Near field microscopy and optical spectroscopy
Bringing some color to materials science
Julio A. Soares, Ph.D.
Optical characterization

• Visual characterization:
  • Color
  • Transparency
  • Reflectivity
  • Refractivity
  • Luminosity

• absorption bands,
  • thickness,
  • homogeneity,
  • composition,
  • temperature,
  • index of refraction,
  • surface morphology/ nanostructure,
  etc.

Colored glass optical filters
Optical characterization

• Visual characterization:
  • Color
  • Transparency
  • Reflectivity
  • Refractivity
  • Luminosity

• absorption bands,
  • thickness,
• homogeneity,
• composition,
• temperature,
• index of refraction,
• surface morphology/
  nanostructure,
  etc.

SiO$_2$ thin film with variable thickness
Optics Express 12, 5789 (2004)
Optical characterization

- Visual characterization:
  - Color
  - Transparency
  - Reflectivity
  - Refractivity
  - Luminosity

- Absorption bands,
- Thickness,
- Homogeneity,
- Composition,
- Temperature,
- Index of refraction,
- Surface morphology/nanostructure, etc.

Solimões and Negro rivers joining to form the Amazon river (right), and Amazon river joining with Tapajós river (left)
• Visual characterization:
  • Color
  • Transparency
  • Reflectivity
  • Refractivity
  • Luminosity

• Absorption bands,
• Thickness,
• Homogeneity,
• Composition,
• Temperature,
• Index of refraction,
• Surface morphology/ nanostructure, etc.

Steel being forged.
Optical characterization

• Visual characterization:
  • Color
  • Transparency
  • Reflectivity
  • Refractivity
  • Luminosity

• absorption bands,
• thickness,
• homogeneity,
• composition,
• temperature,
• index of refraction,
• surface morphology/ nanostructure,
  etc.

Birefringent crystal.
Optical characterization

- Visual characterization:
  - Color
  - Transparency
  - Reflectivity
  - Refractivity
  - Luminosity

- absorption bands,
- thickness,
- homogeneity,
- composition,
- temperature,
- index of refraction,
- surface morphology/nanostructure,
  etc.

Structural color of butterfly wings
Optical spectroscopy

- Spectrophotometry (UV-VIS-NIR).
- Fourier transform infra-red spectroscopy (FTIR).
- Raman spectroscopy.
- Luminescence spectroscopy – photoluminescence (PL).
- Ellipsometry.
- Sum frequency generation (SFG).
- Modulation spectroscopy – thermoreflectance (pump-probe).
What is measured?

The transmission, reflection and absorption of light as a function of the incident photon energy.

Basic principle:
When a material interacts with light, the manner it does so depends on the material electronic, atomic, and morphological structure. Thus by measuring the optical spectra of a material, we are indirectly probing its electronic, chemical, and structural properties.
Spectrophotometry (UV-VIS-NIR)

**Instrumentation:**
Light passes through a monochromator, and is directed to the sample. A detector measures the intensity of light that is transmitted by the sample as a function of wavelength. For quantitative measurements, the signal is compared to the intensity of the light transmitted by a reference sample.
Spectrophotometry (UV-VIS-NIR)

**Instrumentation:**
Light passes through a monochromator, and is directed to the sample. A detector measures the intensity of light that is transmitted by the sample as a function of wavelength. For quantitative measurements, the signal is compared to the intensity of the light transmitted by a reference sample.

