A Method for Atomic Layer Deposition of Complex Oxide Thin Films

Brian R. Beatty

M.S. Thesis in Materials Science and Engineering

Drexel University, Philadelphia, PA

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Outline

- Objectives
- Atomic Layer Deposition
- Thin Film Growth
- Characterization Methods
- Results
- Conclusions

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Project Objectives

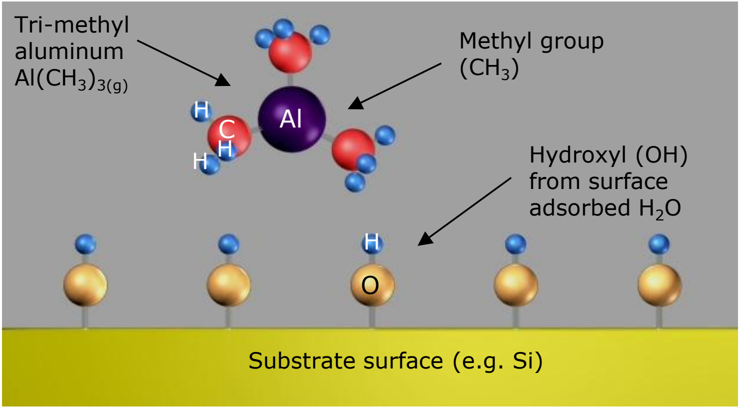
- Develop method for identifying best candidate precursors for depositing complex oxide films
- Determine optimal deposition parameters to obtain desired film stoichiometry
- Characterization of various film properties, for use in further optimizing subsequent depositions
- Successful deposition of desired material:
  Perovskite Lead Titanate ($PbTiO_3$)

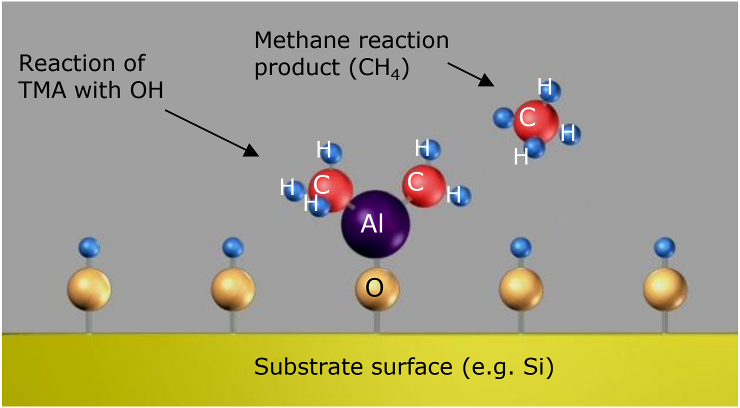
Outline

What is ALD?

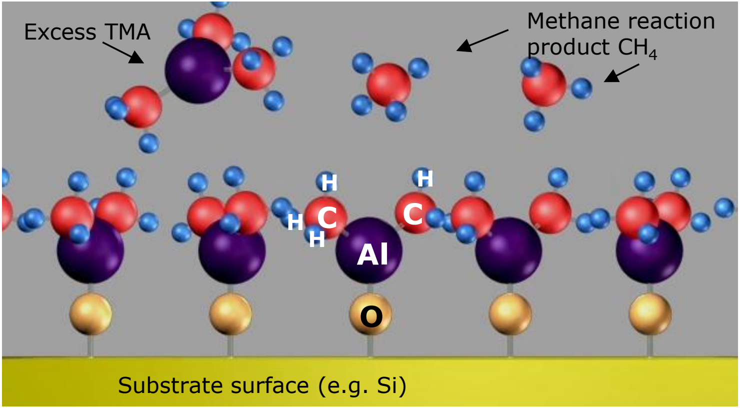
- Chemical deposition method, similar to CVD
- Separation of deposition reaction into metal chemisorption and subsequent oxidation
- Restricts reactions to surface-vapor interactions, no vapor-vapor reactions possible

