A Method for Atomic Layer Deposition of Complex Oxide Thin Films

Brian R. Beatty

Brian.R.Beatty@Drexel.edu

Matricola #: 780703

Politecnico di Milano

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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 ($PbTiO_3$)

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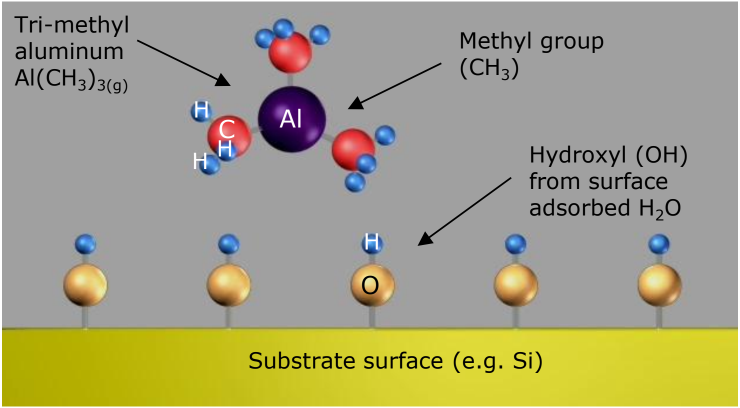
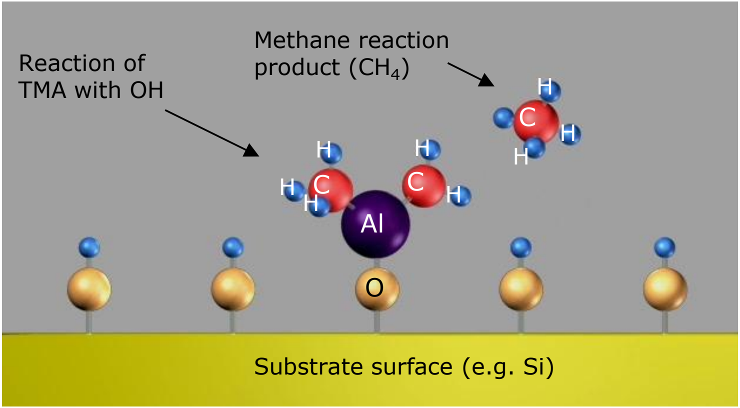
Atomic Layer Deposition

What is ALD?

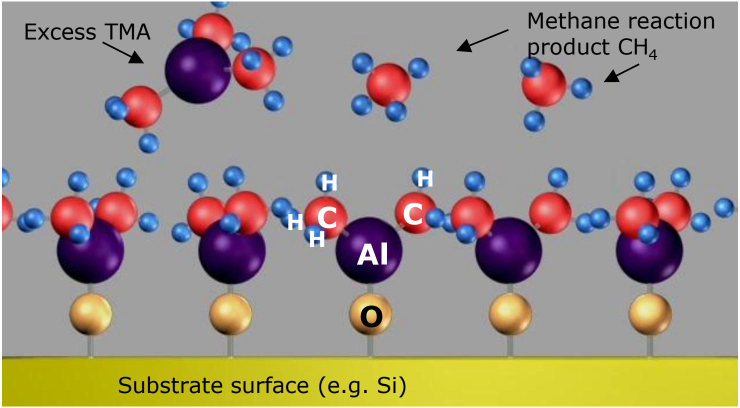
- Chemical deposition method, similar to CVD
- Separation of deposition reaction into metal chemisorption and subsequent oxidation
- Restricts reactions to surface-vapor interactions, no vapor-vapor reactions possible

