Dielectric Phenomenology

- What controls the magnitude, temperature dependence, and electric field dependence of these thin films?
Fundamental Question

BST 70/30
Bulk Ceramic
(after Hilton & Ricketts,

BST 70/30
Thin Film
52% Ti, 53 nm
Dielectric Response

Curie-Weiss Law: \( \varepsilon(T) = \frac{C}{(T-\theta)} \)

C. Basceri, North Carolina State University, J. Appl. Phys. 82, 2497 (1997)
ATMI MOCVD BST - Thickness and Composition

- Strong effect of thickness and Ti content on zero-bias permittivity


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Thickness and Temperature

- Thickness and temperature dependence contained entirely in zero-bias permittivity

C. Basceri, North Carolina State University, J. Appl. Phys. 82, 2497 (1997)
\[ \frac{A}{C_{\text{tinal}}} = \frac{2A}{C_{\text{int}}} + \frac{2A}{C_{\text{film}}} \approx \frac{2A}{C_{\text{int}}} + \varepsilon_0 \varepsilon_{\text{film}} t \]
Origin of Dielectric Tunability

- Ferroelectricity arises because of long range dipole-dipole interactions / correlations

- Can also be thought of (at least for the displacive case) as a phonon catastrophe
  - A transverse optical phonon vibrational frequency approaches zero as a function of temperature (“softens”); i.e. the polar, atomic displacements intrinsic to the phonon become static.
  - As this temperature is approached, the zero bias polarizability increases because of the increasing softness to the polar displacements
  - Application of an electric field hardens this phonon mode, causing the permittivity to decrease.
Origin of Dielectric Tunability

- Thomas Model (1969)
  - Begin with a vibrational degree of freedom
  - Include intercell interactions (dipole-dipole)
  - Anharmonicity in the vibrational degree of freedom leads to ferroelectric behavior, Curie-Weiss behavior above $T_c$

\[ H = \sum_l (V(p_l) - E_{p_l}) - \frac{1}{2} \sum_{l \neq l'} v_{ll'} p_l p_{l'} \]

\[ V(p_l) = \frac{1}{2} w_0 p_l^2 + \frac{1}{2} u p_l^4 \]

- Consistent with mode-softening
- Yields results consistent with Landau Ginzburg Devonshire (mean field) theory (2\(^{nd}\) order phase transition) correct to 3\(^{rd}\) order in polarization

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Phenomenological Approach to the Effect of Stress in Ferroelectric Thin Films

Mean Field Theory: Illustration for \((100)_{\text{pseudocubic}}\) films

- Free energy functional for film under plane biaxial stress (Legendre transformation of elastic Gibbs function \(G\)) given in:

\[
\tilde{G}(\vec{P}, x, T) = G + x_1 \sigma_1 + x_2 \sigma_2 + x_6 \sigma_6
\]

- Empirically, our BST described by:

\[
E_{\text{app}} \approx 2\alpha^*_3 P_3 + 4\alpha^*_{33} P_3^3
\]

\[
\approx 2\left(\frac{\beta}{t} + \gamma(T)\right) P_3 + 4\alpha^*_{33} P_3^3
\]
Origins of Stress

- **Hydrostatic**
  - Point defects
  - Nonstoichiometry

- **Biaxial plane stress**
  - Temperature-dependent “lattice” mismatch
    - Matching/relaxation at growth/anneal temperature
    - Difference in coefficients of thermal expansion
      \[ \sigma_1 = Mx_1 = M(\alpha_s - \alpha_f)(T - T_{freeze}) \]
  - Defect dipoles
FIG. 3. X-ray $\omega$-2$\theta$ scans for $\sim$1400 Å thick homoepitaxial SrTiO$_3$ layers grown with background oxygen pressures of 100, 10, and 1 mTorr.

E.J. Tarsa, E.A. Hachfeld, F.T. Quinlan, J.S. Speck, and M. Eddy,
Need to understand the strain-polarization coupling.

