Ferroelectric Thin Films and Their Applications

Application of ferroelectric films:
- DRAM storage capacitor
- Microactuator
- Piezoelectricity
- Polarizability
- NVFRAM memory cell
- High permittivity
- Thermal infrared switch
- Electro-optic activity
- Pyroelectricity
- Infrared sensor

Conventional Radar

Phased Array Radar

Phase Shifter
Ferroelectrics are polar materials that have at least two equilibrium orientations of a spontaneous polarization. The spontaneous polarization can be switched by an applied external electric field.
Ferroelectricity and Applications

Below $T_c$
- Bistable polarization
- Nonvolatile memory

Near $T_c$
- $\varepsilon = dP/dE$

Well above $T_c$
- $\varepsilon_{para} >> \varepsilon_{sio_2}$
- DRAM
- Multilayer Capacitor

Microwave Tuning
**Tunable Ferroelectric Materials**

- **Large dielectric tunability**
  \[ n = \frac{\varepsilon(0)}{\varepsilon(E)} \]
  \[ n_t = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \]

- **Low dielectric losses**
  \[ \tan\delta = \frac{\varepsilon''}{\varepsilon} \]
  \[ Q = \tan\delta^{-1} \]

\( \varepsilon', \varepsilon'' \) real, imaginary part of relative permittivity

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**Graph:**
- **Mn:BSTO (60:40) films on (001) MgO**
- Dielectric constant (x1000)
- Field (V/\(\mu\)m)
- tunability = 80%
Electronic Properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ Bulk Ceramics Measured at 1 K Hz and 300 K

<table>
<thead>
<tr>
<th>Barium Content</th>
<th>Dielectric Constant</th>
<th>Loss Tangent</th>
<th>Tunability % (2.0V/μm)</th>
<th>Curie Temperature</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.000</td>
<td>-240 °C</td>
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<tr>
<td>0.30</td>
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<td>0.00025</td>
<td>2.200</td>
<td>-105</td>
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<td>0.00961</td>
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<td>10</td>
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<td>0.70</td>
<td>4322.86</td>
<td>0.03355</td>
<td>48.60</td>
<td>40</td>
</tr>
<tr>
<td>1.00</td>
<td>2082.38</td>
<td>0.03675</td>
<td>18.00</td>
<td>135</td>
</tr>
</tbody>
</table>

Dielectric tunability $\Delta = \frac{\epsilon(0) - \epsilon(E)}{\epsilon(0)} \times 100\%$

Data from U. S. Army Research Laboratory, Ceramics Research Branch, 1997
\[ \Delta G = \alpha_{11} (p_1^2 + p_2^2 + p_3^2) + \alpha_{111} (p_1^4 + p_2^4 + p_3^4) \]
\[ + \alpha_{12} (p_1^2p_2^2 + p_2^2p_3^2 + p_3^2p_1^2) + \alpha_{11} (p_1^6 + p_2^6 + p_3^6) \]
\[ + \alpha_{12} (p_1^4(p_2^2 + p_3^2) + p_2^4(p_3^2 + p_1^2) + p_3^4(p_1^2 + p_2^2)) \]
\[ + \alpha_{11} (p_1^8 + p_2^8 + p_3^8) + \alpha_{111} (p_1^{10} + p_2^{10} + p_3^{10}) \]
\[ + \alpha_{12} (p_1^6(p_2^2 + p_3^2) + p_2^6(p_3^2 + p_1^2) + p_3^6(p_1^2 + p_2^2)) \]
\[ + \mu_{33} (p_3^4 + p_3^2p_1^2 + p_3^2p_2^2 + p_1^2p_2^2) \]
\[ + \mu_{44} (p_1^4 + p_2^4 + p_3^4 + p_1^2p_2^2 + p_1^2p_3^2 + p_2^2p_3^2) \]
\[ + \beta_{11} (e_1^2 + e_2^2 + e_3^2 - e_1e_2 - e_2e_3 - e_3e_1) \]
\[ + \gamma_{11} (p_1^4 + p_2^4 + p_3^4 - p_1^2p_2^2 - p_2^2p_3^2 - p_3^2p_1^2) \]
\[ + \gamma_{11} (p_1^6 + p_2^6 + p_3^6 - p_1^4p_2^2 - p_2^4p_3^2 - p_3^4p_1^2) \]
\[ + \gamma_{11} (p_1^8 + p_2^8 + p_3^8 - p_1^6p_2^2 - p_2^6p_3^2 - p_3^6p_1^2) \]


Shaw et al., APL 75, 2129 (1999)
Biaxial film strain due to the lattice and thermal mismatch with the substrate shifts the phase transformation temperature to higher temperatures (increases the stability of the ferroelectric phase).