Atomic Layer Deposition

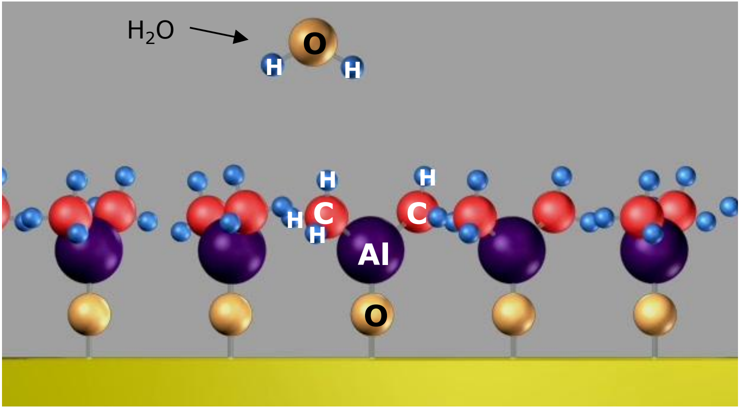


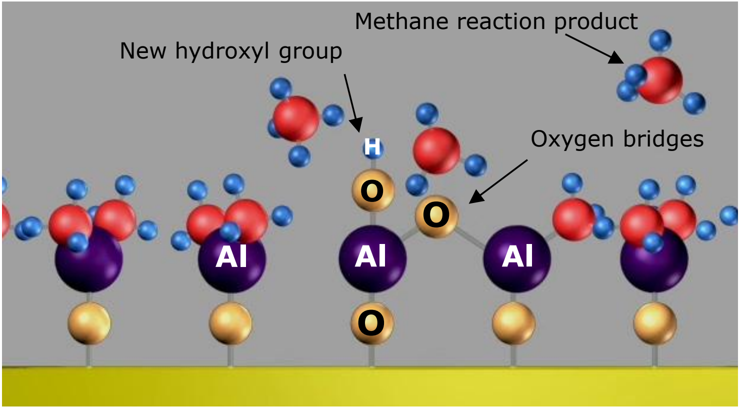

Reaction of
TMA with OH
Methane reaction
product (CH_4)
H
C
H
H
H
H
H
C
H
H
C
H
Al
O
Substrate surface (e.g. Si)

Atomic Layer Deposition

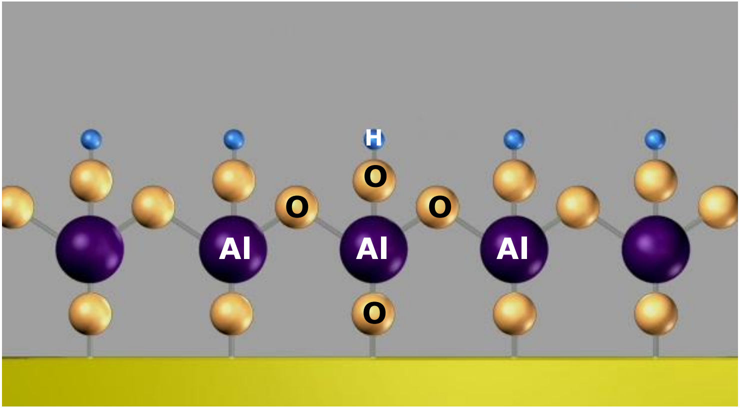


Atomic Layer Deposition




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: Deposition Parameters

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

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Characterization Methods: Thermal Analysis

Thermogravimetric Analysis

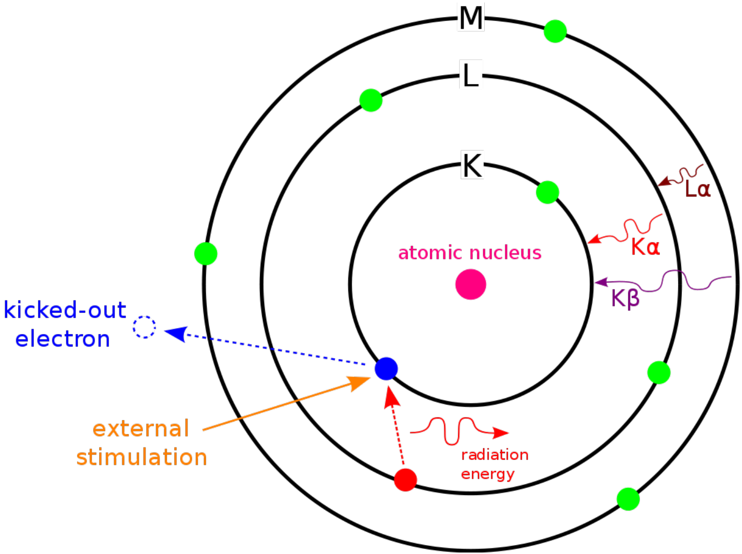
- Method for analyzing mass loss rates as function of temperature
- Useful for determining optimal evaporation temperatures
- Can indicate multi-step evaporation/chemical conversion

