Lecture 20
Optical Characterization 2
Schroder: Chapters 2, 7, 10

Announcements

Homework 5/6:
• Is online now.
• Due **Wednesday May 30th at 10:00am**.
• I will return it the following Wednesday (6\textsuperscript{th} June).

Homework 6/6:
• Will be online on Wednesday 30\textsuperscript{th} June.
• Due **Wednesday June 6th at 10:00am**.
• I will return it at the final exam (14\textsuperscript{th} June).
• I will make the solutions available on June 6\textsuperscript{th}. 
Lecture 20

- Overview of Optical Properties
- Optical Microscopy.
- Ellipsometry.
- Transmission & Reflection Measurements.

Overview of Optical Properties
Optical Spectroscopy

- We have up to now focused primarily on the electronic properties of materials.
- It is worth spending some time on the optical properties of materials as well.
- These are important characteristics of electronic materials.

Optical Processes

- A lot can happen when light (or electromagnetic radiation generally) is incident on a material:
Optical Processes

- There are entire courses (or even degrees) dedicated to optical processes in materials. Here I will only provide an overview.

- At the first interface, some of the incident light is **reflected** and the rest is **transmitted** into the bulk.

We will call it light, despite the fact it could be of any wavelength.

Optical Processes

- There are entire courses (or even degrees) dedicated to optical processes in materials. Here I will only provide an overview.

- Inside the substrate, some of the radiation may be **absorbed** or **scattered**, and the rest of the light is either transmitted through the sample or is reflected off of the back interface.
Optical Processes

- There are entire courses (or even degrees) dedicated to optical processes in materials. Here I will only provide an overview.
- The absorbed electromagnetic radiation may be dissipated as heat or re-emitted at a different frequency (photoluminescence).

Optical Processes

- Scattering of light can involve:
  - Acoustic phonons (Brillouin scattering).
  - Optical phonons (Raman scattering).
  - Plasmons (collective oscillations of the ‘electron gas’, consisting of free carriers in a metal or heavily-doped semiconductor, or valence band electrons for a semiconductor or insulator).
Light

- Light is of course just a particular form of electromagnetic radiation.
- The energy of a photon \( E \), frequency \( \nu \) and wavelength are related by:
  \[
  E = h\nu = \frac{hc}{\lambda}
  \]
  \( h \) is Planck’s Constant.
  \( c \) is the speed of light in a vacuum.

Light

- Light is of course just a particular form of electromagnetic radiation.
- For our purposes we will define light as:
  - Near-Infrared (NIR): \( \lambda = 5\mu m - 700 nm \) \( (E = 0.248 - 1.77 \text{ eV}) \).
  - Visible: \( \lambda = 700 \text{ nm} - 380 \text{ nm} \) \( (E = 1.77 - 3.26 \text{ eV}) \).
  - Near-Ultraviolet: \( \lambda = 380 \text{ nm} - 200 \text{ nm} \) \( (E = 3.26 - 6.2 \text{ eV}) \).
Beer–Lambert Law

- Absorption in a material is described by the Beer-Lambert, or just Beer’s, Law:
  \[ I(x) = I_0 e^{-\alpha x} \]
- \( I(x) \) is the intensity of light at a distance \( x \) into the sample.
- \( I_0 \) is the intensity of light just inside the material.
- \( \alpha \) is the absorption coefficient (normally quoted in cm\(^{-1}\)).
- \( x \) is the distance light has travelled into the material.

Beer–Lambert Law

- The Beer–Lambert Law says that incident radiation is exponentially attenuated in the material and that \( \alpha \) is the \( 1/e \) distance characterizing this attenuation.
- For a sample of thickness \( d \) we can expect to obtain an intensity of \( I_{\text{out}} = I_0 e^{-\alpha d} \).
Absorption

• Consider absorption within a semiconductor or insulator, beginning with light of very long wavelengths.

