Fourier-Transform Infrared Spectroscopic Ellipsometry for Material Identification

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Outline of the talk

• Optical constants of solids
• Ellipsometry basics
• Fourier-transform infrared spectroscopy (FTS or FT-IR)
• Far-infrared/Terahertz setup: detectors, sources
• The case of remote identification of explosives:
  – transmission
  – reflection
  – ellipsometry
Optical constants of solids

INDEX OF REFRACTION (COMPLEX)

Electronic excitations (electron-hole pairs) (Interband transitions)

Dipolar Lattice Vibrations (optical phonons) (normal modes)

Chemical species identification

ULTRAVIOLET

INFRARED

Chemical element identification

Photon energy (eV)

Photon energy (eV)

0.012

0.12

1.2

12

λ (μm)

λ (μm)

0.01

0.1

1

10

100

10³

0.12

1.2

12

0.012

Equivalent formulations:
- Dielectric constant \( \epsilon \)
- Optical conductivity \( \sigma \)

\[ \epsilon_1 = n^2 - k^2 \]

\[ \epsilon_2 = 2nk \]

\[ \sigma_1 = \frac{\omega}{4\pi} \epsilon_2 \]

\[ \sigma_2 = \frac{\omega}{4\pi} (\epsilon_\infty - \epsilon_1) \]

INDEX OF REFRACTION (COMPLEX)

Electronic excitations (electron-hole pairs) (Interband transitions)
Ellipsometry

Fresnel formulae

\[ \tilde{r}_p = \tilde{f}_1(n, k, \varphi) \]
\[ \tilde{r}_s = \tilde{f}_2(n, k, \varphi) \]

Material under analysis
\[ n + \imath k \]

Elliptically Polarized

\[ |r_s|E_s e^{i\delta_s} \]
\[ |r_p|E_p e^{i\delta_p} \]

POLARIZER

Broadband Source

Spectrometer

ANALYZER
Fourier-Transform Infrared Spectroscopy

Infrared spectrometer: Michelson Interferometer

- Reflected and/or Transmitted Power spectra are measured as a function of the frequency $\omega$
- Optical constants are derived by Kramers-Kronig analysis or by Ellipsometry

Frequency range: 0.1 THz – 2 PHz
Energy resolution: up to 0.01 THz
Material identification by Terahertz Spectroscopy

- **Far-Infrared spectra**
  
  “Fingerprint” region: each solid substance has a specific spectrum, or frequency-dependent optical constants 
  *(like a spectrometer)*

- **Terahertz frequencies**
  Clothes, tissues, plastic, paper and atmosphere are partly transparent: remote identification is possible 
  *(like a radar)*

Applications:

⇒ Remote security controls

⇒ Explosive detection
Infrared Spectroscopic Ellipsometry

Fresnel relations: transcendental

\[
\begin{align*}
\tilde{r}_p &= \frac{(n+ik) \cos(\varphi) - \cos(\varphi t)}{(n+ik) \cos(\varphi) + \cos(\varphi t)} = |\tilde{r}_p| e^{i\delta_p} \\
\tilde{r}_s &= \frac{\cos(\varphi) - (n+ik) \cos(\varphi t)}{\cos(\varphi) + (n+ik) \cos(\varphi t)} = |\tilde{r}_s| e^{i\delta_s}
\end{align*}
\]

\[
\sin(\varphi) = (n + ik) \sin(\varphi t)
\]

Michelson: intrinsic beam polarization!

\[
\tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \frac{(n+ik) \cos(\varphi) - \cos(\varphi t)}{\cos(\varphi) - (n+ik) \cos(\varphi t)} = \tan \Psi e^{i\Delta}
\]

\[
\tan \Psi = \frac{|\tilde{r}_p|}{|\tilde{r}_s|} \quad \Delta = \delta_p - \delta_s
\]

Infrared ellipsometry requires calibration!

Normalized Stokes parameters calc with Mueller matrixes

\[
\begin{align*}
\cos 2\Psi \\
\sin 2\Psi \cos \Delta \\
\sin 2\Psi \sin \Delta
\end{align*}
\]

\( n + ik \) in the whole infrared range!
• Room-temperature detectors (Pyroelectrics, Golay cells) are also available, but noise figures are $10^3$ times higher
• Development of sensitive detectors working at higher temperatures is ongoing (e.g. closed-cycle cooled, liquid nitrogen).
• CNR-IFN in Rome is developing superconducting bolometers.
Start user operation: 1999
Circumference of the synchrotron: 96 m
Circumference of the storage ring: 240 m
Number of bending dipoles: 2 x 16
Number of possible insertion devices: 15
Number of beamlines commissioned: ~ 50

Commissioning of the IR-beamline IRIS: 2002

It is the only storage ring producing steady-state Coherent Synchrotron Radiation => high power, pulsed source in the 0.1-1 THz range based on electron bunch acceleration
The Infrared beamline at BESSY

1. Broadband spectrum (MMW to UV)
2. Point-like source (tight focus)
3. High brilliance (photon density at focus)

Far-infrared Ellipsometry
Optical setups for measuring the optical constants

- Normal Incidence Reflectance
- Transmittance
- Variable Angle Reflectance
- Ellipsometry

- Polarizer 0°, 45° and 90°
- Analyzer 45°
- φ = 60° Brewster
Optical setups

- Normal Incidence

\[ \varphi = 8^\circ \]

- Variable Angle

Harrick “Seagull”

Home-made sample
Transmission of pure pellets of explosives and Oxygen-reducing salts

Pure Material pellets
Thickness: 2.0 mm

Bulk Polyethylene sample holder, 15° wedged

High Transparency only below 1 THz

⇒ No strong material-specific features
Absolute Reflectivity of pure explosive pellets for different angles of incidence

- Reference is a gold mirror
- \( R_s \sim R_p \) for \( \phi \sim 0 \), \( R_s > R_p \) anywhere else
- \( R_p \) goes to 0 at the Brewster angle (\( \sim 60^\circ \))
- The slope and the sharp features are material-specific and do not depend much on \( \phi \)
Optical constants of explosives: Absolute Reflectivity and Kramers-Kronig analysis

- High signal intensity
- Practical geometry
- High output quality
- Need a reference measurement on a mirror
- Very sensitive to absolute value (acceptable: ±5%)
- Need for a databank of high frequency extrapolations

Absolute reflectivity $R$ is measured at quasi-normal incidence from 0.7 to 20 THz to correctly evaluate the integral.

$$\phi_\omega(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\ln \sqrt{R(\omega')}}{\omega'^2 - \omega^2} d\omega'$$

$$= R e^{i\phi} \quad \tilde{n} = \frac{1 + \tilde{r}}{1 - \tilde{r}}.$$
Spectroscopic Ellipsometry: optical constants with no reference measurement

Calibration: a known, non-absorbing material at his Brewster angle, where the ellipse is most eccentric

- $n$, $k$ or $\Psi$, $\Delta$ determined from 3 sample spectra only (no mirror)
- the incidence angle has to be large ($>50^\circ$) and known ($\pm 0.5^\circ$)
- High sensitivity to noise (trigonometric functions)
- Low signal at low frequency (2 polarizers + 60° incidence)

Data harvest: close to Brewster angle
Polarizer rotated instead of analyzer (equivalent)
Result 1: NaClO$_3$ (a salt)
Result 2: Octogen (an explosive)
Absorption coefficient of explosives in the THz range

Optical constants determined by Far-infrared ellipsometry

⇒ No need for reference measurements to correct for the frequency-dependent incident power

⇒ Up to 4 THz, no role of surface roughness (common-use objects are “shiny”)