Precision Measurements of Optical Constants using Spectroscopic Ellipsometry

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NSF: DMR-11104934
AFOSR: FA9550-13-1-0022
Flat & uniform films, at least 5 by 5 mm², low surface roughness, films on single-side polished substrate
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http://ellipsometry.nmsu.edu

Graduate Students:
Lina Abdallah, Travis Willett-Cies, Nalin Fernando, Tarek Tawalbeh (Theory)

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Cesar Rodriguez, Nathan Nunley, Khadijah Mitchell, Cayla Nelson, Laura Pineda, Eric DeLong
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Collaborators:
Igal Brener (CINT), Neha Singh, Harland Tompkins (J.A. Woollam Co.), S.G. Choi (NREL)

Samples: Demkov (UT Austin), Alpay (UConn), MTI (LAO), SurfaceNet (NiO)
Key HW accomplishments for smart phones

1. **Power amplifier:**
   InGaP Heterojunction bipolar transistor (HBT)

2. **Low-noise amplifier:**
   Silicon-germanium-carbon HBT

3. **New CMOS materials:**
   Advanced substrate materials (SOI)
   High-k (complex metal oxide) gate dielectrics
   Metal gate
   Si-Ge-C source-drain stressors
   Laser annealing
   Nickel silicide Ohmic contacts
   Copper interconnects
   Low-k interlayer dielectrics

4. **Power, analog, passives**
Why Ellipsometry: InGaP HBT

• How thick is my film?

Table 2. Doping and layer content profile of a typical InGaP double heterojunction bipolar transistor (DHBT). Compare Ref. [28]. See also Ref. [42].

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Doping</th>
<th>Concentration (cm(^{-3}))</th>
<th>Thickness (nm)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>InGaAs</td>
<td>n+</td>
<td>&gt;10(^{19})</td>
<td>100</td>
<td>emitter contact</td>
</tr>
<tr>
<td>10</td>
<td>GaAs</td>
<td>n+</td>
<td>5×10(^{18})</td>
<td>120</td>
<td>contact buffer layer</td>
</tr>
<tr>
<td>9</td>
<td>InGaP</td>
<td>n</td>
<td>3×10(^{17})</td>
<td>40</td>
<td>emitter</td>
</tr>
<tr>
<td>8</td>
<td>GaAs</td>
<td>p+</td>
<td>5×10(^{19})</td>
<td>70</td>
<td>base</td>
</tr>
<tr>
<td>7</td>
<td>GaAs</td>
<td>n</td>
<td>3×10(^{16})</td>
<td>30</td>
<td>collector</td>
</tr>
<tr>
<td>6</td>
<td>GaAs</td>
<td>n+</td>
<td>2×10(^{18})</td>
<td>5</td>
<td>dopant spike for DHBT</td>
</tr>
<tr>
<td>5</td>
<td>InGaP</td>
<td>n</td>
<td>3×10(^{16})</td>
<td>10</td>
<td>DHBT collector</td>
</tr>
<tr>
<td>4</td>
<td>GaAs</td>
<td>n</td>
<td>3×10(^{16})</td>
<td>155</td>
<td>collector layer</td>
</tr>
<tr>
<td>3</td>
<td>GaAs</td>
<td>n</td>
<td>7.5×10(^{15})</td>
<td>400</td>
<td>collector layer</td>
</tr>
<tr>
<td>2</td>
<td>GaAs</td>
<td>n+</td>
<td>5×10(^{18})</td>
<td>1000</td>
<td>subcollector</td>
</tr>
<tr>
<td>1</td>
<td>AlAs (?)</td>
<td>?</td>
<td>?</td>
<td>30</td>
<td>substrate isolation</td>
</tr>
<tr>
<td>0</td>
<td>GaAs ?</td>
<td>?</td>
<td>?</td>
<td>NA</td>
<td>semi-insulating substrate</td>
</tr>
</tbody>
</table>
Polarized light: Electromagnetic waves are transverse

- Jones vectors:
- Linear polarization
- Circular polarization
- Elliptical polarization

\[
\begin{pmatrix}
1 \\
0 \\
\frac{1}{\sqrt{2}} \\
i
\end{pmatrix}
\]

\[
\begin{pmatrix}
\cos \theta \cos \varepsilon - i \sin \theta \sin \varepsilon \\
\sin \theta \cos \varepsilon + i \cos \theta \sin \varepsilon
\end{pmatrix}
\]
Ellipsometry: How does it work?

Reflectance ratio

\[ \rho = \frac{R_p}{R_s} = \frac{E_{rp}}{E_{ip}} \cdot \frac{E_{is}}{E_{rs}} = \tan \Psi e^{i\Delta} \]

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

We measure the change in the polarization state of light, when it is reflected by a flat surface (bulk).

