Combined x-ray Texture-Structure-Microstructure analysis applied to ferroelectric ultrastructures: a case study on $Pb_{0.76}Ca_{0.24}TiO_3$

L. Cont [ab], D. Chateigner [a], L. Lutterotti [b], J. Ricote [c], M.L. Calzada [c], J. Mendiola [c]

LPEC, Univ. Le Mans, France

DIM, Univ. di Trento, Italia

DMF-ICMM-CSIC, Cantoblanco, Madrid, España

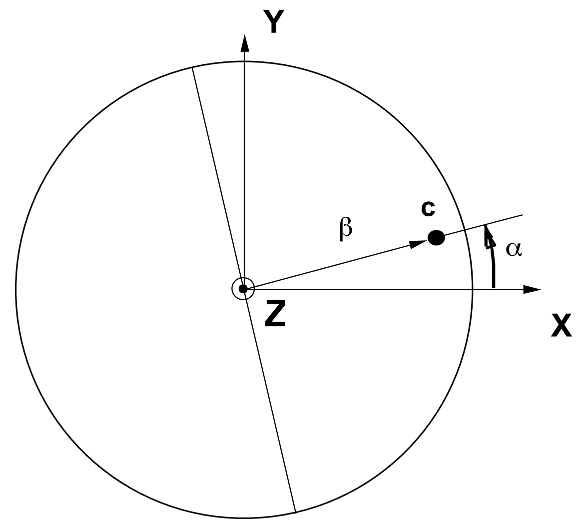
Summary

- 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

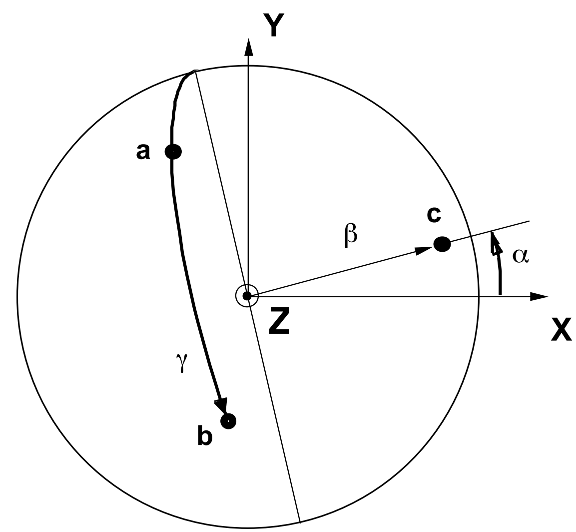
{hkl} pole figure measurement + corrections:

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



We want f(g) (ODF): with g = (α,β,γ)

$$\frac{dV(g)}{V} = \frac{1}{8\pi^2} f(g)\ dg$$



We have to invert (Fundamental equation of Texture Analysis):

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

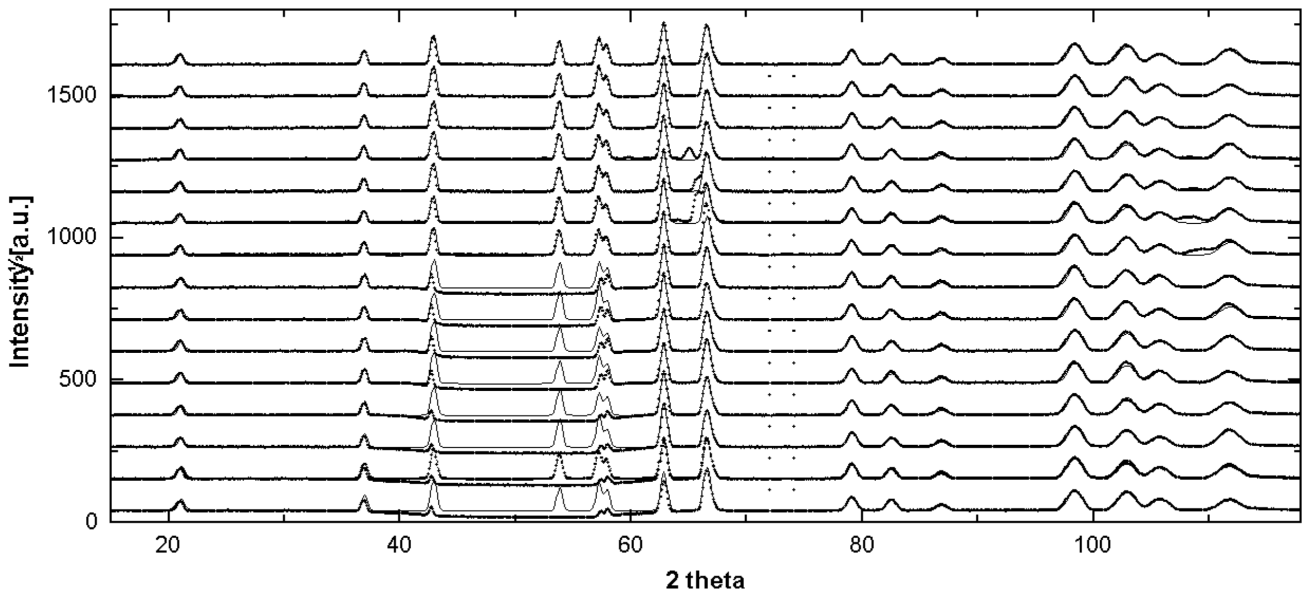
WIMV refinement method:
Williams-Imhof-Matthies-Vinel

