2A: Absorbing Materials
Pt-by-Pt and GenOsc

Nina Hong

U Penn, February 2014
Pt-by-Pt Fit

- UV Absorbing Films
- Point-by-Point Fit Procedure
- Different Fit Types
UV Absorbing Films

- Transparent films with onset of absorption in UV: \( \text{Si}_3\text{N}_4, \text{SiON, Resists, Organics, etc.} \)

Experimental Data
UV absorbing - Analysis Approach

- Fit $n,d$ in transparent region.
- **FIX** $d$ and fit $n,k$ in absorbing region.
Divide analysis into 2 parts:

- **Step 1: Transparent Region.**
  - Range select data where film is transparent \((k=0)\)
    - typically longer wavelengths.
  - Two unknowns \(\rightarrow n(\lambda) \& \text{thickness} \).
  - Two measured parameters \(\rightarrow \Psi(\lambda) \& \Delta(\lambda)\).
  - Cauchy fit \(n(\lambda) \& \text{thickness}\)

- **Step 2: Absorbing Region.**
  - Fix thickness from Step 1.
  - Fit \(n,k\) on a wavelength-by-wavelength basis.
Step 1: Cauchy fit

- Cauchy fit at long wavelengths determines thickness

![Graph showing Cauchy fit and extinction coefficient](image)

- **Cauchy only valid in transparent region**
Range Selecting Data

- User chooses angles, wavelengths and data types for fit

“Range Select” menu from Experimental Data window.

Choose Angles

Choose Wavelengths

Choose Data Types
Step 2: Point-by-Point Fit

- “Point by Point” fits data on a wvl-by-wvl basis.
  - Determines $n, k$ if thickness is correct from Step 1.
  - Start at longest wavelengths where $n$ is known from Cauchy fit and $k=0$.
  - Fit progresses to shorter wavelengths.
Set-Up for Point-by-Point Fit

1. Delete All Parameters

2. Turn on n and k (new fit parameters)
Point-by-Point Fit

Initial starting values.

Where to start the fit.

Previous points averaged together for next wavelength.

- \(\geq 1\) averages previous value(s)
- 0 ignores all previous values (uses current model values)
Advantages

- Small features in $n,k$ are identified.
- QUICK!
- EASY!
Point-by-Point Fit

- **Disadvantages**
  - Requires film to be transparent over some measured wavelengths.
  - Does not enforce Kramers-Kronig consistency (n,k may be unphysical).
  - Noise in $\Psi$, $\Delta$ is incorporated in n, k.
  - Requires accurate starting optical model.
    (*Hence, try to make accurate model for transparent region, account for microstructure if needed)
- **KK consistency can be checked with oscillator model or KK layer.**
Example 1 - Organic on Si

- Use Cauchy-Point by Point Fit procedure to determine optical constants over full spectral range.
Example 2-Organic on Si
Example 3-Organic on Si

(Use si_vuv.mat for substrate)

Fit longer wavelengths with Cauchy.
Fix Thickness and fit n,k using Point-by-Point method.

Save environment file for Example 3 (for later use)!

Are optical constants K-K consistent?
Data Fit Types

- All vary “fit” parameters to find best agreement with Experimental Data

**Normal Fit**
- Works with **ALL** selected data simultaneously.

**Point-by-Point Fit**
- Fit on **wavelength-by-wavelength** basis.

**Global Fit**
- Searches **Grid** of starting values.
“Normal” Fit

- Varies fit parameters to determine the minimum (BEST FIT)
- Fits to all data (all wavelengths, all angles) simultaneously.
- Starting values are important.

![Graph showing MSE vs. Thick.1 with starting point and local minima highlighted.](image)
Point-by-Point Fit

- Fits one wavelength at a time.
- Use in special cases
  - 2 unknowns per wavelength.
  - Fit parameters are wavelength dependent

THICKNESS IS NOT WAVELENGTH DEPENDENT!

Typical Use:
Fit n,k with all other parameters fixed at known values.
Point-by-Point Application

- Cauchy Fit to 3eV gives thickness and index.
- Cauchy doesn’t extend well to absorbing region.
- Normal fit for n,k

- Normal Fit can easily get lost if material n,k are far away from Cauchy “starting point”.