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

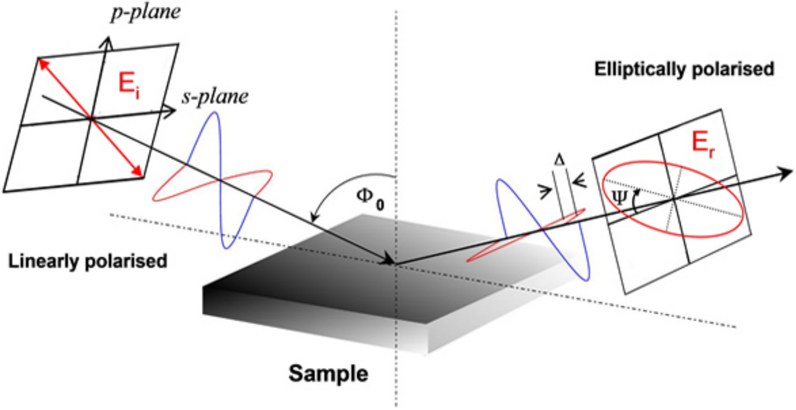
X-Ray Fluorescence Spectroscopy (XRF)

- 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


M
L
K
atomic nucleus
Lα
Kα
Kβ
kicked-out
electron
external
stimulation
radiation
energy

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
Linearly polarised
Φ_0
Sample
Elliptically polarised
E_r
Δ
Ψ

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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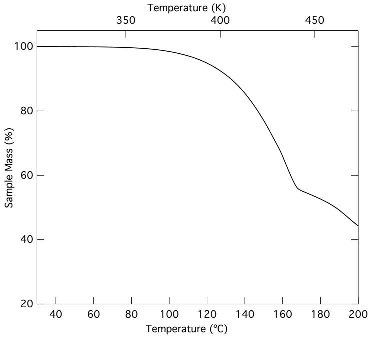
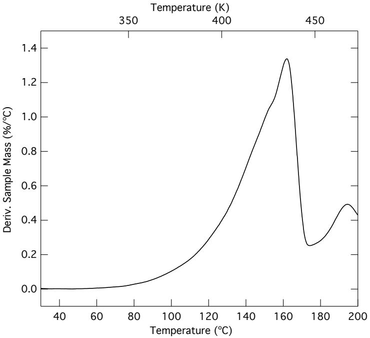
Results: Thermal Analysis