- New ferroelectric phases appear
- The order of the phase transformation is changed

Microwave Phase Shifter

8 element CMPS Au/Ag/BSTO/12 mil MgO array elements
Data taken at 23.675 GHz and 300 K

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Data taken at 23.675 GHz and 300 K

Difficulties in BSTO thin Films

- High frequency soft mode effect
- Multiphase transitions
- Nano phase separation
Previous Works from Other Groups

![Graph showing capacitance (fF) vs electric field (KV/cm) for different compositions of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$/TiO$_2$.](image)

Jia et al., APL (2002)
Previous Works from Other Groups

X-ray Diffraction Studies of Mn:BSTO Films

θ – 2θ scans indicate that the BSTO films are c-axis oriented.

Rocking curve measurements showing that the FWHM value from the (001) reflection of the Mn:BSTO films is about 0.5°, indicating that the Mn:BSTO films have good single crystal quality.

Pole figure studies reveals that only four (111) reflections are appeared in the pattern, verified that the films are single crystalline.
TEM Studies of Mn:BSTO Thin Films on MgO

Appl. Phys. Lett. 87 (2005) 152901
Mn:BSTO Films on (001) MgO

ε = 1200
Tan δ = 0.005
@ 12.84 GHz & RT

Tunability = 80%

Mn:BSTO (60:40) films on (001) MgO

Relative Dielectric Constant

Field (V/μm)

S21(dB)

CPW/MgO

CPW/BST/MgO

Frequency (GHz)

Frequency (GHz)

Dielectric constant (x1000)

Magnitude (dB)

Frequency (GHz)

Appl. Phys. Lett. 87 (2005) 152901
Advantages of \((\text{Pb, Sr})\text{TiO}_3\)

The Curie temperature -- 36K to 760K, varied with increment of lead dopants.

Only one phase transition cubic to tetragonal

High dielectric constant, high tunability and low dielectric loss.
Growth Rate from Vapor Phase

Nucleation rate $N$ is proportional to the stable nuclei concentration $N'$ (number per unit area), the impinging atoms $f$ onto the nuclei of the critical area $A'$.

$$N = N' A' f \left( \frac{\text{nuclei}}{\text{cm}^2} - s \right)$$

where

$$N' = n_s \exp(-\Delta G' / kT), \quad A' = 4\pi r^2,$$

and

$$f = \alpha \frac{N_A (P_V - P_c)}{\sqrt{2\pi MRT}}$$

$\alpha$ is the sticking coefficient, or the ratio of condensed mass over the total impinging atom mass.

$$N = n_s \exp(-\frac{\Delta G'}{kT}) 4\pi r^2 \frac{\alpha (P_V - P_c)}{\sqrt{2\pi MRT}}$$

The no dearth adatom model!
Diffusion-Limited Growth
-- Low Temperature Pattern Formation

Atoms to be crystallized are transported to the crystal surface
-- the chemical diffusion.

The atoms are incorporated in the crystal at the surface
-- surface kinetics

The released latent heat should be transported away from the crystal surface
-- heat conduction
Diffusion-Limited Aggregation

If there are $N(r)$ atoms in a region with a radius $r$, the number of atoms in the radius $br$ is $N(r) = b^{D_f}N(r)$. According to fractal theory,

$$N(r) = r^{D_f} N(1)$$

Au on Ru
Kinetics-Limited Growth Theory

Introducing the adatom surface diffusion, foreign atoms desorbed from the surface, and the solid nucleation structure, we can rewritten it into:

\[ N = n_s \exp\left(\frac{E_{\text{des}} - E_{sd} - \Delta G'}{kT}\right)2\pi r'd \sin \theta \frac{P_v}{\sqrt{2\pi MRT}} \]

Notice: When the film grows on a surface, the growth is controlled by the incorporation of atoms to steps and kinks provided by the two dimensional nuclei and steps. The step density highly depends on the growth condition and the growth law is quiet different from the ideal ones.
Single-Step Growing by Surface Diffusion
Interfaces and Strain Effects in Ferroelectric Thin Films
X-ray Studies of PSTO Thin Films

PSTO on (001) LAO

PSTO on (110) NdGaO$_3$

Cross Sectional TEM Studies of PSTO Films
X-Ray diffraction pattern (θ–2θ scan & rocking curve) of PST/NGO

The film had a single phase with a preferential orientation. FWHM of rocking curve < 0.04°, illustrating the near perfect crystallization of the PST film.

Dielectric Properties of PSTO Films

Dielectric constant and tunability tend to be reduced by compressive strain and improved by tensile strain.

Dielectric Tunability of (Pb, Sr)TiO$_3$ on MgO

![Graph showing room temperature capacitance and tunability as functions of voltage and frequency.](image-url)

Temperature dependent dielectric properties of Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films on MgO

- Ferroelectric phase transition peak is around or above room temperature.
- Dielectric tuning is relatively stable over the measurement temperatures compared to other films (i.e., BST), especially in the tensile-strain films.

Temperature dependent C-V curves of Pb$_{0.35}$Sr$_{0.65}$TiO$_3$ films on MgO

The CV curves below room temperature exhibit ferroelectric hysteresis properties.

TEM Studies of Mn:BSTO Thin Films on MgO

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