Generation of excitons can require less energy than free carriers

I.e. traditional direct-bandgap absorption
Absorption

- Consider absorption within a semiconductor or insulator, beginning with light of very long wavelengths.

- Under high carrier density (e.g. high illumination / electrical injection) available states at band edge will be filled.

- Higher energy photons are required to excite carriers.

Absorption

- Consider absorption within a semiconductor or insulator, beginning with light of very long wavelengths.

- Band structures are more complex than we have considered in this course.

- Interband transitions can occur.
Absorption

• Consider absorption within a semiconductor or insulator, beginning with light of very long wavelengths.

\[ E \text{ (photon energy)} \]

\[ h \nu \text{ (photon frequency)} \]

indirect bandgap (phonon required for momentum conservation)

Refractive Index

• The macroscopic optical properties of an isotropic material are often specified in terms of a complex index of refraction (\( \bar{n} \)):

\[ \bar{n} = n + i\kappa \]

• \( n \) is the real part of the refractive index (what we talk about in high school etc.).
• \( \kappa \) is the extinction coefficient. Sometimes labeled \( k \).
• \( i \) is \( \sqrt{-1} \), you may see it as \( j \).
Refractive Index

- The real part of the refractive index, \( n \), is equal to the ratio of the speed of light in vacuum (\( c \)) compared to the phase velocity of light inside the material (\( v_p \)).

\[
n = \frac{c}{v_p}
\]

- Phase velocity is the velocity at which wave fronts (information travels).

- See Wikipedia for difference between phase and group velocities if necessary.


Refractive Index

- Normally the real part of the refractive index is used to quantify changes in direction (refraction), when light enters or exits a medium:

\[
\frac{n_1}{n_2} = \frac{v_2}{v_1}
\]

- Snell’s Law:

\[
n_1 \sin \theta_1 = n_2 \sin \theta_2
\]
Refractive Index

- The real part of the refractive index of a weakly absorbing material is given by:

\[ n = \sqrt{\varepsilon_r \mu_r} \]

- \( \varepsilon_r \) is the relative permittivity.
- \( \mu_r \) is the relative permeability.
- For non-ferromagnetic materials \( \mu_r \approx 1 \).
- Under these cases we can say:

\[ n = \sqrt{\varepsilon_r} \]

Extinction Coefficient

- The complex index of refraction is given by:

\[ \bar{n} = n + ik \]

- The extinction coefficient, \( k \), describes attenuation of the wave as it travels through space.
- It is related to the absorption coefficient \( \alpha \) by:

\[ \alpha = \frac{4\pi k}{\lambda} \]

- \( \lambda \) is the wavelength of the light in a vacuum.
- \( \alpha \) is normally quoted in cm\(^{-1} \).
Drude Model

- In general, a material exhibits dispersion.
- This means that the index of refraction, or equivalently, the dielectric constant is a function of the frequency or the wavelength: $\varepsilon \rightarrow \varepsilon(\lambda)$.
- This can be described by the Drude Model:

$$\varepsilon(\omega) = \varepsilon_r \varepsilon_0 = \varepsilon_\infty \left[1 - \frac{\omega_p^2}{\omega^2}\right]$$

- $\varepsilon$ is the permittivity of the medium.
- $\varepsilon_0$ is the vacuum permittivity.
- $\varepsilon_r$ is the relative permittivity.

- $\omega$ is the angular frequency of the light. Related to wavelength via:

$$\omega = 2\pi v = \frac{2\pi c}{\lambda}$$

- $\varepsilon_\infty$ is the high-frequency (i.e., optical frequency) material dielectric constant.
- $\omega_p$ is the free carrier plasma frequency.
Drude Model

- The free carrier plasma frequency is defined using:
  \[ \omega_p^2 = \frac{q^2 n}{\varepsilon_{\infty} m^*_n} \]
  - \( n \) is the conduction band electron concentration.
  - \( q \) is the fundamental unit of charge.
  - \( m^*_n \) is the hole effective mass.
  - The equivalent expression exists for holes.

