AMC2023
Advanced Materials Characterization Workshop

Optical Characterization Methods
Part I
Julio A. N. T. Soares
Materials Research Laboratory
University of Illinois at Urbana-Champaign

go.Illinois.edu/AMC2023

© 2023 University of Illinois Board of Trustees. All rights reserved.
- Direction of propagation
- Electric field direction or polarization
- Photon energy or wavelength
- Intensity
Light interactions

- Transmission
- Reflection
- Absorption
- Emission
- Scattering
- Refraction

Non-linear effects
- SFG
- SHG
- DFG
- Multi-photon absorption
Light interactions with matter

- Size
- Lattice structure, dopants
- Temperature
- Thickness
- Microstructure
- Concentration
- Stress
- Composition
Transmission, Reflection, Absorption

What is measured:
The transmitted and reflected light intensity as a function of the incident photon energy, which depends on the material’s electronic, atomic, chemical and morphological structure.
Spectrophotometry (UV-VIS-NIR)

**Instrumentation:**
Optical band gap determination of CdS thin films as a function of growth substrate temperatures

Tauc's relation: \[ \alpha h\nu = A(h\nu - E_g)^m \]

- \( m = 0.5 \) for direct and 2 for indirect allowed transitions.

Spectrophotometry (UV-VIS-NIR)

**Beer-Lambert Law**

\[ \text{Abs} = K \cdot \ell \cdot c = a \cdot \ell \]

\[ \text{Abs} = \log \left( \frac{1}{T} \right) \]

Using absorbance to determine Au/Hg concentration in water solutions
Spectrophotometry (UV-VIS-NIR)

Using transmission interference fringes to determine thickness

- Slope = 2.76 µm
- Slope = 50.99 µm
Spectrophotometry (UV-VIS-NIR)

Al₂Si₄O₁₀(OH)₂

Mg₃Si₂O₁₀(OH)₂

Images from Wikipedia and euortalc.com
Spectra from Developments in Clay Science, Vol. 8, Ch. 5
Excitations in materials

- **Plasmons**

Plasmons are quanta of collective motion of charge-carriers in a gas with respect of an oppositely charged background. They play a significant role on transmission and reflection of light.
Plasmonic crystal Brillouin zone from the transmission spectra measured for many different angles of incidence.
Spectrophotometry (UV-VIS-NIR)

Applied Materials Today 8, 68 (2017)

Optical Materials Express, 332858 (2018)
Vibrational spectroscopy

Normal vibrational modes in molecules:

CO₂ (4 modes)

- \( \nu_1 = 1388 \text{ cm}^{-1} \)
- \( \nu_2 = 667 \text{ cm}^{-1} \)
- \( \nu_3 = 2349 \text{ cm}^{-1} \)

H₂O (3 modes)

- \( \nu_1 (3657 \text{ cm}^{-1}) \)
- \( \nu_2 (1595 \text{ cm}^{-1}) \)
- \( \nu_3 (3756 \text{ cm}^{-1}) \)

PO₄ (9 modes)

Number of modes:

- 3N-6 for non-linear molecules
- 3N-5 for linear molecules
Vibrational spectroscopy

Normal vibrational modes in solids:

Sb/GaAs(110)

GaN

SWCNT

http://www.phonon.fc.pl

http://www.physik.tu-berlin.de/institute/IFFP/richter/naw/research/surface-phonons.shtml

T. A. Beu and A. Farcas 2016 EPL 113 37004
Fourier Transform IR spectroscopy (FTIR)

**IR active vibrations**

The intensity of a vibrational absorption depends on the change of the transition dipole momentum caused by that vibration, so a vibration mode will be “IR active” only when the vibration causes a change in the dipole momentum of the molecule, i.e. $\Delta\mu \neq 0$. 

![Diagram showing IR active and inactive vibrations](image-url)
**Fourier Transform IR spectroscopy (FTIR)**

**Instrumentation:**

The FTIR uses a Michelson interferometer with a moving mirror, in place of a diffraction grating or prism.

\[ \Delta L = n\lambda \Rightarrow \text{constructive interference} \]

\[ \Delta L = (n+1/2)\lambda \Rightarrow \text{destructive interference} \]
Fourier Transform IR spectroscopy (FTIR)

**Instrumentation:**

The FTIR uses a Michelson interferometer with a moving mirror, in place of a diffraction grating or prism.

\[ \Delta L = n \lambda \rightarrow \text{constructive interference} \]

\[ \Delta L = (n+1/2) \lambda \rightarrow \text{destructive interference} \]
Fourier Transform IR spectroscopy (FTIR)

\[ I(\nu) = \int S(t) e^{2\pi i \nu t} dt \]
But what is the Fourier Transform? A visual introduction.
Fourier Transform IR spectroscopy (FTIR)

Polystyrene

Transmission (%)

Wavenumber (cm⁻¹)

3 mil
1.5 mil
Fourier Transform IR spectroscopy (FTIR)

FTIR can be used to identify components in a mixture by comparison with reference spectra.