Atomic Layer Deposition

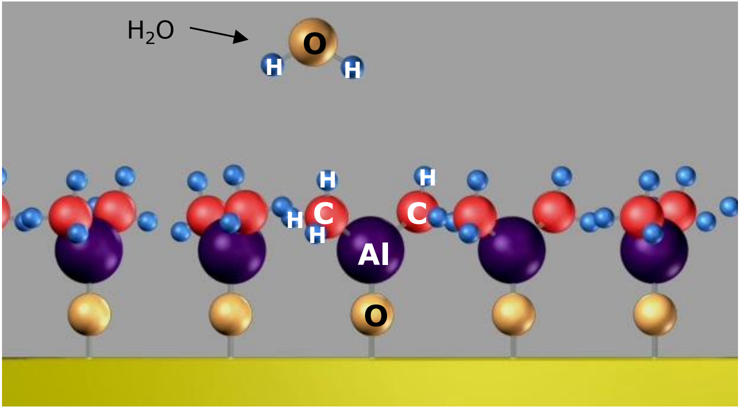


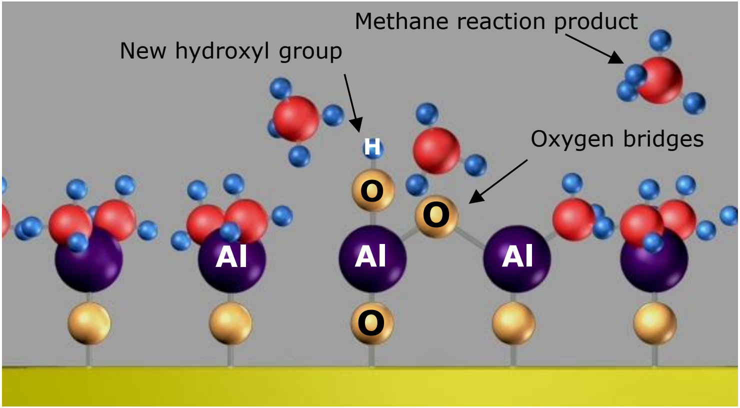

Methane reaction
product (CH_4)
Reaction of
TMA with OH
H
C
H
H
H
H
C
H
C
H
H
Al
O
Substrate surface (e.g. Si)

Atomic Layer Deposition

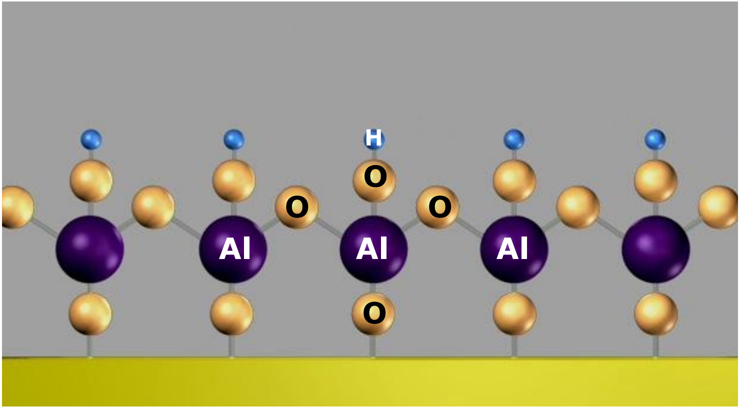


Atomic Layer Deposition




Methane reaction product
New hydroxyl group
Oxygen bridges
H
O
O
Al
Al
Al
O

Atomic Layer Deposition



Atomic Layer Deposition

Advantages

- Ultra-high film thickness resolution (Å-level)
- High film conformality (3D structure coating)
- Lower deposition temperatures
- Potentially lower environmental/economic impact

Disadvantages

- Slow deposition rates
- Precursor chemistry is often difficult and complex (organometallic compounds)
- Many material systems lack developed ALD processes

Atomic Layer Deposition

Where is ALD used?

