Introduction into Spectroscopic Ellipsometry – Basics, Data Interpretation Considerations and Applications to Photovoltaics

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University of Twente, February 11th 2010
Outline

Part 1: Theory and Fundamentals
- What is Ellipsometry?
- Light and Polarization
- Measurements
- Optical Constants
- Models and Data Interpretation

Part 2: PV Applications
- SiNx AR coatings
- Amorphous, microcrystalline, and poly-Si films
- Transparent Conductive Oxides
- CdTe and CdS
- CIGS
- Organic PV layers
Theory & Fundamentals

- Light
- Materials (optical constants)
- Interaction between light and materials
- Ellipsometry Measurements
- Data Analysis
Electromagnetic Plane Wave

- From Maxwell’s equations we can describe a plane wave

\[ E(z, t) = E_0 \sin \left( -\frac{2\pi}{\lambda} (z - vt) + \xi \right) \]

- Amplitude
- Wavelength
- Velocity
- Arbitrary phase
- Electric field \( E(z,t) \)
- Magnetic field \( B(z,t) \)
- Direction of propagation
Intensity and Polarization

- Intensity = “Size” of Electric field. \( I \propto E^2 \)

- Polarization = “Shape” of Electric field travel.
What is Polarization?

- Describes how Electric Field travels through space and time.
What are Optical Constants?

Describe how materials and light interact.

\( n \) = “refractive index”
- phase velocity = \( c/n \)
- direction of propagation (refraction)

\( k \) = “extinction coefficient”
- Loss of wave energy to the material

Together “Complex Refractive Index”: \( \tilde{n} = n + ik \)

or “Complex Dielectric Function”: \( \tilde{\epsilon} = \epsilon_1 + i\epsilon_2 \)

\( \tilde{\epsilon} = \tilde{n}^2 \)
Kramers-Kronig Relation

- Real and imaginary parts depend on each other.

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

- Bumps make wiggles.
- Transparent range: Index increases for shorter wavelengths – **normal dispersion**
- When absorption increases, index will “turn” and decrease with decreasing wavelength - **anormal dispersion**
Absorbing region

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

- Electronic Transitions
- Molecular Vibrations
- Lattice Vibrations
- Free-carriers
Polarized light at interface

- Electric field either parallel (p) or perpendicular (s) to plane of incidence.
- Material differentiates between p- and s- light
Fresnel Coefficients

- Describes reflection and transmission
- Depends on angle and polarization ($p$ or $s$)

\[
\begin{align*}
  r_s &= \left( \frac{E_{0r}}{E_{0i}} \right)_s = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} \\
  t_s &= \left( \frac{E_{0t}}{E_{0i}} \right)_s = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t} \\
  r_p &= \left( \frac{E_{0r}}{E_{0i}} \right)_p = \frac{n_t \cos \theta_i - n_i \cos \theta_t}{n_i \cos \theta_t + n_t \cos \theta_i} \\
  t_p &= \left( \frac{E_{0t}}{E_{0i}} \right)_p = \frac{2n_i \cos \theta_i}{n_i \cos \theta_t + n_t \cos \theta_i}
\end{align*}
\]
Multiple reflections in single film lead to an infinite series

\[ r_{tot} = r_{01} + t_{01} r_{12} t_{10} e^{-2i\beta} + t_{01} r_{12}^2 r_{10} t_{10} e^{-4i\beta} + \ldots \]

\[ r_{tot(p,s)} = \frac{r_{01(p,s)} + r_{12(p,s)} t_{01(p,s)} t_{10(p,s)} e^{-i2\beta}}{1 - r_{01(p,s)} r_{12(p,s)} e^{-i2\beta}} \]

**FILM PHASE THICKNESS**

\[ \beta = 2\pi \left( \frac{d_1}{\lambda} \right) n_1 \cos \theta_1 \]
What is Ellipsometry?

