Optical in-situ characterization techniques for thin film growth processes

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Outline

• Introduction
• Optical in-situ techniques for thin film growth processes
  - Reflectometry
  - Spectroscopic Ellipsometry
  - Reflectance Anisotropy Spectroscopy
  - Raman Scattering
• Summary
In-situ Measurements

In-situ

Measurements performed with a sample mounted in the film growth or processing environment

Advantages of in-situ measurements

• Quick and direct relation between process parameters and sample properties (=> process control option)
• Sensitive samples can be studied without contact to air
• Reduces time and costs
In-situ Measurements

Requirements for in-situ measurements (compared to ex-situ measurements)

- Dynamic processes
  - => Shorter measurement time, and
  - => Less time for data analysis / evaluation
- Harsh environmental conditions
  - => Optical setup typically placed outside process chamber
    (longer working distances, need for optical viewports)
- Process chamber design
  - => Experimental setup needs to be adapted (can include additional optical elements for redirecting or focusing the light)
- Samples can move or rotate
  - => Special attention to substrate positioning, or
  - => Correction algorithms needed
Optical in-situ Measurements Techniques

Optical techniques are ideal tools for in-situ thin film growth monitoring

Advantages
- non-intrusive
- contact-less
- non-destructive
- fast
Optical in-situ Measurement Techniques

Techniques (examples)

- Reflectometry (and transmission spectroscopy)
- Ellipsometry
- Reflectance anisotropy spectroscopy
- Raman scattering
- FTIR spectroscopy
- Photoluminescence
- Emission spectroscopy
- ...

Accessible parameters

- Thickness, growth rates
- Optical properties (index of refraction, absorption index, dielectric function)
- Composition
- Crystal phase
- Crystal properties, stress
- Electronic properties (excitons, transition energies)
- Plasmon properties (free charge carriers)
- Phonon properties (lattice vibrations)
- Temperature
- ...

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**Reflectometry (Transmission Spectroscopy)**

**Principle:** Change of intensity upon reflection (or transmission)

**Measured quantities**
- $I_r$ ... Intensity of reflected beam
- $I_t$ ... Intensity of transmitted beam

**Typically given as relative quantities**
- $R = \frac{I_r}{I_0}$
- $T = \frac{I_t}{I_0}$
- $I_0$ ... Intensity of incident beam (or reference beam)
Reflectometry (Transmission Spectroscopy)

**Principle:** Change of intensity upon reflection (or transmission)

Accessible parameters
- Thickness
- Optical properties (index of refraction, absorption index, dielectric function)

Related properties:
- Growth rate
- Composition
- Electronic transition energies
- Crystal Quality
- Free charge carriers
Reflectometry Example: \((\text{Al}_x\text{Ga}_{1-x})_{0.52}\text{In}_{0.48}\text{P}\) (MOCVD)

In situ transients of normalized reflectance \(R/R_{\text{GaAs}}\) taken during MOCVD growth of \((\text{Al}_x\text{Ga}_{1-x})_{0.52}\text{In}_{0.48}\text{P}\) layers at a wavelength of 563 nm

- Experimental data
- Simulation

\(x\) increases
=> \(n\) and \(k\) decrease

**Reflectometry Example:** \((\text{Al}_x\text{Ga}_{1-x})_{0.52}\text{In}_{0.48}\text{P} \) (MOCVD)

<table>
<thead>
<tr>
<th>(x)</th>
<th>Growth rate (in situ, (\lambda=563\text{nm})) [nm/s]</th>
<th>Growth rate (ex situ, SEM) [nm/s]</th>
<th>(x) (in situ, (\lambda=563\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.451 (0.06)</td>
<td>0.453</td>
<td>0.287 (0.07)</td>
</tr>
<tr>
<td>0.2</td>
<td>0.413 (0.06)</td>
<td>0.426 (0.06)</td>
<td>0.587 (0.11)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.420 (0.07)</td>
<td>0.436 (0.07)</td>
<td>0.747 (0.10)</td>
</tr>
<tr>
<td>0.7</td>
<td>0.423 (0.06)</td>
<td>0.433 (0.06)</td>
<td>0.413 (0.04)</td>
</tr>
<tr>
<td>1</td>
<td>0.400 (0.04)</td>
<td>0.413</td>
<td></td>
</tr>
</tbody>
</table>

Reflectometry (Transmission Spectroscopy)

Advantages:

• Simple setup (low costs)
• Only one viewport is needed (reflectometry)
• Reflectometry: In principle, no initiations concerning the materials to be measured (thickness determination requires transparent films)

Disadvantages:

• Sensitive to intensity fluctuations/losses (due to scattering, misalignment of sample, or beam blocking)
• Transmission spectroscopy: Limited to transparent materials
• Reference measurement needed
Spectroscopic Ellipsometry (SE)

**Principle:** Change of polarization upon reflection (or transmission)

\[ \rho = \frac{R_p}{R_s} = \tan \Psi \cos \Delta \]

\( \rho \) ... parallel to plane of incidence
\( s \) ... perpendicular to plane of incidence
Spectroscopic Ellipsometry (SE)

**Principle:** Change of polarization upon reflection (or transmission)

- Accessible parameters
  - Thickness
  - Optical properties
  - Depolarization

- Related sample properties:
  - Growth rate
  - Composition
  - Electronic transition energies
  - Crystal Quality
  - Free charge carriers
  - Roughness
  - Inhomogeneities
SE Example: ZnO Growth (PLD)

Transient of ellipsometric parameter $\Delta$

Experiment
- $E = 3.317$ eV ($\lambda = 373.8$ nm)
- $E = 2.355$ eV ($\lambda = 526.5$ eV)
- $E = 1.817$ eV ($\lambda = 682.4$ eV)
- $E = 1.252$ eV ($\lambda = 990.3$ eV)

Model
- GVIA

Analysis with General Virtual Interface Approach (B. Johs, J. A. Woollam Co.)