- Integrated Circuits: Transistor Gate Oxides (high-k)
- Alternative Energy: Low tolerances for layer thickness, high film uniformity across surface
- Biomedical: Uniform coating of highly porous structures

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Thin Film Growth: Film Precursors

Titanium Precursor

Titanium(IV) tetraisopropoxide: Ti-o-*i* -Pr

Oxidizer

- H_2O and O_2/O_3 mixtures commonly used in literature
- O_2/O_3 was chosen for higher compatibility with Pb precursors

Lead Precursors

1. Bis(2,2,6,6-tetramethyl -3,5-heptanedionato) Lead(II): $Pb(TMHD)_2$
2. Lead(II) hexafluoro-acetylacetonate: $Pb(HFAc)_2$

Thin Film Growth: Substrates

- 200 nm SiO_2/Si(100)
  - 200 nm of thermally grown silica on crystalline silica.
  - Amorphous top layer
- 15 nm Pt(111)/200 nm SiO_2/Si(100)
  - 15 nm of ALD-grown platinum on the SiO_2/Si(100) substrate
  - Metallic (crystalline) top layer
- $SrTiO_3$(100)
  - Single crystalline oriented strontium titanate wafer.

Thin Film Growth: Deposition Parameters

- Growth Temperature
- Precursor Dosage
- Purge Time
- Precursor Exposure
- Post-Deposition Annealing

Outline

Characterization Methods: Thermal Analysis

Thermogravimetric Analysis

- Method for analyzing mass loss rates as function of temperature
- Useful for determining optimal evaporation temperatures
- Can indicate multi-step evaporation/chemical conversion

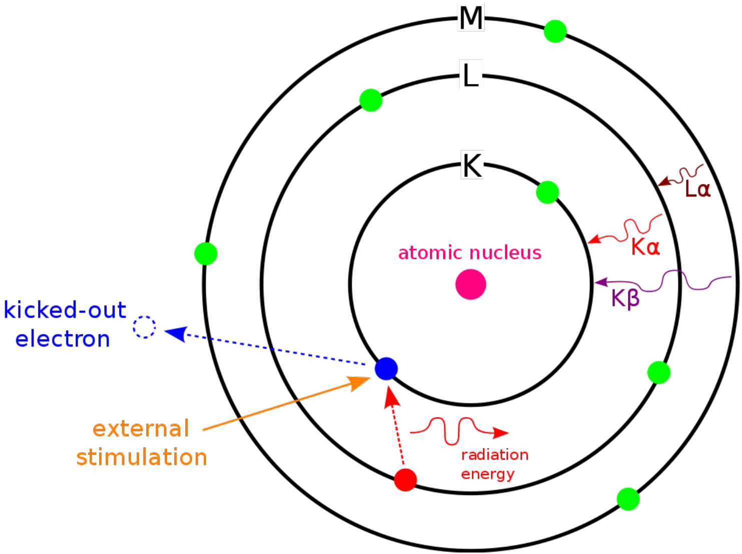
Differential Calorimetry

- Allows insight into energetic transformations as a function of temperature
- Indicates phase changes, evaporation energies, and structural changes
- Useful for analyzing the stability of precursors at desired temperatures

X-Ray Fluorescence Spectroscopy (XRF)

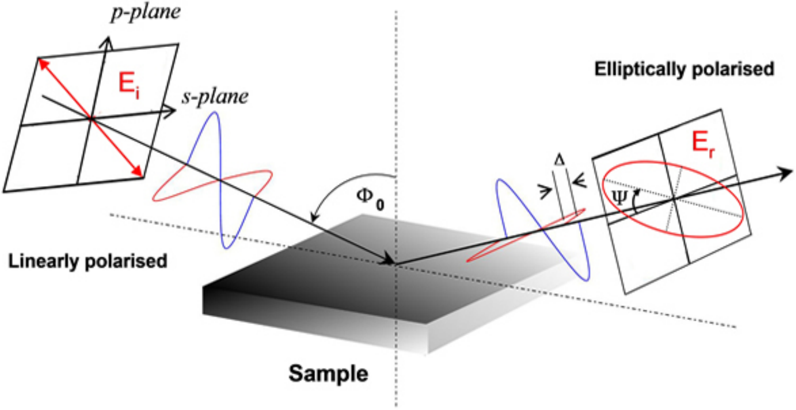
- Similar to EDXS but uses X-rays in place of energetic electrons
- Much lower noise floor (no Bremsstrahlung radiation)
- Capable of quantitative compositional analysis of ultra-thin films