Discovery of beeswax as binding agent on a 6th-century BC Chinese turquoise-inlaid bronze sword
Wugan Luo, Tao Li, Changsui Wang, Fengchun Huang

J. of Archaeological Sci. 39 (2012), 1227
Fourier Transform IR spectroscopy (FTIR)

Images from Wikipedia and eurotalc.com
Spectra from Developments in Clay Science, Vol. 8, Ch. 5
Spectrophotometry (UV-VIS-NIR) and FTIR

Limitations:
- Reference sample is often needed for quantitative analysis.
- Many contributions to the spectrum are small and can be buried in the background.
- Usually, unambiguous chemical identification requires the use of complementary techniques.
- Limited spatial resolution.

Strengths:
- Very little or simple sample preparation.
- Simplicity of use and data interpretation.
- Short acquisition time, for most cases.
- Non-destructive.
- Broad range of photon energies.
- High sensitivity (~0.1 wt% typical for FTIR).

Complementary techniques:
Raman, Electron Energy Loss Spectroscopy (EELS), Extended X-ray Absorption Fine Structure (EXAFS), XPS, Auger, SIMS, XRD, SFG.
Light scattering
Sir Chandrasekhara Venkata Raman

The Nobel Prize in Physics 1930 was awarded to Sir Venkata Raman "for his work on the scattering of light and for the discovery of the effect named after him".

Sir Kariamanikkam Srinivasa Krishnan

Co-discoverer of Raman scattering, for which his mentor C. V. Raman was awarded the 1930 Nobel Prize in Physics.
Raman spectroscopy

What is measured:
The light inelastically scattered by the material.

Basic principle:
The impinging light couples with the lattice vibrations (phonons) of the material, and a small portion of it is inelastically scattered. The difference between the energy of the scattered light and the incident beam is the energy absorbed or released by the phonons.
Impinging light couples with vibration modes of the material:

- Phonons
- Molecular vibrations
Instrumentation:

Raman spectroscopy
| p = 0 |
Raman spectroscopy

\[ E = E_0 \cdot \cos(2\pi \cdot \nu_0 \cdot t) \]

\[ p = \alpha \cdot E_0 \cdot \cos(2\pi \cdot \nu_0 \cdot t) \]
Raman spectroscopy

The $\alpha$ tensor is dependent on the shape, strength, and dimensions of the chemical bond. Since chemical bonds change during vibrations, $\alpha$ is dependent on the vibrations of the molecule:

$$\alpha_i = \alpha_{i0} + \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{k,l} \left( \frac{\partial^2 \alpha}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l + \ldots$$

$$Q_k = Q_{k0} \cdot \cos \left( 2\pi \cdot \nu_k \cdot t + \varphi_k \right)$$

$$\alpha_k = \alpha_0 + \alpha'_k \cdot Q_{k0} \cdot \cos \left( 2\pi \cdot \nu_k \cdot t + \varphi_k \right)$$
The $\alpha$ tensor is dependent on the shape, strength, and dimensions of the chemical bond. Since chemical bonds change during vibrations, $\alpha$ is dependent on the vibrations of the molecule:

\[
\alpha_k = \alpha_0 + \alpha'_k \cdot Q_{k0} \cdot \cos \left( 2\pi \cdot \nu_k \cdot t + \varphi_k \right)
\]

\[
p = \alpha_0 \cdot E_0 \cdot \cos \left( 2\pi \cdot \nu_0 \cdot t + \frac{1}{2} \cdot \alpha'_k \cdot Q_{k0} \cdot E_0 \right) \left[ \cos \left( 2\pi \cdot t \cdot (\nu_0 + \nu_k) + \varphi_k \right) + \cos \left( 2\pi \cdot t \cdot (\nu_0 - \nu_k) - \varphi_k \right) \right]
\]

\[
\alpha'_k = \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \neq 0
\]

the dipole oscillates with three frequencies simultaneously, corresponding to the three possible scattering modes (Rayleigh, Stokes Raman and anti-Stokes Raman).
Fourier Transform IR spectroscopy (FTIR)