**Operation modes:**
- Transmission (liquids and solids)
- Specular reflection
- Diffuse reflection
- Total fluorescence
Applications of spectrophotometry include:

• Transmission / reflectance (measured directly).
• Absorption edges / electronic structure (calculated from the optical data).
• Thin film thickness (from interference fringes, if present).
• Surface plasmonic modes (from optical data).
• Concentration (from optical data and comparison with standards).
Using absorption to determine Au/Hg concentration in water solutions

As Au relative concentration rises, the absorption peak shifts toward shorter wavelengths, increase in intensity, and its FWHM decreases.
High performance plasmonic crystal sensor formed by soft nanoimprint lithography

Viktor Malyarchuk, Feng Hua, Nathan H. Mack, Vanessa T. Velasquez, Jeffrey O. White, Ralph G. Nuzzo and John A. Rogers

Optics Express 13, 5669 (2005)

Plasmonic crystal Brillouin zone from the transmission spectra measured for many different angles of incidence.
Spectrophotometry (UV-VIS-NIR)

Strengths:

• Very little to no sample preparation.
• Simplicity of use and data interpretation.
• Short acquisition time, for most cases.
• Non destructive.

Requirements and limitations:

• Reference sample is often needed for quantitative analysis.
• Different regions of the sample contribute to the final spectrum.
• Many contributions to the spectrum are small and can be buried in the background.

Complementary techniques:

EXAFS, FTIR.
Fourier Transform IR Spectroscopy (FTIR)

What is measured?
The transmission, reflection and absorption of light as a function of the incident photon energy in the mid and far IR region of the electromagnetic spectrum.

Basic principle:
Absorption in the IR is dominated by phonon and vibrational absorption.

The phonon spectrum of a material is very sensitive to variations on atomic arrangement, and bonds length and strength, making FTIR a powerful tool for structural characterization, and molecular identification.
Fourier Transform IR Spectroscopy (FTIR)

Instrumentation:
The FTIR spectrometer is very similar in function to the spectrophotometer, with a fundamental difference. It uses a Michelson interferometer with a moving mirror, in place of a diffractive element for obtaining spectrally resolved data. The beam coming from each mirror will interfere, and different wavelengths will be modulated at different frequencies. The light impinging the sample is not monochromatic as in the spectrophotometer, and all wavelengths are detected at the same time.
Fourier Transform IR Spectroscopy (FTIR)

Spectrum formation:

\[ I(\nu) = \int_{-\infty}^{\infty} S(t)e^{2\pi i\nu t} dt \]
Fourier Transform IR Spectroscopy

An example of an interferogram and its corresponding FTIR spectrum.
Fourier Transform IR Spectroscopy (FTIR)

FT vs. Dispersive optics spectrometers

Advantages:
• Multiplexing (all wavelengths are measured simultaneously).
• No chromatic aberrations or artifacts.
• Higher throughput.
• Improved S/N ratio.
• Better resolution and accuracy.

Disadvantages:
• More complex system.
• More expensive.
• Linearity of detectors (working closer to saturation levels).
• Stray light scattering at low signal level.
Applications of FTIR include:

- Transmission / reflectance in the IR (measured directly).
- Vibrational / rotational levels (calculated from the optical data).
- Thin film thickness (from interference fringes, if present).
- Molecular and crystalline structure (from optical data).
- Concentration (from optical data and comparison with reference standards).
- Detection and identification of compounds – fingerprinting (from optical data and comparison with compiled tables and libraries, and/or to reference samples).
Fingerprinting:
FTIR can be used to identify components in a mixture by comparison with reference spectra.
Fourier Transform IR Spectroscopy

Strengths:
- Very little sample preparation.
- Simplicity of use and interpretation.
- Short acquisition time, for most cases.
- Non destructive technique.
- High sensitivity.

Requirements and limitations:
- Reference sample.
- Overlapping of signal from different regions of the sample.
- Usually, unambiguous chemical identification requires the use of complementary techniques.
- Limited spatial resolution.
- Hard to apply to solutions, due to IR absorption of solvents.

Complementary techniques:
Raman, EELS, Mass spectroscopy, EXAFS, XPS, AES, SIMS, XRD, SFG.
What is measured?

The inelastically scattered light from a sample under strong illumination by a laser beam.