- Films generally under plane biaxial stress from thermal expansion mismatch with substrate, plus hydrostatic stress components due to point defects, etc.

\[
\begin{align*}
\alpha_{\text{SrTiO}_3} &\sim 10 \times 10^{-6} / \text{K} \\
\alpha_{\text{Si}} &\sim 3.5 \times 10^{-6} / \text{K} \\
\alpha_{\text{MgO}} &\sim 13 \times 10^{-6} / \text{K} \\
\alpha_{\text{LaAlO}_3} &\sim 11 \times 10^{-6} / \text{K} \\
\alpha_{\text{Pt}} &\sim 9 \times 10^{-6} / \text{K}
\end{align*}
\]

- Stresses can be very large: 100’s of MPa
Impact of Biaxial Stress on Inverse Permittivity Tensor

Unconstrained, above $T_C$

Biaxial tension, above $T_C$  Biaxial compression, above $T_C$
(100) Fiber-textured BST 70/30: $\tilde{Q}_{12} = 0.023$ m$^4$/C$^2$

**FIG. 3.** Measured capacitance per unit film area as a function of the applied stress. For capacitor 1 data on loading and unloading the capacitor are shown. Capacitor 2 was loaded to the fracture of the substrate.

**FIG. 4.** The relationship between total stress and capacitance and total stress, applied and initial, in a BST film.

T.M. Shaw, Z. Suo, M. Huang, E. Liniger, R.B. Laibowitz, and J.D. Baniecki

Phenomenological Approach to Dielectric Behavior

- Permittivity/susceptibility:
  \[ \varepsilon_0 \chi_i = \frac{\partial P_i}{\partial E_i} \approx f(\alpha_i^*, \alpha_{ii}^*) \]

- Above any phase transitions, \( \varepsilon_0 \chi_i(E=0) = 1/(2 \alpha_i^*) \)
  \[ \alpha_1^* = \frac{T - \theta_1}{2\varepsilon_0 C''} \]
  \[ \alpha_3^* = \frac{T - \theta_3}{2\varepsilon_0 C'} \]
  \[ \theta_i = f(x_1, Q_{ij}, s_{ij}) \Rightarrow \theta_1 > \theta_3 \ (Tension) \]
\[ \varepsilon_{1}, \varepsilon_{3}, \varepsilon_{\text{free}} \]

Inverse Permittivity vs Temperature

- \( P_s \)
- \( \varepsilon_{3} \)
- \( \varepsilon_{1} \)
- \( \varepsilon_{\text{free}} \)
Below $\theta_1$, additional coupling breaks Curie-Weiss law:

$$\alpha_3^* = \frac{T - \theta_3}{2\varepsilon_0 C'} + 2\alpha_{13}^*(P_1(T))^2 + 2\alpha_{113}^*(P_1(T))^4$$

Coefficients:

- $\theta_3$ given earlier
- $C' = \left\{ \frac{1}{C} - \frac{4\varepsilon_0 (\Delta \alpha_{\text{THERM}}) Q_{12}}{s_{11} + s_{12}} \right\}^{-1}$ (est. $C' \sim 20\% > C$)
Effect of Strain on Curie-Weiss Behavior for Different Film Orientations
Summary

In-Plane Coupling

Bulk

Strain

Excess Ti

"Interface Effect"

53.5% Ti
40 nm

Zero-Bias Relative Permittivity vs Temperature (K)
Thickness Dependence: Interface Effect

- **Interface contamination:**
  - TOF-ISARS ion scattering spectrometry (ANL):
    - Hydrogen- and carbon-containing species present on BST surface at Pt TE dep. temperature.

- **Surface/interface discontinuity: Stiffening of ferroelectric soft mode near interface**
  - Our results of same magnitude as those analyzed by Zhou and Newns.

- **Incomplete electrode compensation of polarization**

- **Inhomogeneous strain, composition gradients at the interface(s)**
Magnitude of $\beta$

$$E_{app} \approx 2\left(\frac{\beta}{t} + \gamma(T)\right)P_3 + 4\alpha_{33}^* P_3^3$$

- Thickness effect equivalent to interface capacitance of $\sim 117\text{fF/\mu m}^2$, independent of %Ti up to “reasonable” levels.
Magnitude of $\gamma$

$$E_{app} \approx 2\left(\frac{\beta}{t} + \gamma(T)\right) P_3 + 4\alpha_{33}^* P_3^3$$

![Graph showing the relationship between permittivity and at%Ti](image_url)
TOF-ISARS MSRI Spectrum of 51% Ti BST Surface at 350°C
MSRI Evolution of C/H Species During Heating in Vacuum and Oxygen Ambients