---

©2014 J.A. Woollam Co., Inc.  www.jawoollam.com

19
Point-by-Point Fit!

- Uses previous answer as good "starting point" for next wavelength.

starting $n,k$

PBP Fit Result
Finding the best MSE

![Graph showing MSE vs. film thickness and photon energy. The graph indicates "local" minima and a "global" minimum.](image)

- Film Thickness (mm)
- MSE
- "local" minima
- "global" minimum
- Photon Energy (eV)
- \(\psi\) in degrees
- Model Fit
- Exp E 40°
- Exp E 75°
How to get good start values?

- **Global fit** – Searches a ‘grid’ of starting points for the best match
  - Each parameter has multiple start values in a wide range

- Useful to avoid local MSE minimums
  - New users
  - Complicated models with many parameters
  - Thick films
Global Fit in WVASE

- Check parameter “fit box” in model layer.
  - Actual values of fit parameters do not matter.
- Click “Edit Parms” from “Fit” Window.
1. Highlight a fit parameter
2. Set minimum, maximum and number of guesses
3. “Change Parm Coupling” to update the changes
4. Repeat until all fit parameters have defined ranges and number of guesses
5. Perform “global” fit
Global Fit Guidelines

- Use ~50 guesses per 1 micron thickness range
- Use ~10-20 guesses for Index range of 1 (An)
- Use ~ 5 guesses for Non-ideality
- Avoid global fitting dispersion (Bn, Cn)
- Keep total number of guesses under 5000
- Reduce Wavelengths and Angles to improve speed.

- NOTE: parameter limits will remain for Normal Fit unless adjusted.
GenOsc Outline

- Why use Oscillator models?
- What are Oscillator models?
  - Oscillating systems & resonant frequencies.
  - Kramers-Kronig consistency

- How to use Oscillator models?
  - WVASE Generalized oscillator ("Genosc") layer.
  - Fitting GenOsc models to Reference material file.
  - Using GenOsc to fit real data (Afternoon Session 3B).
Why Use Oscillator Models?

- To check optical constants!

- Are both correct? How to decide?

- Cuves must be physically reasonable:
  
  **Kramers-Kronig Consistency!**
Oscillator models are described as dispersion equations.

Advantages:
- Reduces # of “fit” parameters
  - Fewer parameters in the model.
- Flexible for similar samples.
  - Can be saved on disk and used for later samples.
- Maintains/enforces K-K consistency.
The Dielectric Function $\varepsilon(\omega)$

- The Dielectric Function $\varepsilon(E)$ or $\varepsilon(\omega)$, is the Dielectric Polarization as a function of Energy (or Frequency).

- Regions of transparency, and regions of absorption.

- Where do these features come from?

- Why do we model these with Oscillator functions?
Optical Absorption

Absorptions in the various spectral regions have different shapes & root causes.

- Electronic Transitions
- Molecular Vibrations
- Lattice Vibrations
- Free-carriers

![Graph showing photon energy vs. index of refraction for Lattice Vibrations, Transparent, and Electronic Transitions. The graph indicates transitions from UV to IR with peaks for Rutile TiO₂.]
Dielectric Polarization

- Internal E-field’s response to externally applied E-Field.
  - Different atoms/molecules/crystal structures have different dielectric polarizability.

Single atom example

<table>
<thead>
<tr>
<th>No E-field</th>
<th>External E-field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleus</td>
<td>Dipole Moment</td>
</tr>
<tr>
<td>Electron</td>
<td></td>
</tr>
<tr>
<td>cloud</td>
<td></td>
</tr>
</tbody>
</table>

Molecular example

<table>
<thead>
<tr>
<th>Molecule (with Charge separation)</th>
<th>External E-field</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Change in separation</td>
</tr>
<tr>
<td></td>
<td>= change in Dipole Moment</td>
</tr>
</tbody>
</table>

Material

\[
E_{\text{total (in the material)}} = E_{\text{external}} + D
\]

\[
\varepsilon_p = \frac{D}{E} \quad \varepsilon_p = \varepsilon \cdot \varepsilon_o
\]
Oscillating Systems

- **Light is an oscillating wave**: Alternates positive and negative.
- Absorptions due to different mechanisms can be described by oscillators.

Photon In = Oscillating electron cloud.