Result:

\[ \tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 \]

Optical constants versus photon energy

Monochromator or Interferometer (λ)

detector

polarizer

analyzer

Bulk sample

Angle of incidence
Ellipsometry: Maxwell’s equations in solid

- Gauss’ law (electric field):
  \[ \nabla \cdot \vec{D} = 0 \]
  \( \varepsilon_0 \) permittivity of vacuum

- Gauss’ law (magnetic field):
  \[ \nabla \cdot \vec{B} = 0 \]

- Faraday’s law:
  \[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \]

- Ampere’s law:
  \[ \nabla \times \vec{B} = \mu_0 \frac{\partial \vec{D}}{\partial t} \]

- Dielectric displacement
  \[ \vec{D}(\omega) = \varepsilon_0 \varepsilon(\omega) \vec{E}(\omega) \]

\( \vec{E} \) electric field strength
\( \vec{B} \) magnetic flux density
Lorentz Model: Frequency dependence of $\varepsilon$

\[ F = ma \]
\[ qE - bv - kx = ma \]
\[ x(t) = \frac{-qE_0}{m\omega^2 + ib\omega - k} \exp(-i\omega t) \]

\[ \varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \]

Charge density

Resonance frequency

\[ \omega_p^2 = \frac{nq^2}{m\varepsilon_0} \]
\[ \omega_0^2 = \frac{k}{m} \]
Absorption and dispersion: Frequency dependence of $\varepsilon$

- **Causality (Kramers-Kronig transform):** The polarization cannot precede the external electric field: $\varepsilon_1$ can be calculated from $\varepsilon_2$ by complex residual integration (and vice versa).

- **Dispersion and absorption are related!**

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

\[\varepsilon_2(\omega) = \frac{2\omega}{\pi} P \int_0^\infty d\xi \frac{\varepsilon_1(\xi)}{\omega^2 - \xi^2}\]
Materials properties accessible by ellipsometry

- Mid-infrared spectral range
  - Insulator/semiconductor: Lattice vibrations (phonons)
  - Metal: Free carrier properties (density, scattering rate)

- Visible to UV range:
  - Electronic excitations
  - Band gap, interband transitions

- Ellipsometry allows us to study semiconductors, insulators, and metals.

- Thin films and surfaces can be investigated with proper data analysis (curve fitting).
High Surface Sensitivity

- **Spinel**: MgAl$_2$O$_4$ (high-k oxide)
- At the Brewster angle: phase angle $\Delta$ very sensitive to surface conditions.
- As received: 13 Å surface layer
- After ultrasonic clean: 44 Å surface layer
- After ozone clean: 13 Å surface layer

- **Ni-Pt** alloy on thick thermal oxide.
- Keep in air for a year: 53 Å of water
- Heat in UHVC for an hour: 7 Å of water

C.J. Zollner, T.N. Nunley, 2013

L.S. Abdallah, M. Raymond (GF), IBM, 2013
Si-Si bonds are non-polar.
- Bonds: no dipole moment.
- No infrared absorption.

Ni$^{2+}$-O$^{2-}$ bonds are polar.
- Ni-O vibration has dipole moment.

Silicon: Diamond lattice

NiO or NaCl: Rocksalt lattice

Si-Si bonds are non-polar.

FTIR ellipsometry

NiO

Typical Lorentz oscillator
Vibrational Properties (Phonons)

LaAlO$_3$

$D^6_{3d}$ or $R\overline{3}c$

MgAl$_2$O$_4$

$O^7_h$ or $Fd3m$

Space Group

$\chi(R) = N_R (\det R + 2 \cos \phi)$

$\Gamma(D^6_{3d}) = 2A_{1u} + 3A_{2g} + A_{1g} + 3A_{2u} + 4E_g + 5E_u$

$\Gamma(O^7_h) = A_{1g} + E_g + T_{1g} + 3T_{2g} + 2A_{2u} + 2E_u + 4T_{1u} + 2T_{2u}$

**FTIR Ellipsometry**

Loss function: LO phonons

$\varepsilon = \varepsilon_s \prod \frac{\omega_i^{LO}}{\omega_i^{LO}} = 22.3 \pm 0.3$

Dielectric function: TO phonons


LaAlO$_3$

MgAl$_2$O$_4$


Lattice Dynamics of NiO

- Rocksalt Crystal Structure (FCC), Space Group 225 (Fm-3m).
- Single TO/LO phonon pair.
- Antiferromagnetic ordering along (111).
- Rhombohedral distortion activates zone-edge phonon.