Characterization Methods: Composition Analysis



Ellipsometry

- Non-destructive optical film analysis method
- Capable of determining numerous optical/electronic parameters of film
- Primarily used to determine post-deposition film thicknesses and thus growth rates



p-plane
E_i
s-plane
Elliptically polarised
E_r
Δ
Φ_0
Ψ
Linearly polarised
Sample

X-Ray Diffractometry (XRD)

- Standard technique used to identify materials and phases/orientations
- Analysis produces information about presence of particular lattice spacings
- Identifying lattice spacings (via databases or previous studies in literature) can indicate presence and orientation of specific materials and phases

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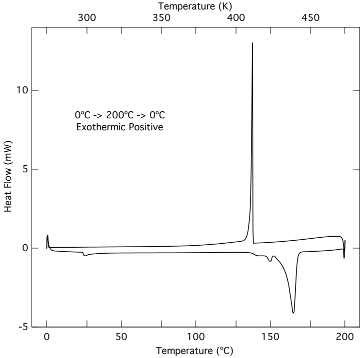
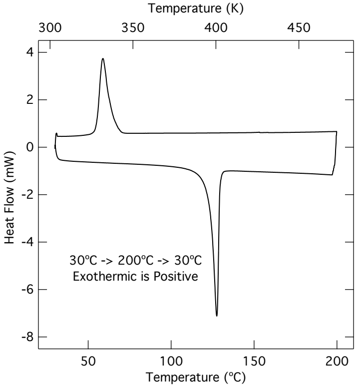
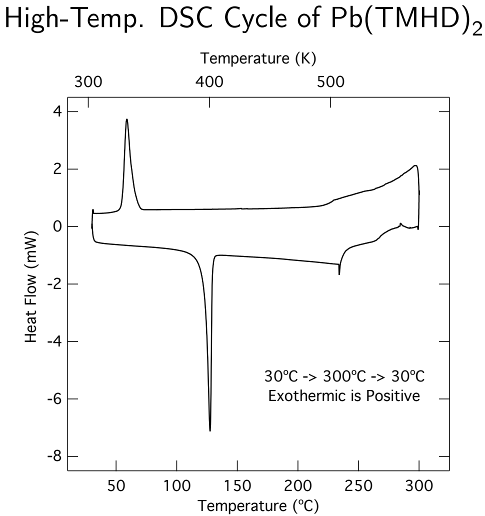
Results: Thermal Analysis

