz Crystal Microbalance and Ellipsometry

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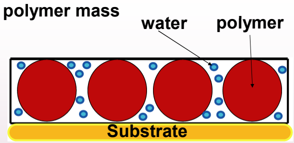
Our message

- Simultaneous measurement of organic thin fim using Quartz Crystal Microbalance (QCM) and Spectroscopic Ellipsometry (SE).
- Synperonic in aqueous phase deposited on octadecane thiol coated gold surface is used as a model system.
- QCM is measures total mass including water entrapped in the thin organic film whereas SE excludes water in the measurement. The combination of the two instruments allows one to determine the porosity and thereby find the water content.

Studying water rich organic thin films

Ellipsometer is sensitive only to polymer mass



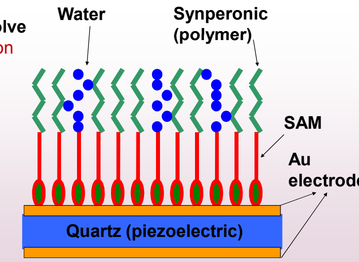
Quartz Crystal Microbalance is sensitive to total mass (polymer + water)

Comparison provides the porosity (f_v) , fraction of polymer in the film

How does the **water content evolve** during organic thin film formation in an aqueous environment?

Porosity holds the key!

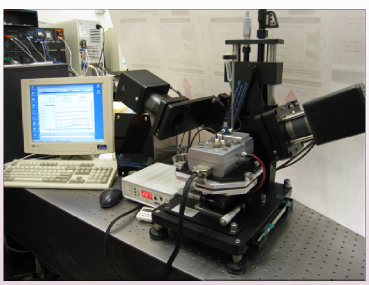
Methods to investigate this phenomena are:
- Optical
- Mechanical
- Combination of optical and
- mechanical methods



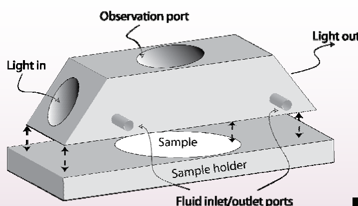
Schematic diagram of film on QCM wafer

Description of System Studied

Instrumentation



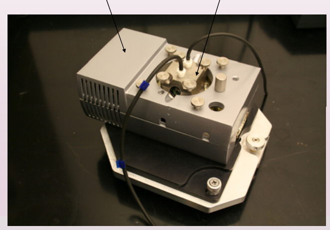
Combined stage for QCM and SE



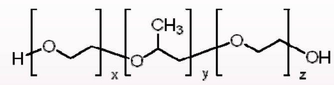
QCM-SE liquid cell
- Specially designed cell allows for simultaneous measurement of mass uptake by SE and QCM.
- QCM and SE readings taken from sample surface.

Quartz Crystal Microbalance unit

Liquid cell



Synperonic

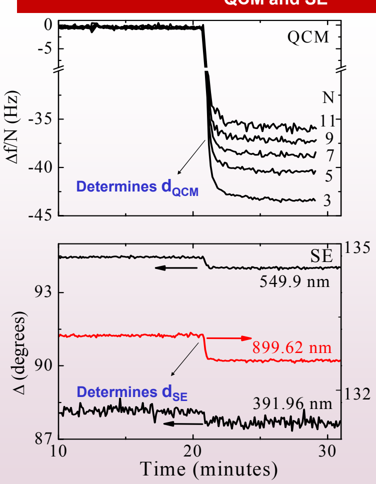


Molecular structure of Synperonic PE/F68

- A self-assembled monolayer (SAM) composed of octadecanethiol was first assembled on to the gold surface. This was done to make the surface hydrophobic.
- Synperonic, a well studied polymer, was introduced to form a thin organic film on the SAM.

Measurement of Film Thickness and Determining the Porosity

QCM and SE



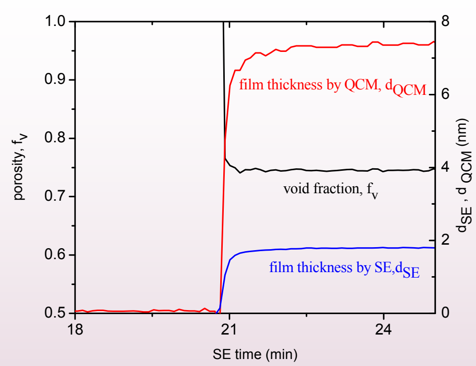
Top panel (QCM): Frequency shift normalized by harmonic number. The graphs do not overlap indicating formation of a viscoelastic film.

Bottom panel (SE): Δ at selected wavelengths from *in-situ* scanning ellipsometry (SE) measurements.

$$f_v = \frac{\rho_o (d_{QCM} - d_{SE})}{\rho_{H_2O} d_{SE} + \rho_o (d_{QCM} - d_{SE})}$$

The formula for porosity (f_v) relates the thickness determined from SE (d_{SE}) & QCM (d_{QCM}) and densities of water and polymer respectively. Monitoring the evolution of f_v gives an idea of whether the film:
1. forms and swells by imbibing water.
2. forms from an initial water rich state to a final denser state by releasing water.

Determination of Porosity, f_v



The graph above displays the variation of thickness of synperonic film over time as calculated from QCM (d_{QCM}) and SE data (d_{SE}). Also shown is the evolution of porosity (f_v) over time. In this case, the film entraps water as it is formed.

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