### Oscillating systems:
- Have \((\omega_0)\) natural frequency of vibration
- A driving force \((F)\) causes oscillations at same frequency
- Oscillator amplitude & phase are usually different than driving force \(F\)

\[
F = A_f \cos(\omega t)
\]

\[
X_r = A_r \cos(\omega t + \delta_r)
\]

\(r = \text{response}\)
Complex Representation of Oscillator

- **Amplitude & Phase** become "Real" & "Imaginary" curves.
  - Amplitude affects peak height. Maximum at $\omega_0$
  - Phase lag $>90^\circ \rightarrow \text{Re}\{X_r\}$ becomes negative
  - More damping (energy absorption) $\rightarrow$ wider $\text{Im}\{X_r\}$

**Instead of**

\[ X_r = A \cos(\omega t + \delta) \]

**We use**

\[ \hat{X}_r = A_r e^{\delta} e^{i\omega t} \]

**To convert back to Real time response**

\[ X_r = \text{Re}\left(\hat{X}_r\right) \]

$r = \text{response}$

**Time dependent term is usually left off**

\[ \hat{X}_r = \text{Re}\{X_r\} + i \text{Im}\{X_r\} \]

\[ = A(\cos \delta + i \sin \delta) e^{i\omega t} \]
Kramers-Kronig Relation

- Real and imaginary parts depend on each other.
- Optical constants **must** satisfy KK-relation to be physical.
- “Bumps make wiggles”, the shape of n & k curves are related.

\[
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'
\]

\[
\varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'
\]

*P* means “principal part”

Integral equation ties area under $\varepsilon_2$ to shape of $\varepsilon_1$ and vice-versa
Ensemble model: Multiple Absorptions

- Optical constants can be modeled as a summation or “ensemble” of various kinds of oscillator functions.
  - Multiple electronic transitions.
  - Sum of oscillators used.
  - Remains KK-consistent.

![Graph showing real and imaginary parts of the dielectric constant for GaAs](image)
Break!!
GenOsc Outline

- Why use Oscillator models?
- What are Oscillator models?
  - Oscillating systems & resonant frequencies.
  - Kramers-Kronig consistency

- How to use Oscillator models?
  - WVASE Generalized oscillator ("Genosc") layer.
  - Fitting GenOsc models to Reference material file.
  - Using GenOsc to fit real data (Afternoon Session 3B).
WVASE Layer “Genosc.mat”

- Oscillator functions that describe $e_1$ & $e_2$ ($n$ & $k$).
- KK-consistent!
Genosc: Transparent Reference Spectra

Load Reference

Absorbing

Add oscillators and fit to match $\varepsilon_2$ (only)

Match $\varepsilon_1$ (only) with offset and poles

Good Fit?

Transparent
Transparent: Sellmeier Model

- Describe \( n(\lambda) \) of transparent materials.

\[
\varepsilon_1 = n^2 = A + \sum_j \frac{B_j \lambda^2}{\lambda^2 - \lambda_0^2_j}, \varepsilon_2 = k = 0
\]

- Kramers - Kronig consistent
Transparent: Sellmeier “Poles”

- Adds dispersion (curvature) to both ends

Absorptions must be outside of spectral range

- Easier to use photon energy scale when describing oscillators…curves are symmetric.
Genosc Window: $\varepsilon_1$ Section

- "Poles" and "$\varepsilon_1$ offset" used to match $\varepsilon_1$ shape.
Genosc Modeling: Transparent Films

1. Fit Pole #1 Amplitude
2. Add Pole #1 Position
3. Add e1 offset.
4. Add Pole #2 Amplitude
   - (should stay zero or very small)
   - (Keep if improves fit, but remove if MSE stays the same or fit goes unphysical.)
Varying Pole Magnitude

- Adjusting $e_1$ offset moves curve up and down.
- Pole 1 adds upward curvature, pole 2 downward.
Example 4-SiO2.mat

- You can open “mat” files in any models.
- Use Examples 4-SiO2.mat file as reference material in GenOsc.

Fit with Genosc.mat.
Fit Pole #1, Pole #2, and e1 offset.
Fitting Transparent Reference Materials: SiO$_2$ example

1) Load **SiO2.mat** as reference material.
2) Select **Fit e1 only**.
3) Note shape of green $\varepsilon_1$ curve:
   - Dispersion upturn at hi-eV. “Pole #1”.
   - Small Dispersion downturn at low eV. “Pole #2”.
Fitting Transparent Reference Material
SiO$_2$ example (part 1)

1) Enter different values in **Pole#1 Position(eV) & Magnitude**
   - Observe how these values change curvature of model $\varepsilon_1$ (black curve).