DSC Cycles of $Pb(HFAc)_2$ and $Pb(TMHD)_2$



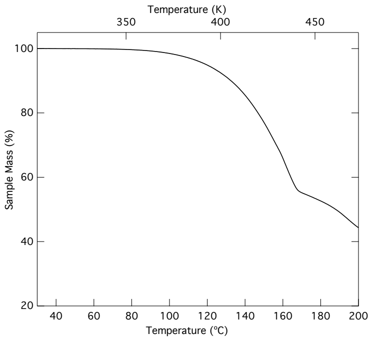


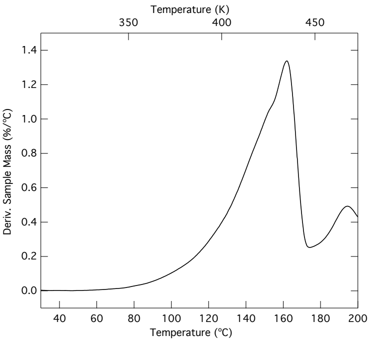
Results: Thermal Analysis



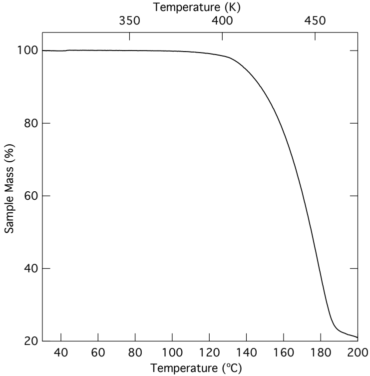
Results: Thermal Analysis

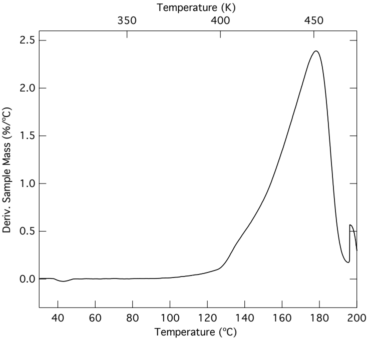
TGA Traces for $Pb(HFAc)_2$



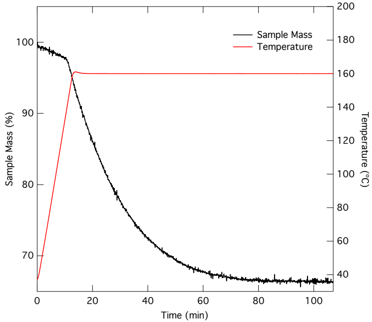


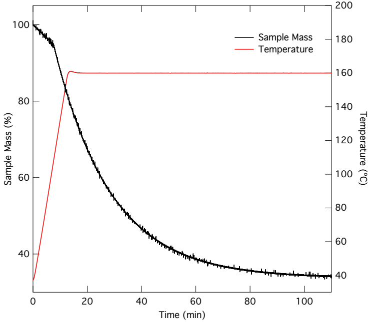
TGA Traces for $Pb(TMHD)_2$





Constant Temperature Studies of $Pb(HFAc)_2$ and $Pb(TMHD)_2$

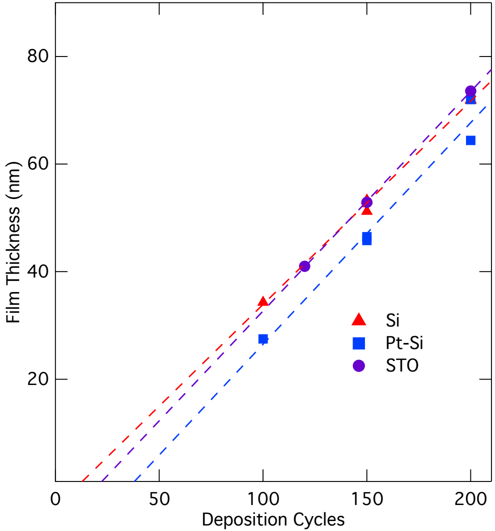




Results: Deposition and Processing Parameters

Temp. (°C)	Run #	Pb:Ti Ratio	Cycles	Subs. Type	Annealing Temp. (°C)	Annealing Time (min)
225	20	3:1	200	Si	N/A	N/A
				Pt-Si	650	90
				STO	650	90
	21	3:1	150	Si	N/A	N/A
				Pt-Si	650	90
				STO	650	90
	22	3:1	150	Si	N/A	N/A
				Pt-Si	650	90
	28	3:1	120	STO	650	90

Results: Film Growth Rates



Results: Film Growth Rates

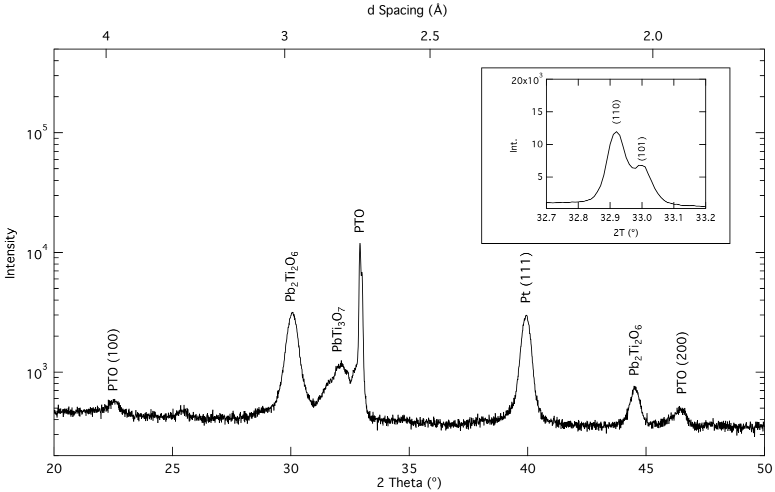
Run #	Subs. Type	Thickness (nm)	Growth Rate (Å/cycle)
20	Si	71.8	3.59
	Pt-Si	64.4	3.22
	STO	73.6	3.68
21	Si	53.2	3.54
	Pt-Si	45.8	3.05
	STO	52.9	3.53
22	Si	53.3	3.55
	Pt-Si	46.5	3.10
28	STO	41.0	3.42