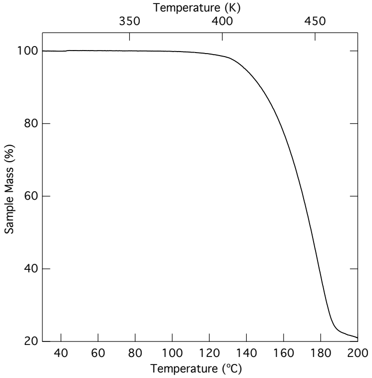
TGA Traces for $Pb(HFAc)_2$

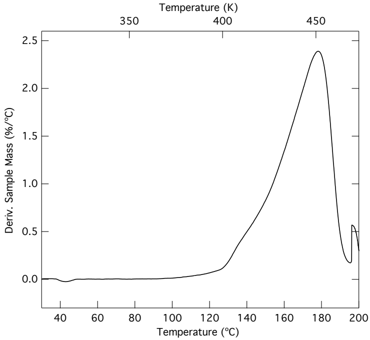




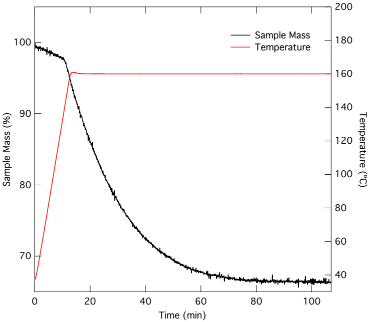
Results: Thermal Analysis

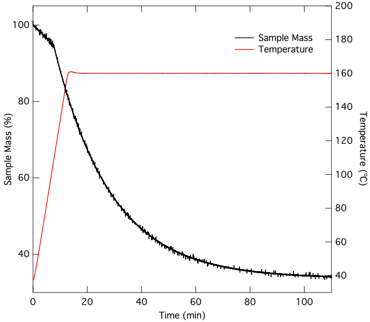
TGA Traces for $Pb(TMHD)_2$





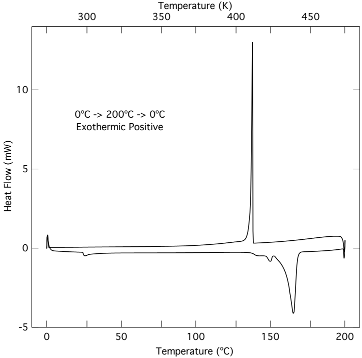
Constant Temperature Studies of $Pb(HFAc)_2$ and $Pb(TMHD)_2$