IR active vibrations

$\Delta \mu = 0 \times$

$\Delta \mu \neq 0$
Raman spectroscopy

Raman active vibrations

The intensity of the Raman scattering linked to a vibrational state depends on the change in the polarizability tensor.
FTIR and Raman:
The two techniques are complementary (different selection rules).

\[ \Delta \mu \neq 0 \]

\[ \alpha'_{\text{k}} = \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 \neq 0 \]
Studying the characteristic Raman frequencies, we can estimate the identity and composition of materials. Raman peak intensity allows us to determine the volume of material probed. The Raman peak frequency shift helps in identifying strain, stress, crystal lattice distortion. Raman peak width gives insight into the crystallinity of the material. Raman peak polarization dependency reveals the crystal orientation and symmetry.
Molecular and crystalline structure characterization

Presence of N vacancies yields poor crystallinity

Substitutional C fills N vacancies improving the crystallinity

C content

C incorporates interstitially causing a degradation of the crystal lattice

PHYSICAL REVIEW B 68, 155204 (2003)
Crystalline structure and defect characterization

The inset shows the linear dependence between the two parameters at low defect concentration.
Strain/stress

(a) Raman spectroscopy

- Gr / flat SiO₂
- Gr / 50 nm NSs
- Gr / 20 nm NSs

(b) Gr / 20 nm NSs

(c) 2685

(d) 0.4

Nano Lett. 18, 2098 (2018)
Phase transitions

<table>
<thead>
<tr>
<th>Different Raman Modes</th>
<th>Si-I (cm⁻¹)</th>
<th>Si-III (cm⁻¹)</th>
<th>Si-XII (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300, 520</td>
<td>466, 171</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>a-Si (cm⁻¹)</td>
<td>384</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>475, 510</td>
<td>432, 463</td>
<td>397</td>
<td></td>
</tr>
</tbody>
</table>

Ref 2,3

J. Raman Spectroscopy 41, 334 (2010)
**Primary Strengths:**
- Very little sample preparation.
- Structural characterization.
- Non destructive technique.
- Chemical information.
- Complementary to FTIR.

**Primary Limitations:**
- Expensive apparatus (for high spectral/spatial resolution and sensitivity).
- Weak signal, compared to fluorescence.
- Limited spatial resolution (diffraction limited).

**Complementary techniques:**
FTIR, EELS, Mass spectroscopy, EXAFS, XPS, AES, SIMS, XRD, SFG.
Optical Characterization Methods
Part II
Julio A. N. T. Soares
Materials Research Laboratory
University of Illinois at Urbana-Champaign

go.Illinois.edu/AMC2023

© 2023 University of Illinois Board of Trustees. All rights reserved.
Luminescence

Lifetime: Phosphorescence, fluorescence

Mechanism: Photoluminescence, bioluminescence, chemoluminescence, thermoluminescence, piezoluminescence, etc.
What is measured:
The emission spectra of materials due to radiative recombination following photo-excitation.

Basic principle:
- Conduction band
- Valence band
- Direct band gap
- Indirect band gap
Instrumentation:

Photoluminescence
Room temperature absorption in GaAs

Infrared Physics, 1961, Vol. 1, pp. 111
**Fig 3** Exciton absorption in GaAs; ○ 294 K, □ 186 K, △ 90 K, ● 21 K.

**Lattice constant**
Photoluminescence

Excitonic molecule emission in Si


Conduction band

Valence band

Defect emission in GaAs

**Photoluminescence**

**Number of layers in 2D materials**

a) PL spectra for mono- and bilayer MoS$_2$
   Inset: PL QY of thin layers for $N = 1$–6.

b) Normalized PL spectra by the intensity of peak A of thin layers of MoS$_2$ for $N = 1$–6. Feature I for $N = 4$–6 is magnified for clarity.

c) Band-gap energy of thin layers of MoS$_2$, inferred from the energy of the PL feature I for $N = 2$–6 and from the energy of the PL peak A for $N = 1$. The dashed line represents the (indirect) band-gap energy of bulk MoS$_2$.

Defects in 2D materials

Defect induced PL emission.

a) Schematic diagram of electron beam irradiation on monolayer WSe₂ sample during the EBL processing.

b) PL spectrum of pristine monolayer WSe₂ and monolayer WSe₂ after EBL. The inset shows optical image of WSe₂ with PMMA patterned by EBL, scale bar is 5 μm.

c) PL spectra of a pristine WSe₂ under different e-beam irradiation density.
Photoluminescence spectra of InN layers with different carrier concentrations.