Results: Composition Analysis

Compositions of Selected Sample Films

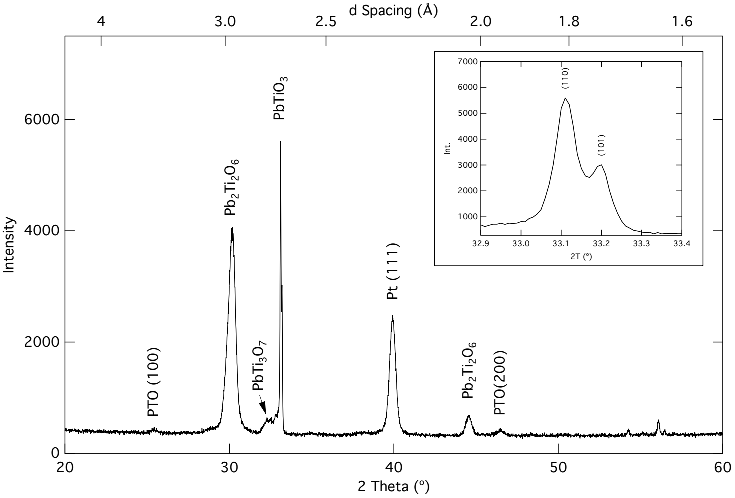
		Composition (%)		
Run #	Substrate	Lead	Titanium	Ti:Pb Ratio
20	SiO_2	56.6	43.4	0.769
	Pt-Si	51.5	48.5	0.944
21	SiO_2	69.6	30.4	0.437
	Pt-Si	56.1	43.9	0.783
22	SiO_2	67.7	32.3	0.478
	Pt-Si	56.1	43.9	0.784
24	SiO_2	69.0	31.0	0.450
	Pt-Si	62.2	37.8	0.609

XRD of 20 on Pt-Si

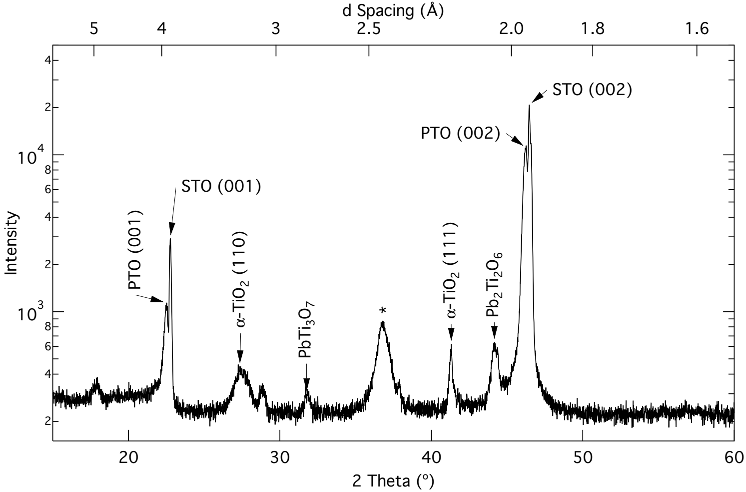


Results: Phase Identification

XRD of 23 on Pt-Si



XRD of 28 on STO(100)



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Conclusions

- A procedure for identifying best precursor compounds for ALD deposition of oxides was created
- A method for designing and implementing an ALD process for a novel material has been developed
- Successfully deposited thin films containing the target material: perovskite $PbTiO_3$
- Films contain significant amounts of impurity phases

Conclusions: Future Work

- Refine process to maximize phase purity and film epitaxy
- Characterize ferroelectric character of crystallized films
- Investigate doping of thin films (e.g. $PbZr_xTi_{1\text{-}x}O_3$)
- Apply process to other oxide families (e.g. $BaSrTiO_3$)

Questions?

