Texture-Structure-Microstructure: a combined analysis by x-ray diffraction of Pb$_{0.76}$Ca$_{0.24}$TiO$_3$ / Pt / TiO$_2$ / SiO$_2$ / Si-(001)

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Summary

• Usual up-to-date approaches for polycrystals
  – Texture
  – Structure-Microstructure
  – Problems on ultrastructures

• Combined approach
  – Experimental needs
  – Methodology-Algorithm
  – Ultrastructure implementation
  – Case study on Pb$_{0.76}$Ca$_{0.24}$TiO$_3$

• Future trends
Usual Texture Analysis

\{hkl\} pole figure measurement + corrections:

\[
\frac{dV(\chi \phi)}{V} = \frac{1}{4\pi} P(\chi \phi) \sin \chi \, d\chi \, d\phi
\]

We want \(f(g)\) (ODF): with \(g = (\alpha, \beta, \gamma)\)

\[
\frac{dV(g)}{V} = \frac{1}{8\pi^2} f(g) \, dg
\]
We have to invert (Fundamental equation of Texture Analysis):

\[
P_{hkl} (\vec{y}) = \frac{1}{2\pi} \int_{<hkl> // \vec{y}} f(g) \, d\vec{\varphi}
\]

WIMV refinement method: Williams-Imhof-Matthies-Vinel

\[
f^{n+1}(g) = N \left[ \frac{f^n(g) f^0(g)}{\prod_{hkl} \left( P_{hkl} (\vec{y}) \right)_I^{1}} \right]
\]
Usual Structure-Microstructure Analysis

(Full pattern fitting, Rietveld Analysis)

$\text{Si}_3\text{N}_4$ matrix with SiC whiskers:

Random powder:  \[ I(2\theta) = \sum_{\text{hkl, phases}} I_{\text{hkl, phases}}(2\theta) S_{\text{hkl, phases}}(2\theta) + \text{bkg}(2\theta) \]
\[ I_{hkl}(2\theta) = S|F_{hkl}|^2 m_{hkl} \frac{L_P}{V_c^2} \]

**S**: scale factor (phase abundance)

**F_{hkl}**: structure factor (includes Debye-Waller term)

**V_c**: unit-cell volume

\[ S_{hkl}(2\theta) = S^I_{hkl}(2\theta) \ast S^S_{hkl}(2\theta) \]

**S^I**: instrumental broadening

**S^S**: Sample aberrations

- crystallite sizes (iso. or anisotropic)
- rms microstrains \( \varepsilon \)
Problems on ultrastructures

- Strong intra- and inter-phase overlaps
- Mixture of very strong and lower textures
- Texture effect not fully removable: structure
- Structure unknown: texture

Ferroelectric film (PTC)
Electrode (Pt)
Antidiffusion barrier (TiO$_2$)
Oxide (native, thermally grown)
SC Substrate (Si)

Sum diagram

001/100 PTC
011/110 PTC + Si (λ/2)
111 PTC + 111 Pt

Need something!!
Combined approach

Experimental needs

Mapping Spectrometer space for correction of:

- instrumental resolution
- instrumental misalignments
Rietveld and WIMV algorithm are alternatively used to correct for each others contributions: Marquardt non-linear least squares fit is used for the Rietveld.

Correction of intensities for texture:

\[ I_{hkl}(2\theta, \chi, \varphi) = I_{hkl}(2\theta) P_{hkl}(\chi, \varphi) \]

Pole figure extraction (Le Bail method):

\[ P_{hkl}(\chi, \varphi) \]
Ultrastructure implementation

Corrections are needed for volumic/absorption changes when the samples are rotated. With a CPS detector, these correction factors are:

\[
C_{\chi}^{\text{top film}} = g_1 \left( 1 - \exp \left( -\mu T g_2 / \cos \chi \right) \right) / \left( 1 - \exp \left( -2\mu T / \sin \omega \cos \chi \right) \right)
\]

\[
C_{\chi}^{\text{cov. layer}} = C_{\chi}^{\text{top film}} \left( \exp \left( -g_2 \sum \mu_i T_i / \cos \chi \right) \right) / \left( \exp \left( -2 \sum \mu_i T_i / \sin \omega \cos \chi \right) \right)
\]

Gives access to individual Thicknesses in the refinement.
Case study on \( \text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3 \)

- \( a = 3.945(1) \) Å
- \( c = 4.080(1) \) Å
- \( T = 4080(10) \) Å
- \( t_{\text{iso}} = 390(7) \) Å
- \( \varepsilon = 0.0067(1) \)

- \( a = 3.955(1) \) Å
- \( T' = 462(4) \) Å
- \( t'_{\text{iso}} = 458(3) \) Å
- \( \varepsilon' = 0.0032(1) \)
WIMV vs Entropy modified WIMV approach

Better refinement with E-WIMV:

- lower reliability factors (structure and texture)
- better high density level reproduction

<table>
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<th>Texture</th>
<th>Pt Text</th>
<th>PTC Text</th>
<th>Pt</th>
<th>PTC</th>
<th>Rw</th>
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<td>18.4</td>
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Future trends

- Combining with reflectivity measurements: independently measured and refined thicknesses, electron densities and roughnesses
- Adding residual stress determinations

- **Multiple Analysis Using Diffraction**, a web-based tutorial for the combined approach: search MAUD (Luca Lutterotti)
- **Quantitative Texture Analysis Internet Course**: http://lpec.univ-lemans.fr/qta (Daniel Chateigner)

Acknowledgements

This work is funded by EU project ESQUI (http://lpec.univ-lemans.fr/esqui: an x-ray Expert System for microelectronic film QUality Improvement, G6RD-CT99-00169), under the RTD program.