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.
**Instrumentation:**

The laser beam is focused on the sample. Scattered radiation from the same spot on the sample is collected and focused on the monochromator entrance slit. The triple monochromator filters out the elastically scattered light. The spectrum is collected by a liquid nitrogen cooled CCD camera.
Applications of Raman spectroscopy include:

• Vibrational / rotational levels (from peak position).
• Structural characterization (from peak position, width and integrated area).
  • Defects and Structural disorder.
  • Non crystalline solids structure
  • Stress analysis.
  • Dopant levels.
• Fingerprinting (from peak position and width).
• Micro Raman.
  • Grain analysis.
  • Crystal zoning.
  • Precipitates / liquid-solid interfaces / Inclusions.

Both, Raman spectroscopy and FTIR measure the vibrational spectra of materials, but the physical processes behind each of them are very different, and different selection rules apply.

The two techniques are complementary, rather than equivalent.
Surface enhanced Raman scattering (SERS)

On this example SERS is used to determine the mechanism of oxygen electroreduction on a roughened gold surface.

Peak 1 is associated to the O-O stretch mode of superoxide (O$_2^-$), demonstrating that it is one of the main intermediates during electroreduction of O$_2$. 
Using Raman spectroscopy we were able to observe structural changes as a function of carbon incorporation, which allowed us to determine C preferred incorporation sites on cubic GaN.
Raman Spectroscopy

Strengths:
- Very little sample preparation.
- Very powerful technique for structural characterization.
- Non destructive technique.
- Complementary to FTIR.

Requirements and limitations:
- Overlapping of signal from different regions of the sample.
- Expensive apparatus (for high resolution).
- Weak signal, compared to fluorescence.
- Laser heating or damage may occur to certain samples.

Complementary techniques:
FTIR, EELS, Mass spectroscopy, EXAFS, XPS, AES, SIMS, XRD, SFG.
Photoluminescence

**What is measured?**

The emission spectra of materials due to radiative recombination following photo-excitation.

**Basic principle:**

The impinging light promote electrons from the less energetic levels to excited levels, forming electron-hole pairs. As the electrons and holes recombine, they may release some of the energy as photons. The emitted light is called luminescence.

![Diagram of direct and indirect band gaps](attachment:diagram.png)

- **Direct band gap**
- **Indirect band gap**
Instrumentation:

The laser beam is focused on the sample. Radiation emitted from the sample is collected and focused on the monochromator entrance slit. The emission spectrum is collected by a photomultiplier, a solid state detector, or a liquid nitrogen cooled CCD camera. A liquid He bath cryostat can keep the sample at temperatures between 2 and 300 K.
Applications of PL include:

- Electronic structure and defect levels (from peak position).
- Impurity and exciton binding energy (from peak position).
- Impurity species (from peak position and width).
- Compound identification (from peak position and width).
- Alloy composition (from peak position – band gap determination).
- Quantum well width and quality (from peak position width and area).
- Structural quality / crystallinity (mainly from peak width).
- Carrier and doping concentration (from peak position and area).
- Internal strain (from peak width and area).
- Excited state life-time (from time-resolved experiments).
Photoluminescence

Conduction band

D
(D^+, X)

F Eagles
(D^0, X)

(A^0, X)

Valence band

A

GaAs

GaAs 4.2K

PL INTENSITY (arb. unit)

PHOTON ENERGY (eV)

1.52 1.51 1.50 1.49 1.48

(D^0, X)

(D^+, X)

(A^0, X)

WAVELENGTH (nm)

820 830 840

P = 17 Torr
n = 2.3 \times 10^{14} \text{ cm}^{-3}
\mu_77 = 105,000 \text{ cm}^2/\text{V} \cdot \text{s}

Shigenori Takagishi and Hideki Mori

Japanese Journal of Applied Physics
Photoluminescence

Mechanism of photoluminescence blue shift in InGaAsN/GaAs quantum wells during annealing

C.S. Peng*, H.F. Liu, J. Konttinen, M. Pessa

Example of the use of PL to determine the width and quality of InGaAsN/GaAs quantum wells.