- Measures change in polarization of reflected light.
- Sample is defined by reflection of p- and s- polarized light.

\[
\begin{pmatrix}
E_{p}^{\text{out}} \\
E_{s}^{\text{out}}
\end{pmatrix} = \begin{pmatrix}
\tilde{r}_{p} & 0 \\
0 & \tilde{r}_{s}
\end{pmatrix}
\begin{pmatrix}
E_{p}^{\text{in}} \\
E_{s}^{\text{in}}
\end{pmatrix}
\]

\[
\frac{E_{p}^{\text{out}}}{E_{p}^{\text{in}}} = \frac{\tilde{r}_{p}}{r_{p}} = e^{i(\delta_{p} - \delta_{s})} = \tan(\Psi)e^{i\Delta} = \rho
\]

\[
\tan(\Psi) = \frac{|r_{p}|}{|r_{s}|}
\]

\[
\Delta = \delta_{p} - \delta_{s}
\]
What can SE determine?

Ellipsometry Measures:

Psi (Ψ)
Delta (Δ)

Properties of Interest:

Film Thickness
Refractive Index
Surface Roughness
Interfacial Mixing
Composition
Crystallinity
Anisotropy
Uniformity
Data Analysis Flowchart

Measurement → Model → Fit → Results

Exp. Data
n, k
n
n-1
1
0

Gen. Data

Compare

Fit Parameters

n, k
Thickness Roughness Uniformity
Ellipsometry Advantages

• Repeatable & accurate:
  – Self-referencing, measures ratio of $E_p/E_s$. Thus, reduced problems with:
    • fluctuation of source intensity
    • light beam spilling over small samples
• Measure two parameters
  – $\Psi$ and $\Delta$ at each wavelength/angle combination.
  – increased sensitivity to multiple film parameters
Ellipsometry vs. Reflectometry

- Phase information gives Ellipsometry higher sensitivity to very thin films.
Thin Film Interference

- Each reflected wave will have a different phase and amplitude.
- Coherent waves (same freq. and direction) combine constructively/destructively.
Motivation

- Data Interpretation:
  - Estimate sample based on “raw” data.
  - Reduce analysis time and improve ability to identify correct models.

![Experimental Data](Image)

**Data interpretation not quantitative**
Role of Optical Constants

- Index difference leads to reflection
  - Large $\Delta N$ ➔ Large Reflection
  - Small $\Delta N$ ➔ Small Reflection

<table>
<thead>
<tr>
<th>Material 1</th>
<th>Material 2</th>
<th>Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (N=1)</td>
<td>SiO$_2$ (N=1.5)</td>
<td>~3.3%</td>
</tr>
<tr>
<td>Air (N=1)</td>
<td>Si (N=3.5)</td>
<td>~31%</td>
</tr>
<tr>
<td>a-Si (N=3.4)</td>
<td>Si (N=3.5)</td>
<td>~0.02%</td>
</tr>
</tbody>
</table>
Bare Substrates

- What do we expect?
  - Psi features follow optical constant structure.
  - Psi curves minimize at Brewster condition, but remain higher when absorbing.
  - Delta at 180° or 0°, except when absorbing or in presence of surface film.
Substrate Optical Constants

- **Semiconductors**
  - Silicon

- **Dielectrics**
  - SiO₂
  - Si₃N₄

- **Metals**
  - Aluminum
Dielectrics

- Psi flat and smooth
- Delta = 0°, 180° - except for surface films

0.5nm roughness
Semiconductors

- Psi follows shape of absorption
- Delta between 0° or 180° when absorbing
Metals

- Significant absorption:
  - Psi stays near 45°, Delta away from 0° or 180°.
“Pseudo Optical Constants”

- $<n> & <k>$ or $<\varepsilon_1> & <\varepsilon_2>$

  ➢ Assumption: Optically thick bulk substrate with no surface layers or roughness

$$\langle \varepsilon \rangle = \langle \tilde{n} \rangle^2 = \sin^2(\phi) \cdot \left[ 1 + \tan^2(\phi) \cdot \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right]$$

  where,

  $\rho = \tan \Psi \ e^{i\Delta}$

  $\phi = \text{AOI}$

![Graphs showing Psi, Delta, and other parameters vs. Wavelength (nm)]
“Pseudo Optical Constants”

- Angle independent way of viewing experimental data.

⇒ All angles give same values implies:
  Light path is same
  Optically thick bulk substrate
  No film (or very thin surface layer)
Thin Films

- “Very Thin” \[\Rightarrow\] thickness < 100 Å
- determining thickness when OC’s are known
  - SE deals with this well
- determining OC’s
  - very difficult, if not impossible
Determining Thickness

- mainly Delta (Phase) is sensitive to very thin films
  - 20, 40, 65, 80, 100 Å
Very Thin Film Index?