2) Enter different values for **e1 Offset**
   - Observe how this value changes the model’s $\varepsilon_1$ constant offset.
Fitting Transparent Reference Material
SiO$_2$ example (part 2)

1) Enter small values (<0.5) into Pole#2 Magnitude
   - (do not change Position value from 0.001eV)
   - Note how different values change curvature of model $\varepsilon_1$ curve (black curve) downward at low energies.
Fitting Transparent Reference Material: SiO₂ example (part 3)

1) **Approximate** the **green reference curve** by entering appropriate values in the **Pole#1, Pole#2, & e1 Offset** quantities.

2) **Check** **Pole#1 Position & Magnitude, Pole#2 Magnitude, & e1 Offset** as fit parameters.

3) **Click Fit Osc. to Ref.** button to start fit
   - Final fit should look something like figure below.
Sellmeier: General Guidelines

- Do not fit Position of pole if Amplitude = 0.
- Do not fit Position of Pole#2.
- Pole#1 and e1-offset often correlated
  - Both increase index, but Pole#1 Amplitude also adds curvature (dispersion).
  - Often possible to fix either pole 1 position or pole 1 magnitude.
More Transparent mat files

- Example 5-Al2O3.mat
- Example_6-CaF2.mat
- Example_7-f3_Schott.mat

(from 0.6 to 3.7 ev)

Fit Pole #1, Pole #2, and e1 offset.
UV-Absorbing Reference Materials

Load Reference

Absorbing

Add oscillators and fit to match \( \varepsilon_2 \) (only)

Transparent

Match \( \varepsilon_1 \) (only) with offset and poles

Good Fit?
Types of Absorption, Types of Oscillators

Different oscillators used for different absorptions.
Absorption features & Suggested oscillators:

- **Organics and Dielectrics**: UV Resonant Absorptions.
  - Gaussian, Tauc-Lorentz, Cody-Lorentz.

- **Metals**: Free electron absorption.
  - Drude or Lorentz oscillator functions.

- **Semiconductors**: Electronic Transitions.
  - Direct Bandgap: Psemi-E0
  - Indirect Gap / Amorphous: Tauc-Lorentz or Cody-Lorentz.
  - Higher Energy Transitions: Gaussian or PSEMI.
Lorentz Oscillator

- "Classic" response function derived in textbooks.
- Has long absorption tails, can cause unwanted absorption in transparent regions.
- Works best for metals (where absorption exists over all wavelengths).
- Also works well for IR phonons (crystal lattice vibrations).

\[ \tilde{\varepsilon} = \frac{A}{E_0^2 - E^2 - i\gamma E} \]

All oscillators have Amplitude (A), Position (E₀), and width (γ).
Drude Model: Lorentz Oscillator for Metals

- Lorentz oscillator with $E_0 = 0$.

- Describes free carriers because no restoring force (set $E_0 = 0$ in Lorentz).

- Use for Metals, doped semiconductors, and conductive dielectrics.

- Optical method for Non-contact measurement of resistivity (conductivity).

\[
\tilde{\varepsilon} = - \frac{A}{E^2 + i\gamma E}
\]
Gaussian Oscillator

- Shorter absorption tails than Lorentz.
  - Absorption drops rapidly to 0.
- Use for:
  - Materials which become transparent at longer wavelengths.
  - Multiple UV absorptions in amorphous materials.
  - Infrared absorptions in amorphous materials.

\[
\varepsilon_2 = A_n e^{-\left(\frac{E - E_n}{B r_n}\right)^2} + A_n e^{-\left(\frac{E + E_n}{B r_n}\right)^2}
\]

\[
\varepsilon_1 = \frac{2}{\pi} P \int_{R_s}^{\infty} \frac{\xi \varepsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi
\]
Tauc-Lorentz Model

- Includes band-gap energy ($E_g$), with NO absorption allowed below gap Energy. Goes exactly to zero.

- Good for amorphous semiconductors & other UV absorptions. Asymmetric shape is more accurate for amorphous materials.

Cody-Lorentz Model

- Ferlauto & Collins (2002).
  - Includes band-gap $E_g$,
    - NO absorption allowed below gap energy.
    - Goes exactly to zero.

- Adds extra flexibility to fit shape of absorption edge.
  - Extra fit term $E_p$
  - Urbach tail function also incorporated for defect absorption.

- Asymmetric shape is more accurate for amorphous materials.

**ε₂ Section: Oscillator Types**

- Choose oscillator ‘Type’ and ‘Style’, then Add oscillator.

- Use to describe ε₂ shape of material.

- Add/Delete Oscillator(s).

