Title: Polymer assisted deposition – a solution route to new materials

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Intended for: Talk at Argonne
Title:
Polymer assisted deposition – a solution route to new materials

Abstract:
Most advanced deposition of thin films involves high vacuum techniques such as pulsed laser deposition, chemical vapor deposition or atomic layer deposition. Each technique has its strengths and weaknesses. The scaling up of these techniques is very challenging involving significant capital investment. This talk will show results of a new solution route that is highly amenable to being scaled up with little capital cost. The talk will show the versatility and advantages of this new solution technique in making well controlled oxide films, ternary nitride films, high surface area conductive electrode materials, phosphors and modified photonic crystals.
Polymer Assisted Deposition – A Solution Route to New Materials

• T. Mark McCleskey, Eve Bauer, Hongmei Luo, Gavin Collis, Menka Jain, Piyush Shukla, Quanxi Jia, and Anthony K. Burrell.

• Los Alamos National Laboratory
Why a Solution Route?

Goal - Develop a controllable, reproducible, and cost effective growth technique for thin film oxides

Why
✓ CVD, PLD, MBE, ALD all require high vacuum
✓ Large surface area coatings
✓ Non line of site coatings
✓ Practical route to metal-oxide films of the actinides

Issues
✓ Control stoichometry
✓ Control dopants
✓ Extension to nitrides and metals
Why Not Sol-gel Process?

Overview of the sol-gel process

- A sol is a reactive suspension
- Different hydrolysis rates of various alkoxides.
- Need to prepare reactive materials as precursors
- High quality thin films are not the normal result of sol-gel
Polymer Assisted Deposition

- Water-based process
- Metal precursor, polymer
- Metals are bound directly to the polymer or as metal complexes
- Polymer used to control viscosity
- Purification
PAD process

- Water-based process
- Non-volatile Precursors for Actinides
- Metals bound directly to the polymer or as complexes

Select precursor → Mix with polymer

Adjust pH, actinide concentration to assure total complexation

Apply coating Spin coating → Thermal treatment De-polymerization

Polymer volatilizes in reducing atmosphere
What do we have to work with?
Lattice Engineering

Schematic representation of the growth of Eu₂O₃ on LaAlO₃
Epitaxial Films by PAD

Versatile solution route with control of stoichiometry

Oxides

Nitrides

Carbides

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Highly conductive epitaxial BaZrN$_2$ films on STO by PAD

*BaZrN$_2$, tetragonal*

- $a = 4.08$ Å
- $c = 8.52$ Å

STO ($a = 3.901$ Å)

**The epitaxial relationships**

- $(001)_{\text{film}} \parallel (001)_{\text{STO}}$
- $[102]_{\text{film}} \parallel [101]_{\text{STO}}$

FWHM = 2°

FWHM = 0.7°
NbC by PAD

(a) 
(b) 
(c) 

30° in-plane rotation

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Control of Valence State

$\text{UO}_2$ on LAO lattice

$\text{U}_3\text{O}_8$ on hexagonal sapphire lattice

First epitaxial films of $\text{U}_3\text{O}_8$ allow for measurement of band gap

First epitaxial films of $\text{U}_3\text{O}_8$ allow for measurement of band gap

$\text{Adv. Mater.} \ 19, \ 3559-3563 \ (2007)$.

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Epitaxial PuO$_2$ Films on YSZ

C-axis oriented - only 200 and 400 peaks
Extremely high quality epitaxy - rocking curves 0.05°
In plane orientation shown by Phi scan

(200) rocking curve 0.05°
shoulder – YSZ substrate

(220) of PuO$_2$

(400) rocking curve 0.05°
shoulder – K$_\alpha_2$ line

(220) of YSZ

Phi Scan
in plane orientation
XANES Confirm Oxidation State

- bulk PuO$_{2.0}$

Normalized Pu $L_{III}$ Absorbance

18050 eV

18150 eV

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Epitaxial Ge films successfully grown on Si by PAD

Intensity

2θ (degree)

50 60 70 80

Ge (004) Si (004)

Intensity

ϕ (degree)

0 50 100 150 200 250 300 350

Ge (220)

Si (220)

5 nm

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Mobility (@RT) of Ge films by PAD is 1500 cm²/Vs

\[ E_g = 0.66 \text{ eV} \]
\[ \mu_n = 3900 \text{ cm}^2/\text{Vs} \]
Large areas with no cracks

SEM of CuGaO$_2$ film on sapphire

SEM image for BaTiO$_3$ film on Si.
Coating Nanoporous Materials

- Known phosphors on anodiscs to limit waveguiding
- Unique emission observed from Hf, Zr coatings on photonic crystals
PAD provides the ability to incorporate nanoparticles into epitaxial matrixes

Silica/metal-oxide composites have a wide range of applications in catalysis, sensors, optics, magnetism and electronics

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Combinatorial Epitaxy

Line array of two different polymer solutions deposited onto silicon wafer.
Drop diameter – 200 µm, vol. – 20 nL
XRF image of Hf top left
XRF close up image of Hf bottom left
XRF spectrum of spot bottom right (prior to annealing)
Electrical and magnetic properties of multilayer-coated ferromagnetic films

(a) $\rho(T)/\rho(5K)$ vs. $T$ (K)

(b) MR (%) vs. $T$ (K)

Sample ID: ML1, ML2

Number of coatings:
- LSMO
- LCMO
- LaAlO$_3$
Real time video
Nitrides are Possible

UN$_2$ obtained on LAO, N appears to come from EDTA
Can UN$_2$ $\rightarrow$ UN in the thin films?
Typically as one heats UN$_2$ $\rightarrow$ U$_2$N$_3$ $\rightarrow$ UN

UN$_2$ and UN lattices are both cubic contraction of the unit cell
nitrogen moves from octahedral to tetrahedral sites

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN$_2$</td>
<td>5.30</td>
</tr>
<tr>
<td>UN</td>
<td>4.89</td>
</tr>
<tr>
<td>LAO (45°)</td>
<td>5.37</td>
</tr>
<tr>
<td>YSZ</td>
<td>5.13</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>5.47</td>
</tr>
<tr>
<td>NpO$_2$</td>
<td>5.44</td>
</tr>
</tbody>
</table>
Lattice parameters of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ correspond to Ba/Sr ratios.