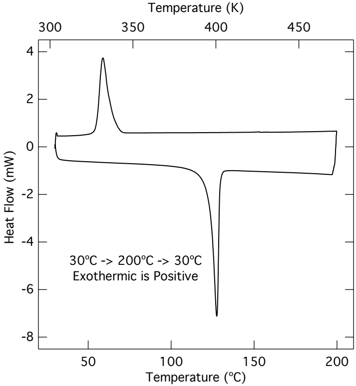




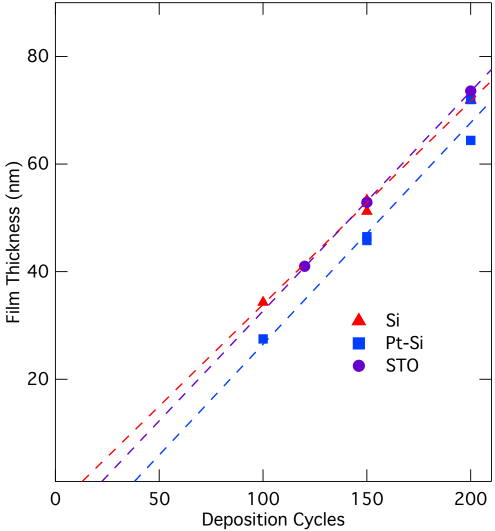
Results: Thermal Analysis

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





Results: Film Growth Rates

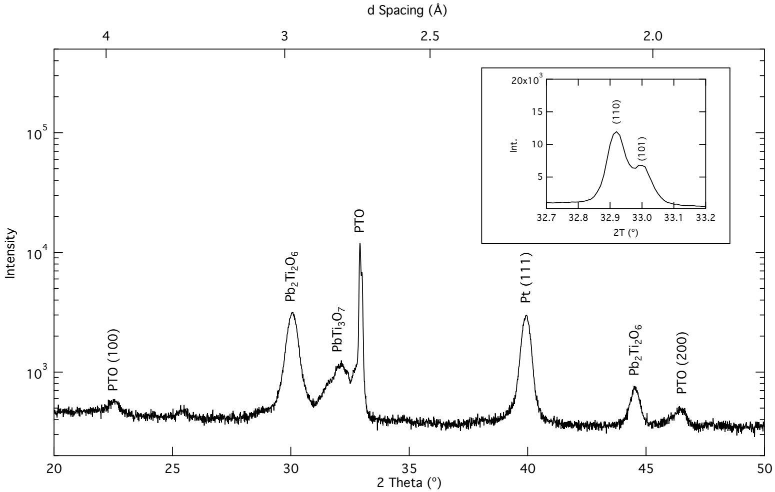


Results: Composition Analysis

Compositions of Selected Sample Films

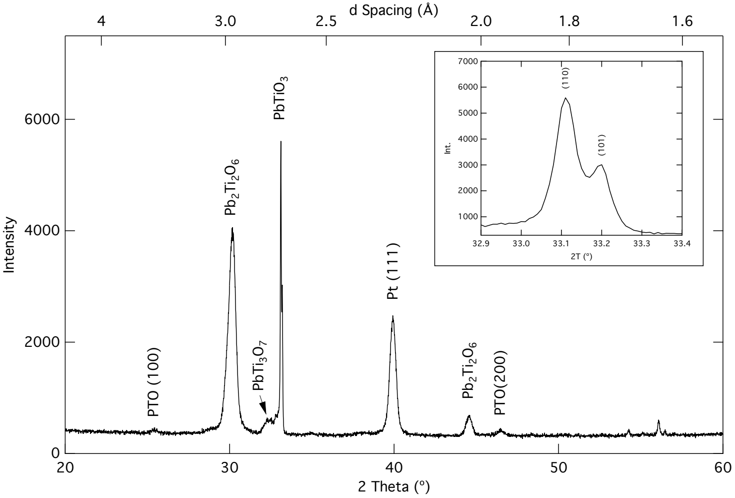
		Composition (%)		
Run #	Substrate	Lead	Titanium	Ti:Pb Ratio
19	SiO_2	65.9	34.1	0.518
	Pt-Si	42.9	57.1	1.333
20	SiO_2	56.6	43.4	0.769
	Pt-Si	51.5	48.5	0.944
21	SiO_2	69.6	30.4	0.437
	Pt-Si	56.1	43.9	0.783
22	SiO_2	67.7	32.3	0.478
	Pt-Si	56.1	43.9	0.784
23	SiO_2	66.9	33.1	0.495
	Pt-Si	49.1	50.9	1.038
24	SiO_2	69.0	31.0	0.450
	Pt-Si	62.2	37.8	0.609

XRD of 20 on Pt-Si

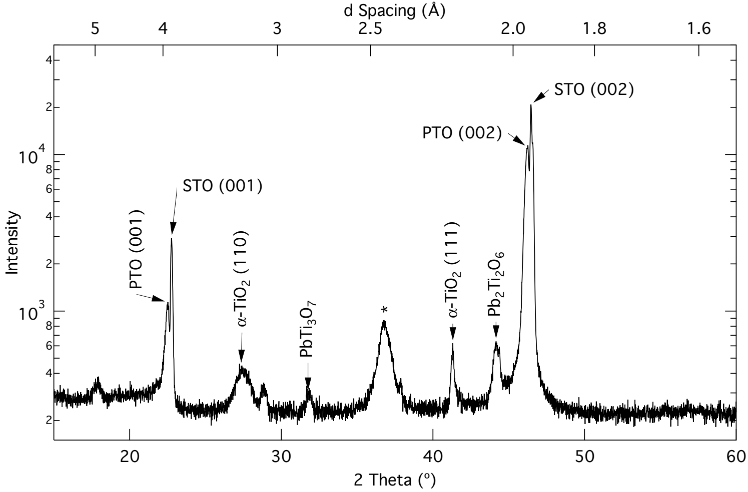


Results: Phase Identification

XRD of 23 on Pt-Si



XRD of 28 on STO(100)



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Conclusions

- A 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?