- Temperature (°C)
- Normalized "C" Peak Counts
- Normalized "H" Peak Counts

(a) Vacuum
(b) P(O₂) = 0.5 mTorr
(c) P(O₂) = 1 mTorr

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J-V Behavior of 60 nm Pt/BST/Pt Heterostructures
Native vs. Cleaned

Both BST capacitors without post-top electrode deposition anneauing

Typical BST capacitor
(25 °C, vacuum)

BST capacitor with cleaned interface

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Processing and Integration Challenges

- Deposition Methods
- Electrodes and Barriers
- Etching
- Compatible Subsequent Processing
- Fab Acceptance
## Candidate Growth Technologies

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape-Casting</td>
<td>¥ Inexpensive, ceramic process ¥ Large area</td>
<td>¥ Morphology</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ High thermal budgets</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Thick film process</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Poor microstructural control</td>
</tr>
<tr>
<td>Chemical Solution</td>
<td>¥ Inexpensive, low capital investment ¥ Rapid sampling of materials ¥</td>
<td>¥ Phase control</td>
</tr>
<tr>
<td>Deposition</td>
<td>Quickly produce new materials</td>
<td>¥ Morphology</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Scalability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Reproducibility</td>
</tr>
<tr>
<td>Pulsed Laser Deposition</td>
<td>¥ Rapid sampling of materials ¥ Quickly produce new materials</td>
<td>¥ Morphology (boulders)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Point defect concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Scalability (small areas only)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Uniformity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ High residual stresses</td>
</tr>
<tr>
<td>Sputtering</td>
<td>¥ Cost ¥ Uniformity ¥ Scalability ¥ Standard IC processing ¥ Low growth</td>
<td>¥ Point defect concentration</td>
</tr>
<tr>
<td></td>
<td>temperatures</td>
<td>¥ Residual stresses</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Composition control</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Slow</td>
</tr>
<tr>
<td>MOCVD</td>
<td>¥ Uniformity ¥ Morphology ¥ Composition selection ¥ Low point defect</td>
<td>¥ Immature technology</td>
</tr>
<tr>
<td></td>
<td>concentration ¥ High conformality ¥ Scalability</td>
<td>¥ Precursor stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Precursor availability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Expensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¥ Down-times</td>
</tr>
</tbody>
</table>
Sputtered BST

- Commercial Edwards 306 RF magnetron sputtering system
- ANL substrate holder for rotation and heating (800°C in oxygen)
Sputtering Parameters

- **Substrates:** Pt/SiO₂/Si or Pt/TiO₂/SiO₂/Si
- **Deposition temperature:** RT-750°C
- **Pressure (O₂+Ar):** 22 mTorr – 58 mTorr
- **Reactive gases:** O₂ and N₂O
- **P(O₂)/P(Ar):** 1/5
- **Deposition rate:** 10 Å/min
- **Substrate-Target Distance:** 10 cm
- **RF Power:** 95 watts
- **Substrate Rotation:** ~ 30 R.P.M.
Sputtered BST Films

**Structural Properties**
- Polycrystalline orientation
- RMS surface roughness: 2 nm

**Current Electrical Properties**
- Capacitance density of 6 µF/cm²
- Dielectric loss ~ 0.005
- Breakdown strength ~ 3 MV/cm
- Energy stored ~ 20 J/cc
- Scaling to larger thickness

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BST Composition vs. Sputtering Pressure

(a) Total Pressure (Ar+O₂)

(b) O₂/Ar Ratio

P = 22 mTorr

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Sputtered BST Permittivity & Loss

Permittivity vs. Field (kV/cm)

Loss tangent vs. Field (kV/cm)

(Ba+Sr)/Ti = 0.98
(Ba+Sr)/Ti = 0.9
(Ba+Sr)/Ti = 0.85
(Ba+Sr)/Ti = 0.73

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Multilayer Thin Films

- Individual layers with unique compositions and microstructures can be deposited by MOCVD and sputtering.

- Multilayer schemes can be developed to obtain improved electrical properties.