NiO Reststrahlen Band

Theory: $\varepsilon_0 = 13.1$ (Louie)

$\varepsilon_0 = 11.3$

$\varepsilon_\infty = 5.0$

Nelson & Willett-Gies (unpublished)

Rooksby, Nature, 1943

Not much at 0.24 eV (1880 cm$^{-1}$).
NiO Band Structure I

- Atomic electron configurations:
  
  \[
  \text{Ni:} \quad [\text{Ar}] \quad 3d^8 \ 4s^2 \\
  \text{O:} \quad [\text{He}] \quad 2s^2 \ 2p^4 
  \]

- \( \text{Ni}^{2+}\text{O}^{2-} \): 4s electrons of Ni are transferred to O 2p:
  
  \[
  \text{Ni}^{2+}: \quad [\text{Ar}] \quad 3d^8 \ 4s^0 \\
  \text{O}^{2-}: \quad [\text{He}] \quad 2s^2 \ 2p^6 
  \]

- This should be a metal, because only 8 of 10 d-states are filled.

- However:

- Transmission measurements show that NiO is an insulator with a fundamental band gap of about 0.8 eV.

NiO Band Structure II

- Let’s double the unit cell: 2 Ni and 2 O atoms per crystal cell:
  
  Ni(1): \[\text{[Ar]} \quad 3d^8 4s^0\]
  
  Ni(2): \[\text{[Ar]} \quad 3d^9 4s^0\]
  
  O(1): \[\text{[He]} \quad 2s^2 2p^6\]
  
  O(2): \[\text{[He]} \quad 2s^1 2p^6\]

- Every other O atom (ligand) transfers one electron to a Ni atom. Ligand (O) hole adds an extra d-electron to Ni.

- Antiferromagnetic ordering.

- Charge-transfer gap commonly assumed to be 4.0-4.5 eV.

- Most evidence from photoemission.

- Optical spectroscopy (transmission, ellipsometry) is usually ignored.

NiO looks just like Silicon

- The charge-transfer gap (CTG) of NiO at 4 eV looks just like the E₁ gap of Si.
- NiO CTG energy decreases with increasing temperature.
- NiO CTG broadening increases with temperature.
- Just like Si: Phonon-related?

Compare: Vina, PRB, 1984 (Ge); Lautenschlager, PRB, 1987 (Si).
Failures of the Charge-Transfer Model for NiO

- Optical absorption between 0.8 and 3.5 eV.
- Too strong to be defect-related.
- Absorption decreases above room temperature.
- Several weak critical points between 0.8 and 4.0 eV.
- Charge-gap model is flawed.
- We need a full-zone band structure for NiO to compare with optical experiments.

Electron Structure of NiO: Band Gaps
Peaks indicate interband transitions

- Valence band (flat): Ni(3d) states with some O
- Conduction band:
  Flat: Ni(3d) states (unfilled)
  Curved: Unfilled O(4s) states

- Strong 4.0 eV peak goes from Ni(3d) VB to Ni(3d) CB.
- Also observed in photoemission
- Weak peaks are transitions from many Ni(3d) VB states to the O(4s) band, only at Γ.

- Explains all experimental evidence.

J.L. Li & S.G. Louie, PRB, 2005

New Mexico State University
Another Oxide Example: $\text{Co}_3\text{O}_4$ on spinel (MBE)

Band gap: 0.75 eV

Cubic field splitting

K.N. Mitchell, Kormondy, Demkov (JAP, submitted)
Crystalline CeO₂ films grown using liquid deposition

- Insulating CeO₂ film with band gap near 3.7 eV.
- Determine film thickness from interference fringes in transparent region.
- Fit optical constants with basis spline polynomials.


Variation of CeO$_2$ band gap with Sm doping

- Linear interpolation to find band gap.
- No variation with Sm doping found.
- However:
  Sm doping shifts absorption to higher energies (lower peak absorption).

K. Mitchell,
C.O. Rodriguez, 2013
Strained Ge Epilayers on Si

N.S. Fernando,1 A. Ghosh,2 C.M. Nelson,1 A.A. Medina,1 S.C. Xu,3 J. Menendez,3 J. Kouvetakis,3 S. Zollner1
1New Mexico State University, Las Cruces, NM; 2University of Michigan, Flint, MI; 3Arizona State University

1 relaxed at the growth temperature
2 Thermal expansion mismatch
3 Tensile stress at lower temperatures

\[ \varepsilon = 0.1\% \]

\[ \varepsilon_\parallel (T) = \int_{T_1}^{T_f} [\alpha_{\text{Ge}} (T) - \alpha_{\text{Si}} (T)] \, dT \]

Strain changes band structure

Tensile Ge becomes direct
Critical points in Ge band structure

Determine energies of $E_1$ and $E_1 + \Delta_1$ energies with very high accuracy (<1 meV)

Pseudo-dielectric function

Determine energies of $E_1$ and $E_1 + \Delta_1$ energies with very high accuracy (<1 meV)
Compare Ge on Si with bulk Ge

Theory:
Tensile biaxial stress (thermal expansion mismatch)
Tensile in-plane and compressive out-of-plane strain
Tensile hydrostatic and compressive shear strain

\[ \Delta E_H = \sqrt{3} D_1 \varepsilon_H \]  (~20 meV)