- Correlation prevents exact determination, beyond whether higher or lower than substrate index.
Transparent Films

- Thicker films produce more interference oscillations.

500nm

100nm Oxide

5 micron Oxide
Thicknes Effects

- As thickness increases:
  * Interference shifts to red
  * Peaks closer together
Transparent Films

- Dispersion Relationship, such as Cauchy, can be used to reduce the number of “fit” parameters.

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]

\[ k(\lambda) = 0 \]
Amplitude (An)

- Adjust the An parameter to the approximate index.

\[ n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \]

An = 2.50  
An = 2.25  
An = 2.00  
An = 1.75  
An = 1.50
• **Bn & Cn** provide curvature versus wavelength.

\[ n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \]

- \( Bn = -0.01 \)
- \( Bn = 0.020 \)
- \( Bn = 0.010 \)
- \( Bn = 0.005 \)
- \( Bn = 0.000 \)
Effect of Film Index

Index difference affects oscillations (75° AOI)

$n=1.5$
$n=1.75$
$n=2.0$
$n=2.25$
$n=2.5$
$n=2.75$
$n=3.0$
$n=3.25$
$n=3.5$
$n=3.75$
$n=4.0$
Effects of Dispersion

- Oscillations are primarily due to thickness. Dispersion will affect oscillation position and amplitude slightly.

<table>
<thead>
<tr>
<th></th>
<th>n=2</th>
<th>500 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>n=4</td>
<td>1 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>user</th>
<th>500 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>n=4</td>
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---

No Dispersion

With Dispersion in Film
Multilayers- Envelope

- Oscillations for multilayers is a combination of each film envelope.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>nitride</td>
</tr>
<tr>
<td>1</td>
<td>oxide</td>
</tr>
<tr>
<td>0</td>
<td>substrate</td>
</tr>
</tbody>
</table>

$\Psi$ in degrees

![Graph showing oscillations for multilayers with different layers and thicknesses.](image)
Both oscillation patterns are superimposed!

<table>
<thead>
<tr>
<th>n</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>200 nm</td>
</tr>
<tr>
<td>3</td>
<td>1000 nm</td>
</tr>
<tr>
<td>4</td>
<td>1 mm</td>
</tr>
</tbody>
</table>
Absorbing Thin Film

- If light is absorbed before returning to surface, only top reflection is ‘seen’ (Film appears as Substrate)
Multilayer (Absorbing-Transparent)

- If 2-layer, but 1 is absorbing, then:

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>a-si</td>
<td>300</td>
</tr>
<tr>
<td>1</td>
<td>sio2</td>
<td>3000</td>
</tr>
<tr>
<td>0</td>
<td>si</td>
<td>1 mm</td>
</tr>
</tbody>
</table>

- For 2-layer, but 1 is absorbing:

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<tbody>
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<td>sio2</td>
<td>3000</td>
</tr>
<tr>
<td>1</td>
<td>a-si</td>
<td>300</td>
</tr>
<tr>
<td>0</td>
<td>si</td>
<td>1 mm</td>
</tr>
</tbody>
</table>

Generated Data

- W in degrees vs. Wavelength (nm)
- psi in degrees vs. Wavelength (nm)
PV Applications

- SE is applied to most PV thin films:
  - SiN$_x$ AR coatings
  - Amorphous, microcrystalline, and poly-Si films
  - Transparent Conductive Oxides
  - CdTe and CdS
  - CIGS
  - Organic PV layers
  - …
Ellipsometric study of Photovoltaics

• Measurement challenges:
  – Textured/ Rough surface
  – Low reflection
  – Large samples
  – Industrial integration

• Modeling considerations:
  – Rough surfaces, Rough interfaces, Rough substrates
  – Parameter correlation

• Applications
Textured Si coated with SiN$_y$

<table>
<thead>
<tr>
<th>Wafer treatment</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished, c-Si</td>
<td>Smooth</td>
</tr>
<tr>
<td>Alkaline etched, c-Si</td>
<td></td>
</tr>
<tr>
<td>Alkaline etched, multi c-Si</td>
<td></td>
</tr>
<tr>
<td>Acid etched, multi c-Si</td>
<td></td>
</tr>
<tr>
<td>As-cut, multi c-Si</td>
<td></td>
</tr>
</tbody>
</table>