The graph shows the lattice constant (Å) as a function of $x$ in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, with specific points indicating the lattice constant for different $x$ values. The graph also includes a diagram of X-ray diffraction patterns for different $x$ values, with peaks indicating the crystalline structure for $x=0.0, 0.3, 0.5, 0.7, 1.0$. The graph is labeled with $2\theta$ (degree) on the x-axis and lattice constant on the y-axis.
Dielectric properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ films are a function of Ba/Sr ratios

$$\text{Tunability} = T(\%) = 100 \times \frac{C_0 - C_V}{C_0}$$

Filter
Oscillators
Resonators
Phased array antenna
Complex Oxides

$\text{YBa}_2\text{Cu}_3\text{O}_7$
Control of Metal Oxide Phase

Rutile TiO_2 on Al_2O_3

Anatase TiO_2 on LaAlO_3

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Depolymerization not Combustion

\[ \text{PEI TGA DATA in } H_2 \]

\[ \text{TEMPERATURE (C) TO 450C THEN ISOTHERMAL} \]
Metal Films

- Simulated and experimental XRD patterns of Ir (top) and Pd (bottom)
- Annealed to 450 °C in 6% H₂ atmosphere
Nitride Films

GaN films both hexagonal and cubic

30° in-plane rotation
Lattice mismatch = 14%
Epitaxial superconducting niobium nitride films by PAD

Intensity

35 40 45 50

2θ (degree)

NbN (002) STO (002)

Intensity

-50 0 50 100 150 200 250 300

φ (degree)

NbN (111) STO (111)
NbN film by PAD shows superconducting transition at a temperature of 14 K

\[ \rho_{20\text{K}} = 0.41 \ \mu\Omega \text{ cm} \]

\[ \text{RRR} = \rho_{300\text{K}}/\rho_{20\text{K}} \sim 98 \]
Microstructure of high quality epitaxial NbN films grown by PAD
Both hexagonal $\delta$-MoN and cubic $\gamma$-Mo$_2$N films epitaxially grown by PAD

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Microstructure of high quality epitaxial MoN and Mo$_2$N films grown by PAD
MoN and Mo$_2$N films have different superconducting properties as expected.
Ternary nitride film SrTiN$_2$ epitaxially grown on LaAlO$_3$ by PAD

SrTiN$_2$, tetragonal, $a = 3.88$ Å, $c = 7.7$ Å, mixing Sr and Ti solutions, annealed in NH$_3$ gas

LAO ($a = 3.79$ Å)

STO ($a = 3.901$ Å)

(001)$_{\text{film}}$ $\parallel$ (001)$_{\text{sub}}$

[102]$_{\text{film}}$ $\parallel$ [101]$_{\text{sub}}$

FWHM $= 1.1^\circ$

FWHM $= 0.7^\circ$

Los Alamos Chem. Soc. 130, 15224 (2008)
Smooth and dense SrTiN$_2$ film was epitaxially grown on LAO
SrTiN$_2$: transparent semiconductor

resistivity at room temperature
$\sim 4.7 \times 10^{-4} \ \Omega \cdot \text{cm}$

Direct band semiconductor

$E_g = 3.65 \ \text{eV}$
High quality epitaxial dense $\text{BaZrN}_2$ film

$\text{BaZrN}_2$: $a = 4.08 \, \text{Å}$
$\text{SrTiO}_3$: $a = 3.901 \, \text{Å}$

The lattice misfit: 4.25%

Dislocation spacing $\sim 9.5 \, \text{nm}$

$23 \, a_{\text{BZN}}$ to $24 \, a_{\text{STO}}$
Transport properties show the high quality BaZrN$_2$ films by PAD

\[ \rho (T) = \rho_0 + AT^m \]

Different conduction mechanisms
- electron-electron scattering (5-80 K)
- electron-phonon scattering (80-155 K)
- disordered localized magnetic moment (160-300 K)

Residual resistivity ratio

\[ \text{RRR} = \frac{\rho_{300\text{K}}}{\rho_{5\text{K}}} = 396 \]
SiC film by PAD

Diagram showing the scattering intensity vs. 2θ (degree) and ϕ (degree) for SiC (111) and Si (111) peaks.
Conformal Coatings

- Coating of porous anodiscs without blocking the pores

- Coating is highly uniform across the membrane by XRF across the surface and throughout the thickness

- Coated film lasts 24 hours at pH13 (uncoated is dissolved in 15 minutes)
Phosphors on Porous Anodiscs

- Eu:YVO$_4$ can be deposited as a coating on porous substrates
- Pores remain open
- Waveguiding is limited
Spin Coating

Real time video
Advantages of PAD

• Stability

• Versatility

• Non line of site coating

• Incorporation of nanoparticles

• Control

• New materials?
Microstructure of epitaxial $\text{BaZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ films by PAD on different substrates
Epitaxial metal-oxide films

- High crystallinity Eu$_2$O$_3$ film on LaAlO$_3$ by PAD.
- Sharp interface between the substrate and the film.
- No voids and 2$^{nd}$ phases detectable
The film is oriented not only out-the-plane but also in-the-plane as confirmed from x-ray diffraction 2θ- and φ-scans.