<table>
<thead>
<tr>
<th>3-QWs</th>
<th>PL Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm GaAs cap</td>
<td></td>
</tr>
<tr>
<td>3 nm In_{0.35}Ga_{0.65}As_{0.994}N_{0.06} QW</td>
<td></td>
</tr>
<tr>
<td>35 nm GaAs barrier</td>
<td></td>
</tr>
<tr>
<td>5 nm In_{0.35}Ga_{0.65}As_{0.994}N_{0.06} QW</td>
<td></td>
</tr>
<tr>
<td>35 nm GaAs barrier</td>
<td></td>
</tr>
<tr>
<td>9 nm In_{0.35}Ga_{0.65}As_{0.994}N_{0.06} QW</td>
<td></td>
</tr>
<tr>
<td>100 nm GaAs buffer</td>
<td></td>
</tr>
<tr>
<td>GaAs (001) SUB</td>
<td></td>
</tr>
</tbody>
</table>

QW width: 9nm, 5nm, 3nm

In_{0.35}Ga_{0.65}As_{0.994}N_{0.06}/GaAs 3QWs

RTA Time (min) @ 700°C

PL Intensity (a.u.)

hν (meV)

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Photoluminescence

Strengths:
• Very little sample preparation.
• Non destructive technique.
• Very informative spectrum.

Requirements and limitations:
• Overlapping of signal from different regions of the sample.
• Expensive apparatus.
• Often requires low temperature.
• Laser heating or damage may occur to certain samples.
• Some applications require complex apparatus.
• Data analysis may be complex.
• Many materials do not luminesce.

Complementary techniques:
Ellipsometry, Modulation spectroscopies.
Ellipsometry

What is measured?

The changes in the polarization state of light upon reflection from a mirror like surface. In particular, the phase difference and the intensity ratio between the reflected light with p and s polarizations.
Ellipsometry

Basic principle:
The components of the reflected light in p and s polarizations are generally different in phase and amplitude. Thus the reflected light emerges from the surface elliptically polarized.

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

\[ \tilde{R}_p = \frac{\tilde{n}^2 \cos \phi - \sqrt{\tilde{n}^2 - \sin^2 \phi}}{\tilde{n}^2 \cos \phi + \sqrt{\tilde{n}^2 - \sin^2 \phi}} \]

\[ \tilde{R}_s = \frac{\cos \phi - \sqrt{\tilde{n}^2 - \sin^2 \phi}}{\cos \phi + \sqrt{\tilde{n}^2 - \sin^2 \phi}} \]
Applications of ellipsometry include:

(All characteristics below enter as parameters to a physical model of the measured structure that is used to fit the ellipsometric data).

- Thicknesses of heterostructure layers and thin films.
- Dielectric function of thin films and bulk materials.
- Surface and interfacial roughness.
- Composition.
- Anisotropy.
- Crystallinity.
- Uniformity.
- In-situ monitoring of thin film growth (by monitoring one or more of the above parameters).
Ellipsometry

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>2.19 ± 0.04</td>
</tr>
<tr>
<td>Si</td>
<td>21.9 Å</td>
</tr>
</tbody>
</table>

SiO₂ thickness 2.19 ± 0.04 nm

χ² = 4.31

Model fit

Experiment

- □ Ψ
- ○ Δ

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Ellipsometry

\[ \varepsilon = 1 + \frac{A_1}{E_1^2 - E^2 - iB_1} + \frac{A_2}{E_2^2 - E^2} \]

DLC thickness \(43.89 \pm 0.04 \text{ nm}\)

\(A_1 = 59.7 \pm 0.5 \text{ eV}^2\)

\(B_1 = 5.52 \pm 0.03 \text{ eV}\)

\(E_1 = 4.51 \pm 0.01 \text{ eV}\)

\(A_2 = 113.4 \pm 0.6 \text{ eV}^2\)

