QUANTITATIVE TEXTURE OF FERROELECTRIC MODIFIED LEAD TITANATE THIN FILMS

J. Ricote, D. Chateigner, L. Pardo†, M. Algueró‡, J. Mendiola†, M.L. Calzada†

Laboratoire de Physique de l'Etat Condensé. Université du Maine-Le Mans (FRANCE)
†Instituto de Ciencia de Materiales de Madrid. CSIC. (SPAIN)
‡ Queen Mary and Westfield College, Univ. of London (UK)
WHY TEXTURE STUDIES IN FERROELECTRIC THIN FILMS?

Ferroelectrics:

- Polar materials
- Characterised by a spontaneous electric polarisation
- The polarisation can be inverted by the application of an electric field ⇒ **Hysteresis Loops**.

**Polar axis** for tetragonal compositions is [001]

In polycrystalline materials a **poling process** (application of a strong electric field) is required to obtain spontaneous polarisation.
Polycrystalline thin films showing a preferred orientation with the polar axis perpendicular to the film:

- DO NOT REQUIRE THE POLING PROCESS
- HAVE AN IMPROVED FERROELECTRIC BEHAVIOUR

A THOROUGH TEXTURE CHARACTERISATION IS NEEDED:

FOR THE CONTROL AND OPTIMISATION OF THE PREPARATION PROCESS OF HIGHLY ORIENTED FERROELECTRIC THIN FILMS REQUIRED FOR APPLICATIONS.

UNTIL RECENTLY
QTA HAVE NOT BEEN CARRIED OUT IN THIN FILMS OF FERROELECTRICS
Chateigner et al., Int. Ferro. 19, 1998, 121
Bornand et al., Int. Ferro. 19, 1998, 1
CORRELATION WITH PHYSICAL PROPERTIES NEITHER
MODIFIED LEAD TITANATE THIN FILMS

- interesting piezo and pyroelectric properties
- suitable for infrared sensors and electromechanical applications.

Films were obtained by sol-gel processing and deposition by spin-coating.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Number of Layers</th>
<th>Annealing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTL-4c</td>
<td>Pt/TiO₂/Si (100)</td>
<td>4</td>
<td>10°C/min</td>
</tr>
<tr>
<td>PTL-1 to 5</td>
<td>Pt/TiO₂/Si (100)</td>
<td>1-5</td>
<td>&gt;500°C/min</td>
</tr>
<tr>
<td>PTC-Si</td>
<td>Pt/TiO₂/Si (100)</td>
<td>1</td>
<td>30°C/s</td>
</tr>
<tr>
<td>PTC-Mg</td>
<td>Pt/MgO (100)</td>
<td>2</td>
<td>30°C/s</td>
</tr>
<tr>
<td>PTC-Sr</td>
<td>Pt/SrTiO₃ (100)</td>
<td>2</td>
<td>30°C/s</td>
</tr>
</tbody>
</table>
Experimental X-ray POLE FIGURES:
- asymmetric reflection mode (Cu Kα radiation)
- 4-circle goniometer with Euler cradle + PSD CPS-120
Scans: $5^\circ \times 5^\circ$ grid, at incidence $\omega = 11^\circ$: sum diagrams

Corrections for asymmetry, volume/absorption

*Heizmann et al., J. Appl. Cryst. 19 (1986) 467*
• Cyclic integration of \{100/001\}, \{101/110\}, \{102/201/210\}, \{112/211\} and \{221/103/300\} overlaps

• Corrections for location

  Bunge et al., Text. Micr. 5 (1982) 153

• ORIENTATION DISTRIBUTION (OD) refinement
  - WIMV algorithm (BEARTEX)
  - crystal symmetry: tetragonal, PTL: 3.93 Å x 4Å sample triclinic
    PTC: 3.89 Å x 4.04 Å
  - pole figure ranges: 100/001: 0-70
    101/110: 5-70
    102/201/210: 15-70
    112/211: 35-70 (substrate)
    221/103/300: 25-70
  - Overlaps: as for the powder
Separation of tetragonal peaks appeared better than a cubic perovskite-like refinement.

Hopefully!!

{100} vs {001} separation

polarisation
PTLs INVERSE POLE FIGURE (NORMAL TO THE FILM)

log. scale equal area proj.
PTLs INVERSE POLE FIGURE (NORMAL TO THE FILM)

- PTC-Si
- PTC-Mg
- PTC-Sr

Log. scale equal area proj.

Values:
- 49.16
- 1 mrd
- 0
### RESULTS FOR PTL THIN FILMS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Components of texture</th>
<th>Texture index (m.r.d.$^2$)</th>
<th>RP0 (%)</th>
<th>RP1 (%)</th>
<th>Remanent polarisation ($\mu$C cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTL-4c</td>
<td>485</td>
<td>weak $&lt;110&gt;$,$&lt;101&gt;$</td>
<td>1.3</td>
<td>14</td>
<td>10</td>
<td>13.4</td>
</tr>
<tr>
<td>PTL-1</td>
<td>130</td>
<td>$&lt;001&gt;$,$&lt;100&gt;$</td>
<td>10.5</td>
<td>36</td>
<td>16</td>
<td>7.4</td>
</tr>
<tr>
<td>PTL-2</td>
<td>210</td>
<td>$&lt;001&gt;$,$&lt;100&gt;$</td>
<td>7.5</td>
<td>24</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>PTL-3</td>
<td>420</td>
<td>$&lt;001&gt;$,$&lt;100&gt;$</td>
<td>6.2</td>
<td>22</td>
<td>16</td>
<td>27</td>
</tr>
<tr>
<td>PTL-4</td>
<td>500</td>
<td>$&lt;001&gt;$,$&lt;100&gt;$</td>
<td>4.6</td>
<td>18</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>PTL-5</td>
<td>560</td>
<td>$&lt;001&gt;$,$&lt;100&gt;$</td>
<td>3.9</td>
<td>19</td>
<td>15</td>
<td>10.7</td>
</tr>
</tbody>
</table>

High heating rates results in stronger textures.