- Osc Up/Down buttons.
Section: Oscillator List

- Details of entire oscillator collection.
- Can adjust or fit each parameter.

Oscillator Parameters:

<table>
<thead>
<tr>
<th>Active</th>
<th>Type: T-L: Tauc-Lorentz</th>
<th>Style: eV, Tauc-Lorentz(A,E,C,Eg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amp</td>
<td>En</td>
<td>C</td>
</tr>
<tr>
<td>80</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

*New Osc: Drd.0, Amp=2, Br=0.2
*1: T-L.0, Amp=80, En=4, C=1, Eg=3.5
*2: Gau.0, Amp=1, En=5, Br=0.2
*3: Gau.0, Amp=2.546, En=6.1, Br=0.1
*4: Drd.0, Amp=2, Br=0.5
“Build Genosc” Feature

- Reference materials are often helpful in building Genosc
- References can come from
  - Publications
  - tabulated optical constants data base
  - Similar material
  - Pt by pt fit results
Display Window

- Displays $\varepsilon_2$ and $\varepsilon_1^*$, of model (Black curves).
- Displays Reference Material (if present) $\varepsilon_2$ (in red) and $\varepsilon_1^*$ (in green),
- Displays $\varepsilon_2$ (in blue) of currently highlighted oscillator.

Dielectric Function Display Window:
Example 8-SiNx pbp.mat

- Fit with Genosc.mat.
- Fit Tauc-Lorentz Oscillator for absorption.
- Fit Pole #1, Pole #2, and e1 offset for index.
Fitting UV-Absorbing Reference Material
Silicon Nitride example

1) Load **Demo_2_sinx pbp.mat** as reference material
2) Select **Fit e2 only** (we are going to fit e2 first, then e1).
3) Note **red** $\varepsilon_2$ curve looks like a **Tauc-Lorentz** shape.
Fitting UV-Absorbing Reference Material
Adding Oscillators

1) Select Tauc-Lorentz as oscillator type and add Tauc-Lorentz oscillator
   - Enter the approximate broadening prior to Adding Oscillator ($\approx 4\text{ eV}$)
   - The Eg value might need to be manually set to the right value ($\approx 3\text{ eV}$ in this case).

2) Change oscillator parameters until an approximate fit is achieved (see figure at right).
Fitting UV-Absorbing Reference Material
Preparation before Reference $\varepsilon_2$ fit

3) Check all four fit parameters for Tauc-Lorentz oscillator.
4) Prior to fitting, the GenOsc window should look similar to figure below.
Fitting UV-Absorbing Reference Material
Silicon Nitride example, $\varepsilon_2$ fit to Ref.

5) Click on Fit Osc. to Ref. window & fit Ref. Mat.
6) After fit, the GenOsc window should look similar to below.
Fitting UV-Absorbing Reference Material
Silicon Nitride example, $\varepsilon_1$ fit preparation

7) Select “e1 Offset” as fit parameter & “Fit e1 only” button

8) With e1 Offset = 1.5, window should look similar to below.
Fitting UV-Absorbing Reference Material

Silicon Nitride example, after $\varepsilon_1$ & $\varepsilon_2$ fit

9) Click on Fit Osc. to Ref. window & fit Ref. Mat. (NOTE: fitting $\varepsilon_1$ only)

10) After fit, window should look similar to figure below.

11) Observe post-fit $\varepsilon_1$ Offset & Tauc-Lorentz values.
Genosc fit UV Absorbing Materials

- “Example 9-a-si.mat”
- “Example 10-SiON.mat”
  - NEEDS TWO OSCILLATORS!!
GenOsc Summary: Fitting Reference Spectra

Load Reference

Absorbing

Add oscillators and fit to match $\varepsilon_2$ (only)

Match $\varepsilon_1$ (only) with $E_{\text{inf}}$ and Poles

Transparent

Genosc.mat layer useful for both transparent and absorbing materials.
Summary

1. Data Analysis Strategy for UV absorbing Films
2. Pt-by-Pt Fit Procedure
3. Understand oscillating systems.
   – Mass on spring, etc. Resonant frequency, Amplitude, etc.
4. Optical absorption as oscillators:
   – Light interacts with electrons.
5. Optical Dispersion Functions: “Oscillator Models”
   – Lorentz, Gaussian, Tauc-Lorentz, Drude…many types available.
6. Fitting reference data sets.
   – Used WVASE32 Genosc layer to fit functions to reference values.
Lunch!!