\(E_2 = 6.98 \pm 0.02 \text{ eV}\)

\(\chi^2 = 2.78\)

DLC (Lorentz w/ 2 oscillators) \(438.9 \text{ Å}\)

SiO\(_2\) \(530 \text{ Å}\)

Si
Ellipsometry

**Strengths:**
- Fast.
- Measures a ratio of two intensity values and a phase.
  - Highly accurate and reproducible (even in low light levels).
  - No reference sample necessary.
  - Not as susceptible to scatter, lamp or purge fluctuations.
  - Increased sensitivity, especially to ultrathin films (<10nm).
- Variable Angle Spectroscopic Ellipsometry.
  - More experimental data to constrain the model fit.
  - Data at wavelengths of interest.
  - Optimize sensitivity by choosing the appropriate angle of incidence.
- Can be used in-situ.

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

**Complementary techniques:**
- PL, Modulation spectroscopies, XPS, SIMS, XRD.
Sum Frequency Generation

What is measured?

Sum frequency generation (SFG) is a second order process involving two input laser fields, which induce the generation of a third field, coherently irradiated with the sum frequency of the original fields. This third beam is measured as a function of the wavelength.

Basic principle:

• Second-order non-linear processes are forbidden in the bulk with inversion symmetry

• At the surface and interfaces the symmetry is broken, and SFG is allowed.

• SFG is strongly dependent on the surface state.

• SFG signal is resonantly enhanced when the energy of the IR beam matches a vibrational energy on the surface/interface.
Instrumentation:
In a three wave mixing process like SFG, the signal is proportional to the pulse width $\delta t$. Thus short and ultra-short systems are preferred. The system in the CMM Laser Facility produces pulses of 10 ps in 100 pulses trains with a repetition rate of 25 Hz. Its range is from 4 to 20 $\mu$m.

Applications of SFG include:
- Vibrational spectroscopy of surfaces and interfaces.
- Surface and interface chemistry / electro-chemistry.

Sum Frequency Generation

Potential Dependent Organization of Water at the Electrified Metal–Liquid Interface

Zachary D. Schultz, Scott K. Shaw, and Andrew A. Gewirth

J. AM. CHEM. SOC. 2005, 127, 15916–15922
Sum Frequency Generation

**Strengths:**
- SFG is a second order process.
  - Mostly insensitive to bulk signal.
  - Can be used to probe surface and optically accessible interfaces.
- Very sensitive to surface state.
  - Can detect less than a monolayer of molecules adsorbed to a surface.
  - Sensitive to molecular arrangement on the surface.
- SFG is a coherent optical process.
  - The SFG beam is highly directional.
- SFG is compatible with in-situ monitoring.

**Requirements and limitations:**
- Careful alignment of beams to coincide on the sample surface.
- Interfaces to be studied need to be accessible by all beams, the IR, the visible, and the SFG.
- May require a long acquisition time to get data.
- Expensive and complex apparatus.

**Complementary techniques:**
FTIR, Raman spectroscopy.
Time-domain thermoreflectance (TDTR)

What is measured?

Modulation spectroscopy is an experimental method for taking the derivative of an optical spectrum (reflectance or transmittance), by modifying the measurement conditions through external stimulation. In the case of thermoreflectance, the temperature of the sample is modulated by the pump beam, and its reflectance is measured by a weaker probe beam. In time-domain thermoreflectance, we measure this reflectance with time resolution.

Basic principle:

The dielectric function of a material, and thus its reflectance, is a function of temperature. By modulating the material’s temperature, we can measure the variation in its reflectivity, caused by that modulation. With time resolved measurements, we can calculate the thermal conductivity of the sample.
Time-domain thermoreflectance (TDTR)

**Instrumentation:**
- Ultra-fast fs Ti:Sapphire laser operating in the range 700-800 nm, with 80 MHz repetition rate.
- A variable delay line in the pump beam path for time resolution.
- Scanning sample stages for spatially resolved measurements and mapping of thermal properties.