F$_2$ ↕ with thickness

⇒ low heat. rate

⇒ affected by leakage
# RESULTS FOR PTC THIN FILMS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Components of texture</th>
<th>Texture index (m.r.d.(^2))</th>
<th>RP0 (%)</th>
<th>RP1 (%)</th>
<th>Pyroelectric coef.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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<td>(\gamma_s)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\gamma_p)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>spontaneous</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>poled (8V)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(10^{-8}) C cm(^{-2}) K(^{-1})</td>
</tr>
<tr>
<td>PTC-Si Pt/TiO(_2)/Si</td>
<td>weak (&lt;001&gt;,&lt;100&gt;) (&lt;110&gt;,&lt;101&gt;)</td>
<td>2.4</td>
<td>23</td>
<td>12</td>
<td>0.28</td>
</tr>
<tr>
<td>PTC-Mg Pt/MgO</td>
<td>(&lt;001&gt;,&lt;100&gt;) weak (&lt;111&gt;)</td>
<td>5.2</td>
<td>22</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>PTC-Sr Pt/SrTiO(_3)</td>
<td>(&lt;001&gt;,&lt;100&gt;)</td>
<td>32.1</td>
<td>26</td>
<td>24</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Less textured films are easier to pole

Poled values are not retained with time

Substrate: determinant factor of the final texture.
Similar contribution of texture components

PTL-1  PTL-3  PTL-5

Thickness ↑
Texture index ↓
Polar axis contribution ↓
(\(<001>\))
Spontaneous polarisation ↓

Thicknes 25.72
Texture index 1 m.r.d.
RECALCULATED POLE FIGURES OF PTC THIN FILMS

PTC-Mg

PTC-Sr

Strong contribution of <100> component

<100> contribution ↑ (⊥ polar axis and non-contributing to polarisation)

Spontaneous polarisation ↓

Spontaneous pyroelectricity ↓
The use of a high heating rate enhances the appearance of preferential orientation. During slow heating several variants of texture can be nucleated, resulting in a random thin film. As the number of layers increases the texture index decreases. This seems to indicate heterogeneous nucleation, i.e., when crystals nucleate in sites throughout the thickness of the film.

Except for the very thin PTL-1 and PTL-2 films, which present high leakage currents, the remanent polarisation decreases as the texture strength of the film decreases. An increase of the texture index involves in this case a higher fraction of crystals oriented with the polar axis, <001>, perpendicular to the film surface. The largest contribution to the net polarisation comes from these crystals. Therefore, there is an increase of the polarisation of the film.
The increase of the film thickness by increasing the number of deposited layers leads to a decrease of the texture strength that results in a reduction of the remanent polarisation.
- DIFFERENT SUBSTRATES LEAD TO:
  DIFFERENT OVERALL DEGREE OF ORIENTATION
  DIFFERENT CONTRIBUTIONS FROM <100> AND <001> COMPONENTS

USE OF THE TRADITIONAL Pt/TiO₂/Si SUBSTRATE RESULTS IN:
  WEAKLY TEXTURED FILMS
  LOW SPONTANEOUS PYROELECTRIC COEFFICIENTS

- PTC-Sr: largest <100>⊥ component: lowest PYROELECTRIC COEFFICIENTS

THE USE OF A Pt/SrTiO₃ SUBSTRATE, COMPARED TO Pt/MgO, PRODUCES HIGHLY TEXTURED FILMS, BUT WITH A STRONG CONTRIBUTION FROM CRYSTALS WHOSE POLAR AXIS IS IN THE PLANE OF THE FILM, WHICH REDUCES THE SPONTANEOUS PYROELECTRIC COEFFICIENTS OF THE FILMS.
SUMMARY

A QUANTITATIVE TEXTURE ANALYSIS HAS BEEN CARRIED OUT FOR THE FIRST TIME ON SEVERAL FERROELECTRIC THIN FILMS OF MODIFIED LEAD TITANATE.

The effects of different processing parameters on the final texture have been studied:

- rapid thermal annealing gives highly texture films
- heterogeneous nucleation of the perovskite: for higher thicknesses, lower texture strengths
- choice of substrate: determinant factor for texture, then properties

Remanent polarisation and pyroelectric coefficients can be correlated to the texture strength and the contribution of the different texture components.

ACKNOWLEDGEMENTS

Grant awarded by the regional government of Pays de Loire and the French Education Ministry Work financed by projects MAT98-1068 (Spanish CICYT) and COPERNICUS CIPA-CT94-0236 Declared of technological interest by the EU COST514 action on ferroelectric thin films.
REFERENCES

J. Ricote & D. Chateigner: Aplicación del Análisis Cuantitativo de la Textura al Estudio de Láminas Delgadas Ferroeléctricas. *To appear Boletín de la Sociedad Española de Cerámica y Vidrio*


