Optical Properties of Zinc Oxide and Strontium Titanate Thin Films by Reflectometry and Ellipsometry

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Objectives and Motivation

Objectives
1. Develop a reliable model to determine the optical properties of zinc oxide (ZnO) and strontium titanate (SrTiO$_3$ or STO) thin films.
2. Determine how optical constants are affected by deposition conditions and substrates.

Motivation
1. Need for reliable data on optical constants of thin films for use in device applications.
2. Very few systematic studies of how deposition temperatures and substrate type affect optical properties of ZnO, STO thin films
Newton’s rings: concentric ring pattern of rainbow colors because different wavelengths of light interfere at different thicknesses
Optical Constants

- When light is incident on a plane-parallel interface between two media it may be reflected or refracted.
- The second medium is characterized by a complex index of refraction:

\[ \tilde{N} = n - ik \]
Optical Constants

- **n**: (real) index of refraction; inverse measure of the phase velocity of light in the material

- **k**: extinction coefficient; measure of how rapidly intensity decreases as the light passes through the material

- **ε**: dielectric function; degree to which a material may be polarized by an applied electric field
  \[ \varepsilon = \varepsilon_1 + i\varepsilon_2; \quad \varepsilon_1 = n^2 - k^2; \quad \varepsilon_2 = 2nk \]

- Both n and k are functions of wavelength; optical constant spectra show n and k as functions of wavelength or photon energy – dispersion spectra
Reflection of Light

- Light incident on the sample has two components of polarization: in plane (p-waves) and perpendicular (s-waves) to the plane of incidence.
- **Reflectance** ($R$): ratio of *intensity* of outgoing light to incoming light – measured in reflectometry.
- Ratio of the *amplitudes* of outgoing and incoming light ($r$) is also of interest – measured in ellipsometry. For a single interface, this ratio is called the Fresnel Reflection Coefficient and is based on Snell’s Law.
Fresnel Reflection Coefficient for single interface:

\[ r_p = \frac{\tilde{N}_b \cos \theta_a - \tilde{N}_a \cos \theta_r}{\tilde{N}_b \cos \theta_a + \tilde{N}_a \cos \theta_r} \]

Reflectance,
\[ \mathcal{R}_p = |r_p|^2 \]

Ratio of amplitude of outgoing resultant wave to amplitude of incoming wave is defined as the **total reflection coefficient**. For a single film (two interfaces) this is:

\[ R^p = \frac{r_{ab}^P + r_{bc}^P e^{-i2\beta}}{1 + r_{ab}^P r_{bc}^P e^{-i2\beta}} \]

\[ \beta = 2\pi \left( \frac{d}{\lambda} \right) n_b - k_b \cos \phi_b \]

d = film thickness; \( n_b \) = index of refraction of layer b;
\( k_b \) = extinction coefficient of layer b

Reflectance, \[ \mathcal{R}_p = |R^p|^2 \]
Ellipsometry

- **Delta**, $\Delta = \delta_1 - \delta_2$ is the phase shift induced by reflection in the p and s-waves ($0 - 360^\circ$ or -180 to +180°)

- Phase shift also induces an amplitude reduction for both p- and s-waves:
  \[
  \tan \psi = \frac{|R_p|}{|R_s|} \quad (\psi: 0 \text{ to } 90^\circ)
  \]

- $\rho = \frac{R_p}{R_s} = \tan \psi e^{i\Delta}$ or $\tan \psi e^{i\Delta} = \frac{R_p}{R_s}$ (fundamental equation of ellipsometry)

- Ellipsometers measure $\Delta$ and $\psi$: from these quantities optical constants and thickness can be calculated using a theoretical model.
Zinc Oxide
ZnO
Zinc Oxide Structure

- Hexagonal wurtzite structure – non-central symmetry
- Alternating planes of \( T_d \) coordinated zinc and oxide ions stacked alternately along the \( c \)-axis
- Positively charged (0001)-\( \text{Zn}^{2+} \) and negatively charged (0001)-\( \text{O}^{2-} \) polar surfaces result in a normal dipole moment and spontaneous polarization along the \( c \)-axis
- Uniaxial with optical axis being the hexagonal \( c \)-axis – gives rise to two independent refractive indices, \( n_0 \) and \( n_e \)
Zinc Oxide Properties and Applications

- II-IV, *n*-type semiconductor (band gap 3.3 eV)
- High excitonic binding energy (60 eV) - optically pumped UV lasing at room temperature demonstrated by Yu et al and Bagnall et al\(^1\)
- Due to the non-central crystal symmetry, ZnO is piezoelectric: useful for electromechanical coupled sensors, varistors and transducers\(^2\)
- Transparent conductive oxide, exhibiting high transmittance in the visible region and low electrical resistivity: ideal material for solar cells and flat panel displays\(^3\)

Zinc Oxide Thin Film Preparation

Films were deposited using radio frequency (RF) planar magnetron sputtering using a 3 inch diameter Zn target reactively sputtered in Ar-O\(_2\) (1:1) plasma discharge.