Drude Model

- Thus, this free carrier plasma equation offers a way to estimate the carrier concentration, if the effective mass is known or, alternatively, of the effective mass, if the carrier concentration is known.
  \[ \varepsilon(\omega) = \varepsilon_{\infty} \left[ 1 - \frac{\omega_p^2}{\omega^2} \right] \]
  - According to this Drude model relation, for \( \omega > \omega_p \) (i.e., for shorter wavelengths or larger photon energies, beyond the singularity at \( \omega = \omega_p \)), the dielectric constant is real and positive, so the material is non-absorbing and transparent.
Drude Model

- In contrast, the Drude model says that for \( \omega < \omega_p \) (longer wavelengths or smaller energies), the dielectric constant is negative, corresponding to total internal reflection.
- In this ideal picture we would expect:
  
  ![Graph showing transmittance (T) versus energy (h\nu) with a horizontal line at 100% transmittance and a vertical line at \( \omega_p \) and \( E_G \).]

  - In reality we see:

Drude Model

- Valence electrons oscillating with respect to their atomic core charge constitutes another type of plasma, sometimes denoted as a valence electron plasma.
- However, the energy of this valence electron plasma is significantly larger (~15 eV) than for the free carrier plasma since valence band electrons are not screened from the core charge.
- This means that the relative dielectric constant and the effective mass is not present in the equation for the valence electron plasma frequency,
Optical Microscopy

- This is a technique that you will be familiar with.
- We magnify light to image a sample.
- Optical microscopy is useful for imaging feature sizes larger than \(~0.6-0.8\ \mu\text{m}\).
- Beyond that you will need to use surface techniques (AFM, SEM,...).
Resolution

- **Far-field optical imaging** involves a trade-off between resolution, as specified by a minimum distance between two resolvable points, $S$, as given by:

$$S = \frac{0.61\lambda}{n \sin \theta} = \frac{0.61\lambda}{NA}$$

- $2\theta$ is the acceptance angle and NA is the **Numerical Aperture** of the objective lens.

Depth of Field

- The depth of field $D$ is the distance along the optical axis in which the object is in focus. It is given by:

$$D = \frac{\sqrt{n^2 - NA^2} \lambda}{NA^2}$$

- $NA$ is a measure of the objective lens’ ability to collect diffracted light.
- Bigger is better, with an upper bound of $\sim 0.95$.
- Since both the resolution and depth-of-field depend inversely on $NA$, it is evident that image quality involves a trade off.
Resolution

- Returning to the far-field resolution equation:
  \[ S = \frac{0.61 \lambda}{n \sin \theta} \]

- There are three ways to improve resolution:
  - Reduce the wavelength.
  - Get a better lens, with a larger \( NA \).
  - Immerse the sample in a fluid to increase the index of refraction between the sample and the objective lens.

- The maximum magnification of an optical microscope is \(~750\times\).

Bright-Field Microscopy

- **Bright-field microscopy** involves vertical incident light.

- Horizontal features give maximum contrast.
**Dark-Field Microscopy**

- **Dark-field microscopy** refers to light incident from a shallow angle, nearly horizontal.

- Vertical features give maximum contrast.

- Thus, the contrast is inverse for bright and dark-field microscopy.

**Interference / Phase Contrast**

- **Phase-contrast microscopy** and interference microscopy involve phase shifting so that there is more constructive interference between reflected (transmitted) and diffracted optical beams and, hence, better visual contrast.

- The basic idea is that reflected (transmitted) and diffracted beams are out-of-phase, which means that they destructively interfere with one another.

- These techniques exploit the fact that light amplitude can be positive or negative.
Interference / Phase Contrast

- Until now we talked just about intensity \( I \) of light.
- But the wave has an amplitude, \( E \), which can be negative, positive (or complex).

\[ E(x, t) = A \cos[kx - \omega t - \theta] \]

- The intensity is the square of the amplitude

\[ I = |E^2| \]
Confocal Optical Microscopy

• Confocal Optical Microscopy involves sampling only a very small, submicron region of the sample at a time.