**Applications of TDTR include:**
Spatially resolved thermal and elastic properties of materials:
- Thermal effusivity (ΛC) and conductivity.
- Mechanical properties (by determination of the speed of sound).

Ultralow Thermal Conductivity in Disordered, Layered WSe$_2$ Crystals

Catalin Chiritescu, David G. Cahill, Ngoc Nguyen, David Johnson, Arun Bodapati, Pawel Keblinski, Paul Zschack


Time domain thermoreflectance was used to measure the thermal conductivity of WSe$_2$ films as a function of temperature, and film thickness. Thermal conductivities 6 times lower than the minimum predicted conductivity for single crystalline WSe$_2$.

The lowest thermal conductivity obtained (50 mWm$^{-1}$K$^{-1}$) is the lowest so far observed for a fully dense solid.

The low conductivity is produced by random stacking of crystalline WSe$_2$ sheets.
Elastic constants of single-crystal TiN$_x$(001) (0.67 ≤ x ≤ 1.0) determined as a function of x by picosecond ultrasonic measurements

Taeyoon Lee, K. Ohmori, C.-S. Shin, David G. Cahill, I. Petrov, and J. E. Greene

PHYSICAL REVIEW B 71, 144106 (2005)
Time-domain thermoreflectance (TDTR)

**Strengths:**
- No sample preparation.
- Non destructive technique.
- Spatial and temporal resolution.
- Measurements can be made over a large range of temperatures.
- Fast.

**Requirements and limitations:**
- Careful alignment of beams to coincide on the sample surface.
- Complex and expensive apparatus.

**Complementary techniques:**
Raman spectroscopy, Nanoindentation.
• Near-field scanning optical microscopy (NSOM).
Near-field Scanning Optical Microscopy

Background

Based on the Airy discs formation Abbé derived a theoretical limit to the optical microscope resolution.

*Arch. Microskop. Anat.* 9, 413 (1873)

He defined the resolving power of the microscope as the distance between two point sources for which the center of one Airy disk coincides with the first zero of the other:

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

Rayleigh criterion
Near-field microscopy: resolution beyond the diffraction limit!

The near field microscope resolves objects much smaller than the wavelength of light by measuring at very short distances from the sample surface, through sub-wavelength apertures.

Basic principle:

The principle of operation of the NSOM was devised by Synge in 1928 †.

- The sample is kept in the near-field regime of a sub-wavelength source. Resolution quickly degrades with sample source separation distance.
- If $z \ll \lambda$, the resolution is determined by the aperture, not wavelength.
- The image is constructed by scanning the aperture across the sample and recording the optical response.

† Philos.Mag. 6, 356 (1928).
Near-field Scanning Optical Microscopy

Instrumentation:

- Fiber-coupler
- Lamp
- Confocal microscope
- PMT/APD spectrometer
- Data acquisition
- Shear-force feedback
- Scan control
- Flip mirror
- XYZ-stage
- PMT

- Laser
- Adapter ring
- Counternut
- Screw to hold the endcap
- Magnet
- Washer
- Cantilever

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Spatially resolved photoluminescence in InGaN/GaN quantum wells by near-field scanning optical microscopy

M. S. Jeong, J. Y. Kim, a) Y.-W. Kim, and J. O. White
E.-K. Suh b C.-H. Hong and H. J. Lee


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**Near-field Scanning Optical Microscopy**

**Strengths:**
- No sample preparation.
- Non destructive technique.
- Sub diffraction limit resolution (50 nm).

**Requirements and limitations:**
- Careful alignment required.
- Interaction between tip and sample may make analysis difficult.
- Very low throughput.
- Slow data acquisition.
- Limited to fairly flat samples (20 μm).

**Complementary techniques:**
AFM, SEM, TEM, Confocal microscopy.
Acknowledgements

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