1. \( n = 6 \times 10^{18} \text{ cm}^{-3} \) (MOCVD);
2. \( n = 9 \times 10^{18} \text{ cm}^{-3} \) (MOMBE);
3. \( n = 1.1 \times 10^{19} \text{ cm}^{-3} \) (MOMBE);
4. \( n = 4.2 \times 10^{19} \text{ cm}^{-3} \) (PAMBE).
**In$_x$Ga$_{1-x}$N alloys. Luminescence peak positions of cathodoluminescence and photoluminescence spectra vs. concentration x.**

The plots of luminescence peak positions can be fitted to the curve

$$E_d(x) = 3.48 - 2.70x - bx(1-x)$$

with a bowing parameter of $b=2.3$ eV.

Width and quality of semiconductor quantum wells.

3-QWs

<table>
<thead>
<tr>
<th>Depth (nm)</th>
<th>Material</th>
<th>Layer Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>GaAs</td>
<td>cap</td>
</tr>
<tr>
<td>3</td>
<td>InGaAsN</td>
<td>QW</td>
</tr>
<tr>
<td>35</td>
<td>GaAs</td>
<td>barrier</td>
</tr>
<tr>
<td>5</td>
<td>InGaAsN</td>
<td>QW</td>
</tr>
<tr>
<td>35</td>
<td>GaAs</td>
<td>barrier</td>
</tr>
<tr>
<td>9</td>
<td>InGaAsN</td>
<td>QW</td>
</tr>
<tr>
<td>100</td>
<td>GaAs</td>
<td>buffer</td>
</tr>
</tbody>
</table>

Photoluminescence

Photoluminescence

Pitfalls, artifacts, corrections...

[Graph showing wavelength vs. signal with peaks at 300, 600, 900 nm]

[Diagram showing grating with normal, incident light, and orders m = 0, ±1, ±2 with wavelengths 300, 200, 100 nm]
Pitfalls, artifacts, corrections ...

Non-ideal components introduce spectral distortions

(b)

Uncorrected DCM Spectrum

Corrected DCM Spectrum

Normalised Emission

Wavelength (nm)
Photoluminescence

Strengths:
- Very little to none sample preparation.
- Non-destructive technique.
- Very informative spectrum.

Limitations:
- Often requires low temperature.
- Data analysis may be complex.
- Many materials luminescence weakly.

Complementary techniques:
- Ellipsometry, Modulation spectroscopies,
- Spectrophotometry, Raman.
- Direction of propagation
- Electric field direction or polarization
- Photon energy or wavelength
- Intensity
**Ellipsometry**

**Basic principle:**
The reflected light emerges from the surface elliptically polarized, i.e., its p and s polarization components are generally different in phase and amplitude.

\[ \tan(\Psi') e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} \]
Ellipsometry

\[ \tilde{n} = n + ik \]
\[ \tilde{n}_1 \sin \phi_1 = \tilde{n}_2 \sin \phi_2 \]

\[ \tilde{r}_{12} = \frac{\tilde{n}_{2,1} \cos \phi_1 - \tilde{n}_{1,2} \cos \phi_2}{\tilde{n}_{2,1} \cos \phi_1 + \tilde{n}_{1,2} \cos \phi_2} \]

\[ \tilde{R}_{p,s} = \frac{\tilde{r}_{p,s} + \tilde{r}_{p,s} e^{-2i\beta}}{1 + \tilde{r}_{p,s} \tilde{r}_{p,s} e^{-2i\beta}} \]

\[ \beta = \frac{2\pi d}{\lambda} \tilde{n}_b \cos \phi_b \]

\[ \tan(\Psi) e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} \]

\[ \tan(\Psi) = \frac{\tilde{R}_p}{\tilde{R}_s} \]

\[ \Delta = \delta^r - \delta^i \]
What is measured:
The changes in the polarization state of light upon reflection from a mirror like surface.
What is measured:
The changes in the polarization state of light upon reflection from a mirror-like surface.
Ellipsometric $\Psi(\lambda)$ and $\Delta(\lambda)$ spectra of Cd$_{1-x}$Zn$_x$S thin films deposited under the different concentration of ammonia: 0.19, 0.38, 0.56, and 0.75 M.
Ellipsometry Applications

- Composition
- Surface roughness
- Film thickness
- Band gap energy
- Optical constants (dielectric function)

Graph showing variation of $(c/h)^2$ with $E$ (eV) for different concentrations.
Ellipsometry

Limitations:
- Flat and parallel surface and interfaces with measurable reflectivity.
- A realistic physical model of the sample is required to obtain most useful information.