• A pinhole in front of the detector restricts light to a small sample region in a plane confocal to the pinhole.

• A laser is used for optical scanning across the horizontal plane.

Confocal Optical Microscopy

• Confocal Optical Microscopy involves sampling only a very small, submicron region of the sample at a time.

• Different planes are selected by mechanical repositioning.

• A computer is used to store each voxel of optical information and to then construct a 2D image of this essentially 3D information.
Near-field Optical Microscopy

- Near-field optical microscopy circumvents the normal resolution limit due to ‘far-field’ diffraction by putting the light source very near to the sample (nm).

- If the optical source aperture and the detection distance for reflected or transmitted light are both smaller than the wavelength of the light, resolution is determined by the aperture, size instead of the wavelength.

\[ D \approx \Delta x = \text{nm} \]

Ellipsometry
Polarization

- **Ellipsometry** involves a change of polarization of light as it is reflected off of a surface or interface.
- Light is a transverse electromagnetic wave whose time-varying electric \( E \) and magnetic \( B \) field vectors are perpendicular to the direction of propagation \( z \).

https://www.youtube.com/watch?v=BycPfKvItqg

Polarization

- We define the polarization by the direction of the electric field vector.
- Hence we do not need to picture the magnetic field component.

https://www.youtube.com/watch?v=BycPfKvItqg
Linear Polarization

- We consider the direction of the E-field as the polarization direction.
- Here we would say the polarization angle is 0°.

Angular Polarization

- Each photon has a polarization.
- We can add multiple beams together to create new polarization states.
- These two beams are in phase.
- Hence the resulting beam is also linearly polarized. Just at a different angle.
Circular Polarization
• We can instead combine two beams which are 90° out of phase.
• In this case the average $E$-field vector will not be at a fixed angle.
• It will rotate with time.
• This is called circularly polarized light.

https://www.youtube.com/watch?v=BycPkJRutqg

Elliptical Polarization
• If these two beams do not have the same amplitude, the light result will be elliptically polarized light.
• As you may have guessed from the name, Ellipsometry uses elliptically polarized light.

https://www.youtube.com/watch?v=BycPkJRutqg
Ellipsometry

- In ellipsometry, the polarization state of incident light is measured upon reflection from a substrate.
- The electric field vectors associated with the incident and reflected light are expressed in terms of components parallel and perpendicular to the plane of incidence (POI).

P-Polarized Light

- Light with its electric field vector parallel to the POI is described as \textbf{p-polarized}.
- We say the incident p-polarized light has an electric field strength of $E_{p}^{inc}$.
- We say the reflected p-polarized light has an electric field strength of $E_{p}^{ref}$.
S-Polarized Light

- Light with its electric field vector perpendicular to the POI is described as s-polarized.
- We say the incident s-polarized light has an electric field strength of $E_s^{inc}$.
- We say the reflected p-polarized light has an electric field strength of $E_s^{ref}$.

https://www.youtube.com/watch?v=BycPKfRutog

Reflection

- To carry out an ellipsometry measurement, we assume that p-polarized and s-polarized light reflect differently.
- We can define the following reflection coefficients:
  
  $R_p = \frac{E_p^{inc}}{E_p^{ref}}$  
  
  $R_s = \frac{E_s^{inc}}{E_s^{ref}}$

- The ratio of reflection coefficients is defined as $\rho$:
  
  $\rho = \frac{R_p}{R_s}$
Ellipsometry

• The ratio of reflection coefficients can also be defined by:

\[ \rho = \tan(\Psi)e^{i\Delta} \]

• The parameters \( \Psi (0° \leq \Psi \leq 90°) \) and \( \Delta (0° \leq \Delta \leq 90°) \) are called ellipsometric angles.

• We do not need to know the exact details for this course, but \( \Psi \) and \( \Delta \) are essentially the amplitude and phase polar form components of \( \rho \).