Measurement Challenge:
Textured surface
High scattering
Specular R ~ 0

Solution:
Sample tilting mount
Improved light source and detection system
Including scattering factor

Textured Si Wafer

M-2000X with Intensity Optimizer

![Graph showing standard measurement and special geometry](image)

![Image of M-2000X with Intensity Optimizer](image)
Large Area Mapping

ACCUMAP-SE

Flying-SE

p-layer Si Film Thickness

- 130Å
- 120Å
- 110Å
- 100Å
- 90Å
- 80Å
- 70Å

X (cm)

Y (cm)
Modeling Considerations

- Modeling considerations for PV thin films:
  - SiN_x AR coatings
  - Amorphous, microcrystalline, and poly-Si films
  - Transparent Conductive Oxides
  - CdTe and CdS
  - CIGS
  - Organic PV layers

  Rough surfaces, Rough interfaces, Rough substrates, High absorption, Grading, Anisotropy, Superstrates, Complex sample structure, Parameter correlation, ..
Thin Film Interference

\[\Psi \text{ in degrees} \]

Photon Energy (eV)

- **Transparent-oscillations**
- **Absorbing-oscillation suppressed**
- **Rough Surface – shifts in data**
Thickness determination - UV/VIS

- Difficult in UV/Visible range due to high absorption/surface roughness
Thickness determination
- Near Infrared (NIR) or Infrared (IR)

**UV–VIS - NIR**

- Index of refraction, $n$
- Extinction coefficient, $k$

**Transparent region in NIR/IR spectra**

easy to get thickness!
Modeling of Rough Surfaces

- Bruggeman Effective Medium Approximation (EMA)
  - Mix the optical constants of surface layer with void
SiNₓ AntiReflection Coatings

SiNₓ Optical Constants

Index of Refraction, $n$
Extinction Coefficient, $k$

Wavelength (nm) vs. $\Psi$ in degrees
Wavelength (nm) vs. $\Delta$ in degrees

Layer #2 = PV-SIN-Tauc-Lorentz  Thickness #2 = 70.50 nm (fit)
Layer #1 = NTVE_JAW  Native Oxide = 1.00 nm
Substrate = SI_JAW
With Scattering Factor

<table>
<thead>
<tr>
<th>Layer</th>
<th>Formula</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>sin-tauc lorentz</td>
<td>70.500 nm</td>
</tr>
<tr>
<td>0</td>
<td>ema si_jaw/23% void</td>
<td>1 mm</td>
</tr>
</tbody>
</table>
Amorphous, Microcrystalline, and Poly-Crystalline Silicon

For high crystalline %, the peak is narrower and eventually separates into two distinct regions.
Transparent Conductive Oxides

- **TEC-15 Glass**
  - Characterize Multi-Layer TCO structure
  - TCO intentionally rough - hazy for light trapping

![Diagram of TCO structure](image-url)

SnO$_2$:F

- 320nm

SiO$_2$

- 23nm

SnO$_2$

- 30nm

Glass Substrate

![Graph of wavelength vs. Δ and Ψ](image-url)
Indium Tin Oxide

- NIR absorption used to monitor conductivity
CdTe / CdS on Tec-15 Glass

CdTe  1458nm
CdS   210nm
Tec-15 Glass

CdTe –SEM micrograph-
Courtesy: Nicola Romeo, University of Parma, INFIM, & ARENDI S.p.A. IMRC 2008
CdTe and CdS Films

- Measure optical constants with changing morphology and process conditions.
Organic Solar Cells

- Measurement similar to OLED
- Films may exhibit anisotropy
- SE + Transmission fit, OLED film
Organic Solar Cell Materials

- PEDOT:PSS
- Multi-Sample fit:
Organic Solar Cell Materials

- P3HT / 300nm SiO2 / Si
- Multi-Sample fit:
PV Summary

- **SE has many uses toward PV thin films:**
  - $\text{SiN}_x$ AR coatings
  - Amorphous, microcrystalline, and poly-Si films
  - Transparent Conductive Oxides
  - CdTe and CdS
  - CIGS
  - Organic PV layers
  - ...
Further References on Ellipsometry


ICSE Conference Proceedings: