Optical Constants of Ge and GeO$_2$ from Ellipsometry

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2016 DPG Frühjahrstagung
Regensburg, 9. März 2016, HL 59.10

Wo ist Las Cruces?

NIR/VIS/QUV ellipsometry:
190 to 2500 nm, 77 to 800 K

http://ellipsometry.nmsu.edu

NSF: DMR-1505172
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
Biography

Regensburg
Germany

Motorola (Mesa, Tempe)
Arizona, 1997-2005

Las Cruces, NM
Since 2010

Motorola, Freescale
Texas, 2005-2007

Freescale, IBM
New York, 91-92, 07-10
SiGe:C Metrology: How thick is my film?

Si$_{1-x}$Ge$_x$ alloys

100 thickness measurements
Need precise values of refractive index

Si$_{1-x}$Ge$_x$ alloys

High-resolution XRD

Spectroscopic Ellipsometry

SiGe:C base

Si cap (emitter)

Si substrate

Why Germanium?

- First transistor built with Ge.
- High frequency applications (bipolar).
- Excellent infrared photodetector.
- **Recent interest: PMOS channel material.**
- Training students in semiconductor physics
- Why not?

SciFi CMOS cartoon:
Multi-Sample Analysis

- **Single sample**: Ellipsometry of one GeO$_2$/Ge sample
  - Unknown Ge optical constants
  - Unknown GeO$_2$ (native oxide) optical constants and thickness
  - This problem is under-determined (not enough data).

- **Multi-sample analysis**: 
  - Grow thermal oxides on Ge with different thicknesses.
  - All oxides identical; only thickness varies between samples.
  - Fit all data simultaneously (over-determined).

- **Ellipsometry measurements**:
  - J.A. Woollam VASE ellipsometer with Berek compensator.
  - 0.5 to 6.6 eV (with halogen lamp).
  - 60°-75° angle of incidence.
  - Fit with parametric oscillator model.
Substrate Cleaning and Thermal Oxidation

- **Substrate cleaning:**
  - Remove most of the native oxide.
  - Leave **stable (but thin)** native oxide.
  - No harsh chemicals (BHF, Br:Meth).
  - UV ozone clean at 150°C for 1 hour, followed by cool-down incubation.
  - Ultrasonic clean in DI water followed by isopropanol (20 min each).

- **Thermal oxidation:**
  - 20 by 20 mm² undoped Ge pieces.
  - Single-side polished.
  - Anneal in O₂ (2.7 atm) at 550°C to avoid oxide (GeO) desorption.
  - 1-10 hours; 35 to 130 nm thick.
  - Some spots, but OK.
  - GeO₂ unstable and water-soluble, measure soon.
$d^2 + Ad = B(t + \tau)$
X-ray reflectance of typical sample (550°C, 1 h, 33 nm)

GeO₂ density $\rho$: 90% of bulk
Lower $\rho$ near surface
Higher $\rho$ near substrate
Thickness: 33 nm
Roughness: 0.5 nm (2%, neglect)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Electron Density (eÅ⁻³)</th>
<th>Bulk Electron Density (eÅ⁻³)</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO₂</td>
<td>0.84</td>
<td>1.14</td>
<td>1.67</td>
<td>0.4429</td>
</tr>
<tr>
<td>GeO₂</td>
<td>1.03</td>
<td>1.14</td>
<td>30.8</td>
<td>0.4734</td>
</tr>
<tr>
<td>GeO</td>
<td>1.24</td>
<td></td>
<td>0.79</td>
<td>0.9723</td>
</tr>
<tr>
<td>Ge</td>
<td>1.36</td>
<td>1.36</td>
<td>Substrate</td>
<td>0.6906</td>
</tr>
</tbody>
</table>
Ge wafer with native oxide (2.3 nm)

- Measurement right after cleaning, excellent fit to data.
- Herzinger-Johs parametric oscillator model for Ge.

Jellison-Sales method for transparent glasses:
$\Delta$ at 75° below band gap determines oxide thickness (2.3 nm)
Ge wafer with 34 nm thermal oxide (one hour)

- Cleaned, then oxidized for one hour at 550ºC, 33 nm by XRR.
- 5% non-uniformity.
- Poor fit in deep UV (above 6 eV)
Ge wafer with 89 nm thermal oxide (5 hours)

- Cleaned, then oxidized for five hours at 550°C.
- 7% non-uniformity.
- Poor fit in deep UV (above 6 eV)
Ge wafer with 136 nm thermal oxide (10 hours)

- Cleaned, then oxidized for ten hours at 550ºC.
- 1% non-uniformity.
- 4 nm spectral bandwidth.
- Poor fit in deep UV (above 6 eV)
Preliminary optical constants for Ge and GeO$_2$

- Determined using multi-sample analysis (2, 34, 52, 89, 136 nm)

Similar to Jellison/UNL data
Higher amplitude than Aspnes
Broader spectral range (0.5 to 6.6 eV)
Bigger differences in UV.

Much broader spectral range.
Absorption begins at 6.5 eV.
Tauc-Lorentz oscillator fit.
Remaining issues

- **Depolarization** of reflected light
  - Thickness non-uniformity (20 mm sample size)
  - Insufficient monochromator resolution (4 nm)
- Does the density vary between samples?
- Need to improve XRR fits for some samples.
- Is there a **density gradient** in the oxide?
- Do we need to consider surface roughness (no AFM yet)?
- Is there an interfacial layer at the GeO\(_2\)/Ge interface?
- Is a simple Tauc-Lorentz oscillator sufficient for GeO\(_2\)?
- Need FTIR-SE to study phonons.
Summary

Optical constants for Ge and GeO$_2$

- Developed UV-ozone clean for thermal oxidation of Ge.
- Performed thermal oxidation of Ge at 550ºC for 1 to 10 hours.
- Multi-sample ellipsometry fit of ellipsometric angles.
- Dielectric function of Ge and GeO$_2$ from 0.5 to 6.5 eV.

![Graphs of Ge and GeO$_2$ dielectric functions](http://ellipsometry.nmsu.edu)