- Example: Ti-rich layers at the BST film / Pt electrode interface.
Multilayered $(\text{Ba}_x\text{Sr}_{1-x})\text{Ti}_{1+y}\text{O}_{3+z}$ Films
$(\text{Ba}+\text{Sr})/\text{Ti}=0.73/0.9/0.73$
## Sputtered Ti-rich Interfacial Layers

<table>
<thead>
<tr>
<th></th>
<th>Single layer</th>
<th>Multilayer (interfacial layers)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Permittivity:</strong></td>
<td>480</td>
<td>270</td>
</tr>
<tr>
<td><strong>Zero bias loss:</strong></td>
<td>0.013</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>Breakdown field:</strong></td>
<td>~1 MV/cm</td>
<td>3-4 MV/cm</td>
</tr>
<tr>
<td><strong>% Tunability:</strong></td>
<td>72%</td>
<td>76%</td>
</tr>
<tr>
<td><strong>Figure of merit:</strong></td>
<td>55</td>
<td>152</td>
</tr>
<tr>
<td><strong>Energy density:</strong></td>
<td>11.25 J/cm³</td>
<td>33.51 J/cm³</td>
</tr>
</tbody>
</table>

*Figure of merit = tunability/loss*
Metalorganic Chemical Vapor Deposition (MOCVD)

Thin film formed by reaction of metalorganic vapors on the substrate

- High growth rates
- Ability to tailor composition
- No energetic ion bombardment
- Excellent uniformity (composition and morphology)
- Excellent coverage of complex topographies
- High device reliability and yields

Issues:
- High temperatures (500-700°C)
- Oxidizing environment

from K.F. Jensen, Microelectronic Processing: Chemical Engineering Aspects, p. 200
Deposition Regimes

❖ Reaction limited
  ➤ Lower temperature
  ➤ Conformal coverage
  ➤ May require subsequent anneal to fully crystallize or react species into desired phase

❖ Transport limited
  ➤ Higher temperature
  ➤ May have difficulty achieving desired conformality
Horizontal Reactor with Bubbler Sources

Horizontal Flow
Resistive Heating
Quartz Tube
Table 1. Representative volatile MOCVD precursors used in ferroelectric thin film deposition and their vaporization properties [61].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>Melting Point</th>
<th>Vapor Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(TMHD)$_2$</td>
<td>solid</td>
<td>194-197°C</td>
<td>0.05 torr at 200°C</td>
</tr>
<tr>
<td>Bi(TMHD)$_3$</td>
<td>solid</td>
<td>114-116°C</td>
<td>0.05 torr at 150°C</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$Bi</td>
<td>solid</td>
<td>77-78°C</td>
<td>0.20 torr at 100°C</td>
</tr>
<tr>
<td>(CH$_3$)$_3$Bi</td>
<td>liquid</td>
<td>-107.7°C</td>
<td>9.50 torr at 0°C</td>
</tr>
<tr>
<td>La(TMHD)$_3$</td>
<td>solid</td>
<td>227-231°C</td>
<td>0.20 torr at 210°C</td>
</tr>
<tr>
<td>(C$_5$H$_5$)$_2$Mg</td>
<td>solid</td>
<td>176°C</td>
<td>0.10 torr at 160°C</td>
</tr>
<tr>
<td>Mg(TMHD)$_2$</td>
<td>solid</td>
<td>135-150°C</td>
<td>0.05 torr at 150°C</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_4$Pb</td>
<td>liquid</td>
<td>-136°C</td>
<td>2.00 torr at 50°C</td>
</tr>
<tr>
<td>Pb(TMHD)$_2$</td>
<td>solid</td>
<td>126-128°C</td>
<td>0.05 torr at 180°C</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_4$Pb</td>
<td>solid</td>
<td>229-230°C</td>
<td>0.05 torr at 230°C</td>
</tr>
<tr>
<td>Nb(OC$_2$H$_5$)$_5$</td>
<td>liquid</td>
<td>6°C</td>
<td>0.10 torr at 142°C</td>
</tr>
<tr>
<td>Ru(TMHD)$_3$</td>
<td>solid</td>
<td>120-125°C</td>
<td>0.50 torr at 120°C</td>
</tr>
<tr>
<td>(C$_5$H$_5$)$_2$Ru</td>
<td>solid</td>
<td>194-198°C</td>
<td>0.10 torr at 190°C</td>
</tr>
<tr>
<td>Sr(TMHD)$_2$</td>
<td>solid</td>
<td>125°C</td>
<td>0.30 torr at 230°C</td>
</tr>
<tr>
<td>Ta(OC$_2$H$_5$)$_5$</td>
<td>liquid</td>
<td>21°C</td>
<td>0.10 torr at 140°C</td>
</tr>
<tr>
<td>Sn[OC(CH$_3$)$_3$]$_4$</td>
<td>liquid</td>
<td>45°C</td>
<td>0.30 torr at 65°C</td>
</tr>
<tr>
<td>(C$_4$H$_9$)$_4$Sn</td>
<td>liquid</td>
<td>-112°C</td>
<td>10.0 torr at 145°C</td>
</tr>
<tr>
<td>Ti[OCH(CH$_3$)$_2$]$_4$</td>
<td>liquid</td>
<td>19°C</td>
<td>5.00 torr at 92°C</td>
</tr>
<tr>
<td>Ti[OC(CH$_3$)$_3$]$_4$</td>
<td>liquid</td>
<td></td>
<td>0.20 torr at 70°C</td>
</tr>
<tr>
<td>Ti[OC(CH$_3$)$_3$]$_2$(TMHD)$_2$</td>
<td>solid</td>
<td>220°C</td>
<td>1.00 torr at 240°C</td>
</tr>
<tr>
<td>Zr[OC(CH$_3$)$_3$]$_4$</td>
<td>liquid</td>
<td></td>
<td>1.00 torr at 65°C</td>
</tr>
<tr>
<td>Zr(TMHD)$_4$</td>
<td>solid</td>
<td>308°C</td>
<td>0.10 torr at 180°C</td>
</tr>
</tbody>
</table>