• It turns out that \( \Psi \) and \( \Delta \) are related to the index of refraction, extinction coefficient, and thicknesses of the layers of the sample being measured.

Ellipsometer

• The mathematic is very complicated, requiring numerical techniques.

• We will not discuss these details.

• But the information encapsulated in \( \rho \) can be used to obtain the thickness with the correct calibration and mathematical tools.
Ellipsometer

- The basic idea is to adjust the polarizer and compensator angles to provide elliptically polarized light to the sample which, upon reflection, becomes linearly polarized so that an appropriate analyzer angle minimizes the detector signal.
- More information is available when ellipsometry is accomplished at various angles and as a function of wavelength (spectroscopic ellipsometry).
- Ellipsometry is very sensitive, capable of detecting monolayer changes.

Transmission & Reflection Measurements
UV Vis Spectroscopy

- Optical transmission and reflection measurements are often used in electronic materials work.
- Often called ultraviolet-visible (UV-Vis) spectroscopy.
- Consider light impinging on a sample:

\[
\begin{align*}
\Delta n & \rightarrow \Delta \alpha
\\
I_i & \rightarrow I_t, I_r
\\
\text{Incident intensity} & \rightarrow \text{Reflected intensities}
\\
\text{Internal refractive index} & \rightarrow \text{External refractive index}
\\
\text{Multiple reflections} & \rightarrow \text{Attenuation coefficient}
\\
\text{Transmitted intensities} & \rightarrow \text{Thickness}
\\
ECE / ChE 613 – Electronic Materials Characterization
Spring 2018 - John Labram
\end{align*}
\]

UV Vis Spectroscopy

- Conservation of energy requires that:

\[
T + R + A = 1
\]

- \(T\) = transmittance.
- \(R\) = reflectance.
- \(A\) = absorbance.
- All of these normalized to the incident irradiation intensity, which is assumed to be equal to one.
Transmittance

- For normal incidence, the transmittance of a sample having identical front and back reflection coefficients is given by:

\[ T = \frac{(1 - R)^2 e^{-\alpha d}}{1 + R^2 e^{-2\alpha d} - 2Re^{-\alpha d} \cos \phi} \]

- Where:

\[ \phi = \frac{4\pi n_1 d}{\lambda} \]

Reflectance

- The reflectance is given by:

\[ R = \frac{(n_o - n_1)^2 + k^2}{(n_o + n_1)^2 + k^2} \]

- Be aware that depending on where your detector is, you may only be measuring specular reflectance.

  - Integrating spheres can measure diffuse reflectance.
UV Vis

• Normally in the lab we would just use a spectrophotometer and get out the results.

PDS

• Photo-Thermal Deflection Spectroscopy (PDS) is a technique to evaluate absorbance with extremely high resolution.
  • Absorption leads to small changes in temperature in the sample and a thermosensitive fluid.
  • This then leads to a change in deflection of a probe beam.
**Tauc Plots**

- Once you know $\alpha(\lambda)$ over a wavelength range including the bandgap of the material, you can estimate the bandgap.
- The usual approach is to plot $\alpha^{1/2}$ versus $h\nu$ (indirect bandgap) or $\alpha^2$ versus $h\nu$ (direct bandgap), and extrapolate a linear best-fit back to the $h\nu$ axis.

![Tauc Plots Graph](image)

**Quantization**

- UVVis spectroscopy can also be used to provide evidence of quantization.
- As samples become smaller, their band states will become quantized:
  
  $$E_n = E_{xy} + \frac{n^2h^2}{8m^*L^2}$$

- This will happen in both valence and conduction band.

![Quantization Graph](image)
Quantization

- The lowest energy transition will then increase with as quantization increases.

Next Time...

- Electron Beam Techniques
  - emission
    - AES
    - CL
    - EPMA
    - EBIC
  - absorption
  - reflection
    - SEM
    - LEED
    - RHEED
    - surface potential
    - voltage contrast
  - transmission
    - TEM
    - STEM
    - EELS