- Observed \( E_1 \) shifts yield the correct sign and magnitude of the strain.
- But: Shifts are larger than expected from thermal expansion mismatch.
- Perhaps other influence on \( E_1 \) energy shifts (threading dislocations?).
Metals are described by Drude Model: Dielectric function and optical conductivity

Drude model, $\Gamma/E_p=0.1$

- $\sigma_1$: Conductivity, absorption
- $\sigma_2$: Phase shift, dispersion

$$\sigma_1 = E\varepsilon_0 \varepsilon_2$$

$$\sigma_2 = (1 - \varepsilon_1)E\varepsilon_0$$

$\sigma_2$ has maximum at $E=\Gamma$

$\sigma_1$ and $\sigma_2$ cross at $E=\Gamma$, value is $\sigma_0/2$
Samples and motivation

**METAL ALLOY**

<table>
<thead>
<tr>
<th>100 Å Ni(_{1-x})Pt(_x)</th>
<th>Up to 25% Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
</tr>
</tbody>
</table>

**MONOSILICIDES**

- NiPtSi
- NiPtSi

**SE**: Drude + Drude (two carrier types)

**Drude**: free carriers + intraband transitions

**Applications**: **MOSFET**: metal-oxide–semiconductor field-effect transistor

**SE**: One Drude + Gaussians

**Gaussian**: interband transitions
Nickel-Platinum Alloys for Ohmic Contacts

32nm CMOS on SOI

Ni$_{1-x}$Pt$_x$

100 Å

SiO$_2$

2000 Å

Si

L.S. Abdallah, M. Raymond (GF), 2013
Nickel-Platinum Alloys: Composition Dependence

Pt 5d bands are wider than Ni 3d bands

L.S. Abdallah, M. Raymond (GF), 2013
Ellipsometric angles => Optical conductivity (Fresnel fitting)

Ni$_{0.9}$Pt$_{0.1}$/SiO$_2$/Si (as-deposited)
Ni$_{1-x}$Pt$_x$ alloys: Ni/SiO$_2$/Si

\[ \hbar \omega < 1000 \text{ cm}^{-1}: \quad \sigma_1 \downarrow \text{ with Pt} \uparrow \]
(DC: Litschel & Pop, 1985)

\[ \hbar \omega > 1000 \text{ cm}^{-1}: \quad \sigma_1 \uparrow \text{ with Pt} \uparrow \]
(d-intraband transitions
Pt adds richer d-state band structure)

25% Pt: $\sigma = 16,000/\Omega\text{cm} @ 250\text{cm}^{-1}$
$\sigma_{DC} = 30,000/\Omega\text{cm}$ (Litschel & Pop)

Two Drude oscillators: Two sets of electrons
1) electrons inside crystallites (grains)
2) electrons in the areas between crystallites

Nagel & Schnatterly, PRB, 1973; Hunderi, PRB 1973
Ni films (0% Pt): Different thicknesses

50 Å not metallic

σ₁ with t ↑ reduced grain boundary scattering in thicker films

Ola Hunderi, PRB, 1973
Ni$_{1-x}$Pt$_x$Si monosilicides: Ni$_{1-x}$Pt$_x$/Si followed by annealing

Free carriers

\[ \hbar \omega < 1000 \text{ cm}^{-1} : \quad \sigma \downarrow \text{ with Pt} \uparrow \]

Similar to Ni$_{1-x}$Pt$_x$ alloys: Ni-Pt alloy scattering

\[ \hbar \omega > 1000 \text{ cm}^{-1} : \quad \sigma \uparrow \text{ with Pt} \uparrow \]

More d-d interband absorption as Pt content increases

Si-O vibration fitted using Gaussian oscillator.
Materials properties accessible by ellipsometry

- Mid-infrared spectral range
  - Insulator/semiconductor: Lattice vibrations (phonons)
  - Metal: Free carrier properties (density, scattering rate)

- Visible to UV range:
  - Electronic excitations
  - Band gap, interband transitions

- Ellipsometry allows us to study semiconductors, insulators, and metals.
- Thin films and surfaces can be investigated with proper data analysis (curve fitting).

Hold the date:
October 2016
APS Four Corners Meeting
Las Cruces, NM
Send us your samples: Metals, insulators, semiconductors

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Back: Nathan Nunley, Travis Willett-Gies, Cesar Rodriguez, Tarek Tawalbeh, Stefan Zollner
Front: Khadijih Mitchell, Christine Acheampong, Lina Abdallah, Amber Medina
Not shown: Cayla Nelson, Maria Spies, Chris Zollner, Ayana Ghosh, Laura Pineda, Nalin Fernando. Yuling Li, Dr. Hongmei Luo (Chemical Engineering)

http://ellipsometry.nmsu.edu