Source: N. Ashkenov, M. Schubert (formerly Uni Leipzig, M.S. now Uni Nebraska-Lincoln)
Phase II: - Growth rate decreases with time
   - Index of refraction and absorption index decrease with time

*Source: N. Ashkenov, M. Schubert (formerly Uni Leipzig, M.S. now Uni Nebraska-Lincoln)*
Spectroscopic Ellipsometry (SE)

Advantages:

• Measures (at least) two quantities at each spectral point
• No reference spectrum needed
• Less sensitive to intensity fluctuations/losses
• In principle, no restriction concerning the material to be measured
  (thickness determination requires transparent films)

Disadvantages:

• Experimental setup more complex (requires additional optical elements, such as polarisers, compensators)
• Requires two viewports, which allow specular measurements
  (angle of incidence preferred to be in the range between 60° and 80°)
Reflectance Anisotropy Spectroscopy (RAS)

\[
x = [1\overline{1}0]
\]
\[
y = [110]
\]

Reflectance Anisotropy Spectroscopy (RAS) or Reflectance Difference Spectroscopy (RDS)

= Ellipsometry at (near) normal incidence

\[
\frac{\Delta r}{r} = 2\frac{r_x - r_y}{r_x + r_y} = \text{Re}\left\{\frac{\Delta r}{r}\right\} + \text{Im}\left\{\frac{\Delta r}{r}\right\}
\]

Source: Optical Analysis Laboratory, University of Dublin
http://www.tcd.ie/Physics/opticslab/images/RAS_diagram_big.jpg
Reflectance Anisotropy Spectroscopy (RAS)

RAS is mainly used to monitor the epitaxial growth of III-V semiconductor compounds (MOVPE, MBE, ...) or metal layers in UHV-environments

- Bulk optical response is isotropic, i.e. bulk RAS signal is zero
- Surface can introduce anisotropy because of surface symmetry reduction due to surface reconstruction or relaxation

RAS is very surface sensitive (even though penetration depth can be many atomic layers)

RAS can be used to probe:
- composition in ternary or quarternary compounds
- variation of doping
- temperature
- growth rate
RAS Example: InGaAs/GaAs Superlattice (MOVPE)

RAS response for the MOVPE growth of a InGaAs (5ML)/GaAs(10ML) superlattice with 30 periods

Monolayer growth can be resolved

Reflectance Anisotropy Spectroscopy (RAS)

Advantages:

- (Sub)Monolayer resolution
- Less sensitive to intensity fluctuation (intensity ratio is measured)
- Only one viewport is needed

Disadvantages:

- Modelling of experimental data not (yet) possible, i.e. quantitative analysis of experimental data is not straightforward
- Applications restricted to
  - materials with isotropic bulk optical response
  - clean surfaces
**Raman Scattering (RS)**

**Principle:** Inelastic light scattering at optical phonons (lattice vibrational modes).

- **Incident light** (monochromatic, laser): $\omega_0$
- **Sample**
- **Inelastically scattered light**: $\omega_0 \pm \omega_{\text{Raman}}$
Raman Scattering (RS)

Principle: Inelastical light scattering at optical phonons (lattice vibrational modes).

Accessible parameters:
- Phonon mode frequency
- Broadening, lineshape
- Intensity (ratio)

Related sample parameters:
- Crystal Structure
- Composition
- Crystal Quality
- Free charge carriers
Raman Scattering: In-situ Probe

Main Features:

- Optics and laser combined in one unit
  - No intensity losses due to fibre coupling
  - No 'ghost Raman signal' produced by fibre
- Optics: Achromats (Ø 50 mm) for reduction of aberration
  - Numerical aperture 0.31 at working distance of 70 mm
- Laser: Nd:YAG laser with 100 mW at 532 nm
- Reduction of elastically scattered light by notch filter
RS Example: Cu-In-Se (Evaporation)

Raman spectra of selected Cu-In-Se phases

- CuInSe$_2$
- CuInSe$_2$ + Cu$_2$Se (HT)
- In$_2$Se$_3$
- InSe

Source: Solarion AG
RS Example: Cu-In-Se (Evaporation)

Gray scale plot of in-situ Raman spectra recorded during roll-to-roll process


Source: Solarion AG
RS Example: Cu-In-Se (Evaporation)

Comparison of Raman and X-ray fluorescence data allows to define the target zone.


Source: Solarion AG
Raman scattering (RS)

**Advantages:**
- Setup is (rather) simple
- Only one viewport is needed
- Data analysis

**Disadvantages:**
- Scattering intensity of solids is low (integration time typically > 30 s)
- Number of possible applications is limited (only materials with Raman-active phonon modes can be probed)
Summary

• Variety of optical measurement techniques for in-situ characterization of thin film growth processes (pros and cons)
  - Reflectometry
  - Spectroscopic Ellipsometry
  - Reflectance Anisotropy Spectroscopy
  - Raman scattering
• Optical techniques allow
  - contactless and non-destructive measurements
  - to probe a variety of sample properties
  - to characterize different materials
• In-situ optical techniques can be integrated into PVD (and CVD) processes