Substrates were placed parallel to the target surface in a sputter down geometry and heated with quartz lamps to temperatures varying from 200°C to 600°C.
Data Analysis

Multi-parameter regression analysis:

1. Build model of the thin film structure: estimate thickness, optical characteristics
2. Determine actual change in reflection/polarization over a wide spectral range
3. Measured change is compared to the calculated change and regression analysis based on selected model parameters is performed until a ‘best fit’ is achieved
4. Best fit measured by minimizing the root mean square error (RMSE)

Models of Film Structure

- Silicon substrate
- ZnO thin film (L1)
- EMA Layer
- Platinum film
- Void
- ZnO
Sample Data: ZnO on Si

Figure 1: Measured (-) and simulated (--) 0 and 70 degree reflection data for ZnO film on Si substrate deposited at 500C.

Figure 2: Measured (-) and simulated (--) delta ellipsometric data for the film shown in Fig. 1

Figure 3: Measured (-) and simulated (--) psi ellipsometric data for the film shown in Fig.

- Quality of fit: RMSE 1.437
- Strong interference oscillations below the band edge due to multiple internal reflections between the film and the substrate
- Model is able to fit data above and below the band gap
Optical constant spectra show strong peaks which may be attributed to interband transitions (375 nm) as well as a smaller peak (338 nm) usually attributed to free excitonic and exciton-photon complex transitions.

- n exhibits typical semiconductor dispersion: n decreases with increasing λ and resonant frequency close to visible region (~370 nm).

ZnO film is transparent in region 400 – 920 nm.

Discussion – Si Substrate

- $n$ – indicator of packing density and film stoichiometry. Increasing temperature results in increased surface mobility of impinging species and a more regular lattice structure.

- Index also increases with O: Zn ratio – film is nearly stoichiometric.

- EMA layer has no correlation to temperature – real
Discussion – Pt Substrate

- n increases with substrate temperature
- EMA layer has no correlation to temperature – real. FESEM images confirm significantly higher roughness in RT, 550°C films
- Low temperature films on both substrates exhibit low n and high EMA thickness, i.e., are rough and not very dense.
Discussion: Refractive Index

- Bulk refractive index @ 600 nm ~ 2.00
  (1.99 on sapphire\(^1\); 1.9985 single crystal\(^2\) (ord. ray); 1.997 uniaxial thin film material\(^3\) (ord. ray)

- Measured values are close to ordinary bulk values (1.99 - 2.03 for ZnO/Si and 1.96 – 2.01 ZnO/Pt) indicating a high quality film

- Comparison of substrates indicate high quality films can be grown on both materials

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Strontium Titanate
SrTiO$_3$
Structure and Properties

- Perovskite crystal structure
- Important dielectric material with incipient ferroelectric transition (tetragonal cubic) at 110K and bandgap of 3.22 eV\(^1\)
- High dielectric constant, excellent optical properties and stable stoichiometry at RT offers prospective applications in microelectronics and optoelectronics in thin film morphology
- Isotropic optical behavior as a result of cubic crystal structure

Thin Film Preparation

- Films were deposited using radio frequency (RF) planar magnetron sputtering using a 3 inch diameter SrTiO$_3$ target (IC Mechanics 99.9%) in Ar-O$_2$ (4:1) plasma discharge in an Anelva SPF-332H sputtering system.

- Substrates were placed parallel to the target surface (target to substrate distance of 4.5 cm) in a sputter down geometry and heated with quartz lamps to temperatures varying from room temperature to 800°C.
Sample Data: SrTiO$_3$ Film

- Analysis using multi-angle reflectometry
- Graded model
- Quality of fit: RMSE 1.638
- Strong interference oscillations due to multiple internal reflections between the film and substrate

<table>
<thead>
<tr>
<th>Extracted Data</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Thickness Layer 1 (STO)</td>
<td>564.88 nm</td>
</tr>
<tr>
<td>Maximum Refractive Index @ 632 nm</td>
<td>2.32958</td>
</tr>
<tr>
<td>Extinction coefficient @ 632 nm</td>
<td>0.0000</td>
</tr>
<tr>
<td>RMSE</td>
<td>1.638</td>
</tr>
</tbody>
</table>
Discussion

- Data analysis indicates a graded refractive index - \( n \) increases linearly in the normal direction, reaching a maximum at the film surface.
- Graded index occurs only in films deposited at 400\(^\circ\)C and above.
- Applications: multi-band rugate filters, anti-reflective coatings, edge and dichroic filters.
Discussion

- Clear trend of increasing n with increasing deposition temperature: increased packing density

- Significant increase in n above 300°C (1.989 to 2.274 at 400°C)

- Bulk refractive index of SrTiO₃ is 2.394 at 620 nm; maximum value of 2.385 at 800°C which is very close to the bulk values, indicating very high crystallinity and film quality.
High quality ZnO and SrTiO$_3$ films can be produced via sputtering on Si and Pt substrates.

Film density, as measured by an increase in the refractive index, increases with increasing substrate temperature during deposition.

For ZnO films, model is able to fit data both above and below the band gap.

For STO films, a marked change in crystallinity of the deposited films occurs above 300°C; films also exhibit a graded index at higher deposition temperatures.
Reflectometry Instrumentation

- Intensity of a monochromatic beam of light is measured before and after it reflects from the sample

\[
R_{\text{relative}} = \frac{I_{\text{sample}}}{I_{\text{standard}}}
\]

- Absolute reflectance of the sample can be calculated from absolute reflectance of the standard (bare Si wafer)
Ellipsometry Instrumentation

- Measurement of the change in polarization state of a beam of light upon reflection from the sample.

Detector signal is measured as a function of time then Fourier analyzed to obtain psi and delta.