Cauchy Model as used by WVASE32

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} + \cdots \tag{1a}$$

$$\kappa(\lambda) = A_\kappa e^{B_\kappa\left(\frac{hc}{\lambda}\right) - C_\kappa} \tag{1b}$$

Tauc-Lorentz Model as used by WVASE32

$$\epsilon_1 = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \epsilon_2(\xi)}{\xi^2 - E^2} \, \mathrm{d}\xi \tag{2a}$$

$$\begin{cases} \epsilon_2(E) = \dfrac{A E_0 C \left(E - E_g\right)^2}{\left(E^2 - E_0^2\right)^2 + C^2 E^2} \cdot \dfrac{1}{E} & E > E_g \quad \text{(2b)} \\ \epsilon_2(E) = 0 & E \leq E_g \quad \text{(2c)} \end{cases}$$

Ellipsometry Analysis Procedure

1. High-λ Cauchy Model
2. Direct Calculation of n and κ
3. Conversion to Oscillator Model
4. Refinement of Oscillator Layer Parameters

Ellipsometry Analysis Procedure

- High-λ Cauchy Model
  - Used to determine layer thickness
  - Cauchy model applied to transparent region of film (>600nm)

Ellipsometry Analysis Procedure

- Direct Calculation of n and κ
  - Numeric calculation of n and κ from Fresnel equations
  - Used to provide a starting point to base Tauc-Lorentz oscillator model upon
  - Calculated values are non-physical

- Conversion to Oscillator Model
  - Data set of n and κ are used to approximate initial guesses for T-L oscillator parameters

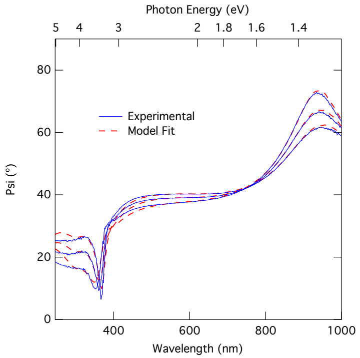
Ellipsometry Analysis Procedure

- Refinement of Oscillator Layer Parameters
  - Software optimization of model parameters

Model Parameters for 20-Pt/Si

Layer	Variable	Thickness (nm)	Value
3. T-L Osc.		75.6	
	ϵ_1 offset		3.62
	Amp		36.54
	E_n		4.51
	C		1.30
	E_g		2.07
2. Pt		15.1	
1. SiO_2		1.1	
0. Si		Substrate	

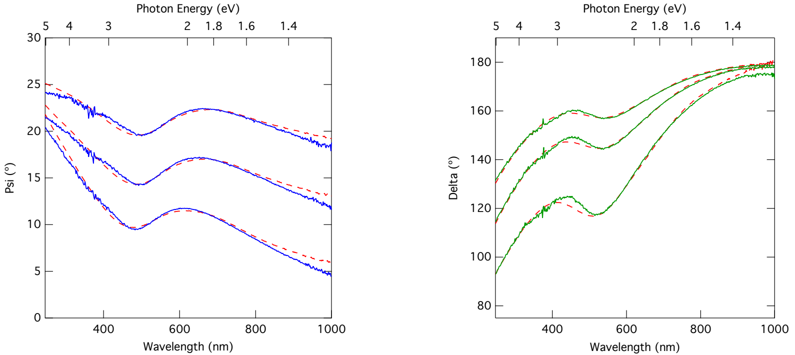
Ellipsometry Data from 20 - Pt/Si



Model Parameters for 20-Pt/Si

Layer	Variable	Thickness (nm)	Value
1. T-L Osc. (2)		49.2	
	ϵ_1 offset		1.42
	Amp_1		64.71
	$\mathrm{E}_{\mathrm{n}1}$		3.69
	C_1		4.44
	$\mathrm{E}_{\mathrm{g}1}$		1.55
	Amp_2		1.55
	$\mathrm{E}_{\mathrm{n}2}$		2.12
	C_2		0.76
	$\mathrm{E}_{\mathrm{g}2}$		0.001
0. STO		Substrate	

Ellipsometry Data from 28 - STO



Model Parameters for 28-STO

Layer	Variable	Thickness (nm)	Value
1. T-L Osc. (2)		49.2	
	ϵ_1 offset		1.42
	Amp_1		64.71
	E_{n1}		3.69
	C_1		4.44
	E_{g1}		1.55
	Amp_2		1.55
	E_{n2}		2.12
	C_2		0.76
	E_{g2}		0.001
0. STO		Substrate	