Adapted from C. Foster, in *Thin Film Ferroelectric Materials and Devices*, ed. R. Ramesh (Kluwer Academic Publishers, Norwell, MA, 1997)
\[ \text{\textbf{\(\beta\)-Diketonates}} \]

\[
\begin{align*}
R_1 &= R_2 = \text{CH}_3 & \text{(acetylacetonate)} \\
R_1 &= R_2 = \text{C(CH}_3)_3 & \text{(tetramethylheptadionate)} \\
R_1 &= \text{C(CH}_3)_3, R_2 = \text{CF}_3 & \text{(trifluorodimethylhexanedionate)} \\
R_1 &= \text{C(CH}_3)_3, R_2 = \text{C}_3\text{F}_7 & \text{(heptafluorodimethyloctanedionate)} \\
R_1 &= \text{C(CH}_3)_3, R_2 = \text{CF}_3 & \text{(hexafluoroacetylacetonate)}
\end{align*}
\]

\[ \text{\textbf{Organometallics}} \]

\[
\begin{align*}
\text{phenyl} & \quad \text{cyclopentadienide} & \text{tetraethyllead}
\end{align*}
\]

\[ \text{\textbf{Alkoxides}} \]

\[
\begin{align*}
R_1 &= \text{CH}_3 & \text{(methoxide)} \\
R_1 &= \text{C}_2\text{H}_5 & \text{(ethoxide)} \\
R_1 &= \text{CH(CH}_3)_2 & \text{(isopropanoxide)} \\
R_1 &= \text{C(CH}_3)_3 & \text{(t-butoxide)}
\end{align*}
\]

Figure 3. Schematic structural diagrams of typical MOCVD precursors used in the growth of perovskite-structured electroceramic oxides films [51].

