In-situ ellipsometry studies of thin swollen films, a review

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Thin polymer films
Why are they important?

Functional coatings
Membranes
Displays

Solar cells
Barriers
Biosensitive films
Sensors
Thin polymer films

Interactions with penetrants

Dry

Swollen
Spectroscopic ellipsometry

in-situ
Spectroscopic ellipsometry

Drawbacks? or opportunities?
**In-situ configurations**

**No cell**

**Advantages:**
- No window effects
- Multi-angle possibility

**Disadvantages:**
- Less defined ambient

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**Delivery of osmotic shocks**

**References:**
- Richardson H., et al., The European Physical Journal E, 2003, 12(0), p. 87-91
In-situ configurations
Trapezoidal cell

Advantages:
- Controlled ambient
- Static or flowing

Disadvantages:
- Window offsets
- Angle offset – cell geometry

Typical angles of incidence: 65° - 75°
In-situ configurations

Backside configuration

Advantages:
- Multiple angles of incidence
- Relative simplicity (no windows)

Disadvantages:
- Bubble formation

**In-situ configurations**

**High pressure cells**

- **Advantages:**
  - $p_{\text{max}} = 200$ bar
  - Broader T range 0 - 220 °C
  - Liquids, vapors, gases, vacuum, …

- **Disadvantages:**
  - Window offsets
  - Ambient optical dispersion

Ogieglo W., et al., Journal of Membrane Science, **2013**, 437(0), p. 313-323

![Diagram of high pressure cell setup](image)
Types of polymeric materials

**Glassy state:**
- Frozen macromolecule
- Non-equilibrium
- History dependence

**Rubbery state:**
- Fast macromolecule
- Equilibrium

Types of polymeric materials

Block co-polymers
**Multilayer films**
Zwitterionic films
Cyclic oligomers
Hydrogels
Particle films
Conducting polymers
Composite films
Metal Organic Frameworks
Saccharides

Types of studied phenomena


Inaccurate at very high swelling

Dry film

Swollen film

Optical contrast - sensors

Good sensor!

Bad sensor!
Types of studied phenomena

Drying processes

Penetrant volume fractions

1. Film dilation

\[ \phi_{dil.} = \frac{h_{SP} - h_{DP}}{h_{SP}} \]

2. Effective medium approximations

\[ \phi_1 \cdot \frac{n_1^2 - n_{mix}^2}{n_1^2 + 2n_{mix}^2} + \phi_2 \cdot \frac{n_2^2 - n_{mix}^2}{n_2^2 + 2n_{mix}^2} = 0 \]

3. Clausius - Mossotti

\[ \frac{n^2 - 1}{n^2 + 2} = \frac{R}{M_w} \cdot \rho \]

\[ \frac{n_{mix}^2 - 1}{n_{mix}^2 + 2} = q_{solv.} \cdot C_{solv.} + q_{polym.} \cdot C_{polym.} \]

Glassy systems?

Ogieglo W., et al., Polymer, 2014, in press


Thermodynamic parameters

\[ \ln(a) = \ln(\phi_S) + (1 - \phi_S) + \chi \cdot (1 - \phi_S)^2 \]

Free-standing film: \[ \Omega = \left(1 - \frac{2M_e}{M}\right) \frac{V_{HE}}{3RT} \left(\frac{1}{\alpha} - \frac{1}{2\alpha^3}\right) \]

Thin supported film: \[ \Omega = \left(1 - \frac{2M_e}{M}\right) \frac{V_{HE}}{3RT} \left(\alpha - \frac{1}{2\alpha}\right) \]
Ellipsometry combined with other techniques

Quartz Crystal Microbalance (QCM)

Highly complementary to ellipsometry

Ellipsometry

QCM-D

Thickness $\varepsilon_1, \varepsilon_2$

Mass (Viscoelastic properties)
Ellipsometry combined with other techniques

Atomic Force Microscopy (AFM)

Source: Aalto University, School of Science, Department of Applied Physics


Roughness increases
Ellipsometry combined with other techniques

Neutron and X-ray reflectivity
Electrochemical methods
Gravimetric methods
Contact angle measurements
Spectroscopy (IR, UV-VIS)
Surface plasmon resonance
Methods to determine mechanical properties

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Ellipsometry combined with other techniques

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Methods to determine **mechanical properties**

In more detail:

Ogieglo W., PhD Thesis, Chapter 1
Thank you for your attention!

Questions?