Strengths:
- Fast.
- Measures a ratio of two intensity values and a phase.
  - Highly accurate (even in low light levels).
  - No reference sample necessary.
  - Not susceptible to scatter, lamp or purge fluctuations.
  - Increased sensitivity, especially to ultrathin films (<10nm).
- Can be used in-situ.

Complementary techniques:
"Conventional" Optical Microscopy

- Eyepiece
- Tube lens
- Objective
- Object
- Image
- Eye
- Perceived image
Optical microscopy

Phase contrast

Bright field

Dark field

Polarizing

Integrated Circuit in Brightfield, Darkfield, and DIC with Reflected Light

Living Cells in Brightfield and Phase Contrast

Phyllite Thin Section in Polarized Light

Microscopy U
THE SOURCE FOR MICROSCOPY EDUCATION
• But how small a thing can we see?
• But how small a thing can we see?
The Airy pattern
Lateral resolution

NA = (n)sin(\(\mu\))

(a) \(\mu = 7^\circ\) NA = 0.12
(b) \(\mu = 20^\circ\) NA = 0.34
(c) \(\mu = 60^\circ\) NA = 0.87
Lateral resolution

Numerical aperture
Resolution

**Airy Disks**

Intensity Distributions

**Rayleigh criterion**

\[ d \approx \frac{0.61 \lambda}{NA} \]

**Abbé criterion**

\[ d = \frac{0.61 \lambda}{NA} \]

\[ d = \frac{0.50 \lambda}{NA} \]

\[ d = \frac{0.47 \lambda}{NA} \]
Confocal microscopy

- Increased contrast \( \Rightarrow \) 200:1.
- Slightly increased in plane resolution (1.5 x)
- Significantly increased resolution along the optical axis.
- Scanning image formation.
Confocal microscopy

- Increased contrast => 200:1.
- Slightly increased in plane resolution (1.5 x)
- Significantly increased resolution along the optical axis.
- Scanning image formation.
Confocal microscopy

The relation of the first ring maximum amplitude to the amplitude in the center is 2% in case of conventional point spreading function (PSF) in a focal plane, while in case of a confocal microscope this relation is 0.04%.
Confocal microscopy combined with spectroscopy

Widefield microscope
PSF

Confocal microscope
PSF

Confocal microscopy reconstruction of a 3D capillary bed

PLOS ONE 7(12): e50582 (2012)
Confocal microscopy combined with spectroscopy

Chemical composition
Component identification
Components distribution

Confocal microscopy for measuring topography

Confocal microscopy z-stack
Confocal microscopy for measuring topography
Scratch on glass
Primary Limitations:
- Expensive apparatus (for high spectral/spatial resolution and sensitivity).
- Weak signal, compared to fluorescence.
- Limited spatial resolution (diffraction limited).
The More Time Approach
Surface Plasmons

Plasmons can be driven by photons at resonance to build large standing wave electric fields. That leads to a strong enhancement of Raman scattering, proportional to fourth power of the E field strength.
Surface Enhanced Raman Spectroscopy (SERS)

Typically achieved with corrugated gold/silver surface or gold/silver nanoparticles with molecules of interest attached.

Capable of boosting Raman signal up to 14 Orders of Magnitude or more! *Science* 275, 1102 (1997)

*Chem. Rev. 117, 5002, (2017)*
Confocal Raman Microscopy

That's cool, but what about ...

- Limited spatial resolution (diffraction limited).

Confocal Raman Image
Carbon Nanotubes

Tip Enhanced Raman Spectroscopy (TERS)

What is really cool is that this also works with a single metalized sharp tip, such as an STM or AFM tip!

Not only do you get the electric field enhancement, but now the source of the Raman signal is extremely localized.

Tip Enhanced Raman Spectroscopy (TERS)

Confocal Raman Image

Tip Enhanced Raman Image

Carbon Nanotubes

Near-field scanning optical nanospectroscopy
Near-field scanning optical nanospectroscopy

Nano-FTIR

Nature Communications 4, 2890

Science 344, 1369
Thanks to our sponsors

Platinum sponsors

Keyence

Kurt J. Lesker Company

Oxford Instruments

Quantum Design

Raith

ThermoFisher Scientific

Sponsors

Angstrom Scientific Inc.

Bruker

Gatan

Edax

Hitachi

Inspire the Next

A.S. Woollam

JEOL

Kratos Analytical

Malvern Panalytical

Midwest Vacuum

Molecular Vista

Pfeiffer Vacuum

Physical Electronics

Protochips

Rigaku

Sanko

Surface Measurement Systems

Teledyne

Teledyne Leec Instruments

Tescan

Waters