### Pb(Zr,Ti)O$_3$ GROWTH CONDITIONS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>700°C</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>8 torr</td>
</tr>
<tr>
<td>OM precursor temperature</td>
<td></td>
</tr>
<tr>
<td>Zr(O(CH$_3$)$_3$)$_4$</td>
<td>29-30 °C</td>
</tr>
<tr>
<td>Ti(OC$_3$H$_7$)$_4$</td>
<td>39-40 °C</td>
</tr>
<tr>
<td>Pb(C$_2$H$_5$)$_4$</td>
<td>27-28 °C</td>
</tr>
<tr>
<td>OM precursor pressure</td>
<td></td>
</tr>
<tr>
<td>Zr(O(CH$_3$)$_3$)$_4$</td>
<td>40 torr</td>
</tr>
<tr>
<td>Ti(OC$_3$H$_7$)$_4$</td>
<td>150 torr</td>
</tr>
<tr>
<td>Pb(C$_2$H$_5$)$_4$</td>
<td>400 torr</td>
</tr>
<tr>
<td>Flow rate of OM and carrier gas (N$_2$)</td>
<td></td>
</tr>
<tr>
<td>Zr(O(CH$_3$)$_3$)$_4$</td>
<td>25 sccm</td>
</tr>
<tr>
<td>Ti(OC$_3$H$_7$)$_4$</td>
<td>35 sccm</td>
</tr>
<tr>
<td>Pb(C$_2$H$_5$)$_4$</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Flow rate of reactant gas (O$_2$)</td>
<td>150 sccm</td>
</tr>
<tr>
<td>Flow rate of background gas (N$_2$)</td>
<td>600 sccm</td>
</tr>
<tr>
<td>Film thickness</td>
<td>20-5000 nm</td>
</tr>
<tr>
<td>Film growth rate</td>
<td>40 Å/min. SrTiO$_3$/SrRuO$_3$</td>
</tr>
<tr>
<td>Substrates</td>
<td>SrTiO$_3$(001), SrRuO$_3$/SrTiO$_3$(001)</td>
</tr>
</tbody>
</table>
Fig. 8. Equilibrium curves for two reactions governing adsorption-controlled growth of GaAs (dashed lines) and two reactions governing adsorption-controlled growth of PbTiO$_3$ (solid lines).
Compositional Control in PZT Thin Films

![Graph showing the variation of film composition with the carrier-gas-flow-rate ratio.]  

Figure 4. The variation of film composition with the carrier-gas-flow-rate ratio, $x_g = Zr/(Zr+Ti)$, is shown [56], demonstrating compositional control of epitaxial PZT thin films grown at 700°C on epitaxial SrRuO$_3$(001) buffered SrTiO$_3$(001).

Adapted from C. Foster, in *Thin Film Ferroelectric Materials and Devices*, ed. R, Ramesh (Kluwer Academic Publishers, Norwell, MA, 1997)

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Film Synthesis

MOCVD BST

- Ba(thd)$_2$, Sr(thd)$_2$ with adducts
- TiO(thd)$_2$, TiO(O-I-Pr)$_2$(thd)$_2$
- Poor volatility/stability of Ba, Sr precursors
  - Ba(thd)$_2$ m.p. = 220°C, 0.05mm @200°C
- Showerhead for large area uniformity
- Warm walls and showerhead
- Applied Materials Reactor, Varian/Novellus Reactor with ATMI LDS system
As-Deposited Films: MOCVD Parameters

- Substrate heater temperature: 600-750°C
- Reactor pressure: 0.4 – 2.7 Torr
- Reactive gases: O₂ and N₂O
- Reactive gas flow rate: 250-1000 SCCM
- Deposition rate: 30 – 120 Å/min
- Top electrodes: e-beam Pt
- Post electrode anneal: 550°C for 0.5 hrs
Nonstoichiometry

- **Bulk Composition**\(^1\)  
  \[49.98 < \%\text{Ti} < 50.03\]

- **Thin Film Compositions**\(^2\)  
  \[46 < \%\text{Ti} < 57\]

- Many physical properties, although not permittivity, are best when the Ti \% is in the 51.5 to 52.5 \% range.

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53.5% Ti:

Oxygen K-edges

51% Ti

53.5% Ti

SrTiO$_3$

TiO$_2$

53.5% Ti (on GB)

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Titanium L$_{2,3}$-edges

- Changes in Ti content effect the grain interiors as well!
Etching

- Reactive ion etching of non-standard materials is a challenge

Adapted from S. Summerfelt, in *Thin Film Ferroelectric Materials and Devices*, ed. R. Ramesh (Kluwer Academic Publishers, Norwell, MA, 1997)
Integration Challenges

❖ Bottom Electrode
  ➢ Material must resist oxidation, reactions
  ➢ Diffusion barriers
  ➢ Etch

❖ Conformal BST
  ➢ Require excellent properties, low thermal budget

❖ Top Electrode
  ➢ Material
  ➢ Etch

❖ Post-processing
  ➢ Interlayer dielectric depositions
  ➢ H₂ anneals

❖ Fab Compatibility
  ➢ Tool sharing
  ➢ Error tolerance / recovery