$$f^{n+1}(g) = N \left[\frac{f^{n}(g)\, f^{0}(g)}{\prod_{hkl} \left(P^{n}_{hkl}(\vec{y})\right)^{\frac{1}{I}}} \right]$$

Usual Structure-Microstructure Analysis

(Full pattern fitting, Rietveld Analysis)

Si_3N_4 matrix with SiC whiskers:



Random powder: $$I(2\theta) = \sum_{hkl,\ phases} I_{hkl,\ phases}(2\theta) S_{hkl,\ phases}(2\theta) + bkg(2\theta)$$

$$I_{hkl}(2\theta) = S\left|F_{hkl}\right|^2 m_{hkl} \frac{L_P}{V_c^2}$$

S: scale factor (phase abundance)

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

V_c: unit-cell volume

$$S_{hkl}(2\theta) = S^I_{hkl}(2\theta) * S^S_{hkl}(2\theta)$$

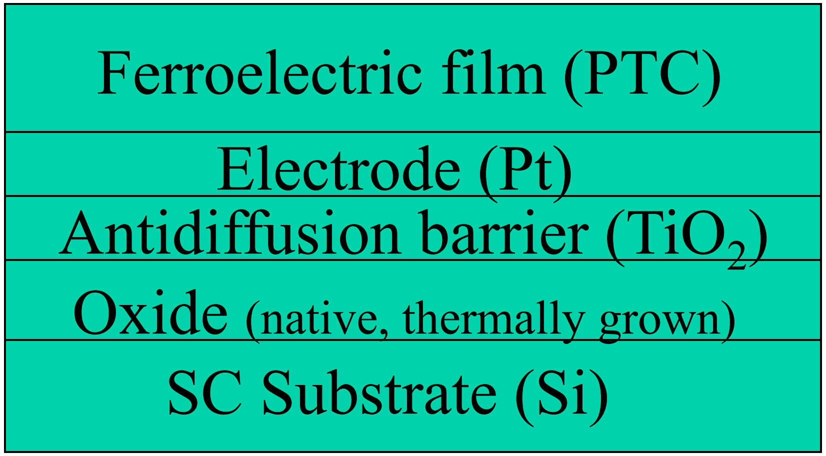
S^I: instrumental broadening

S^S: Sample aberrations

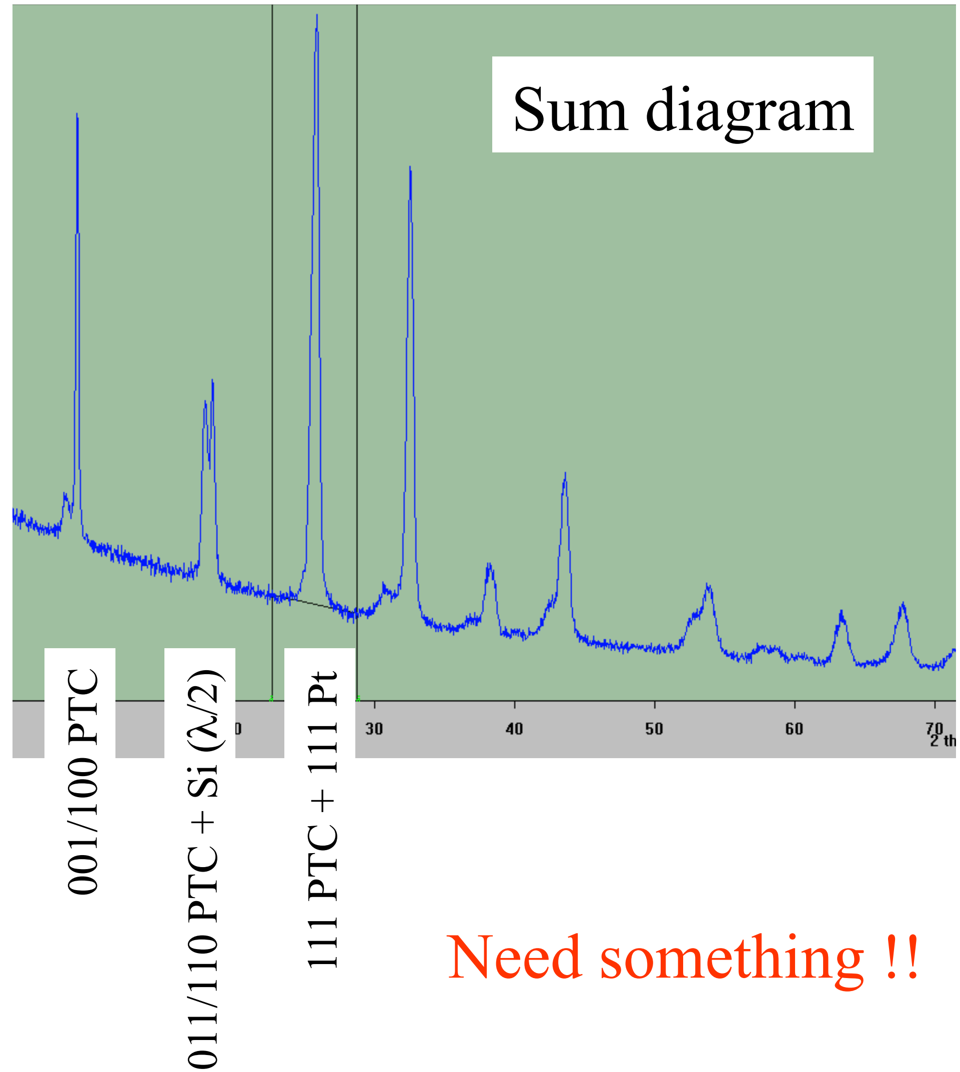
crystallite sizes (iso. or anisotropic)

rms microstrains ε

Problems on ultrastructures



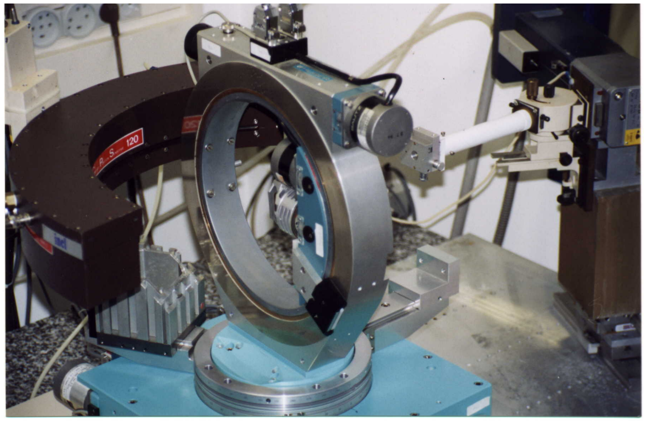
- Strong intra- and inter-phase overlaps
- Mixture of very strong and lower textures
- texture effect not fully removable: ~~structure~~
- structure unknown: ~~texture~~



Need something !!

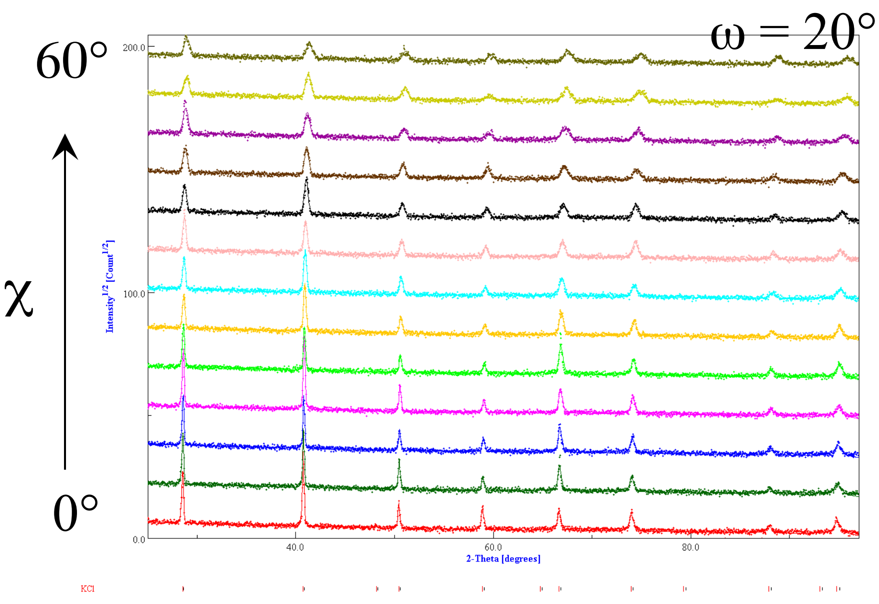
Combined approach

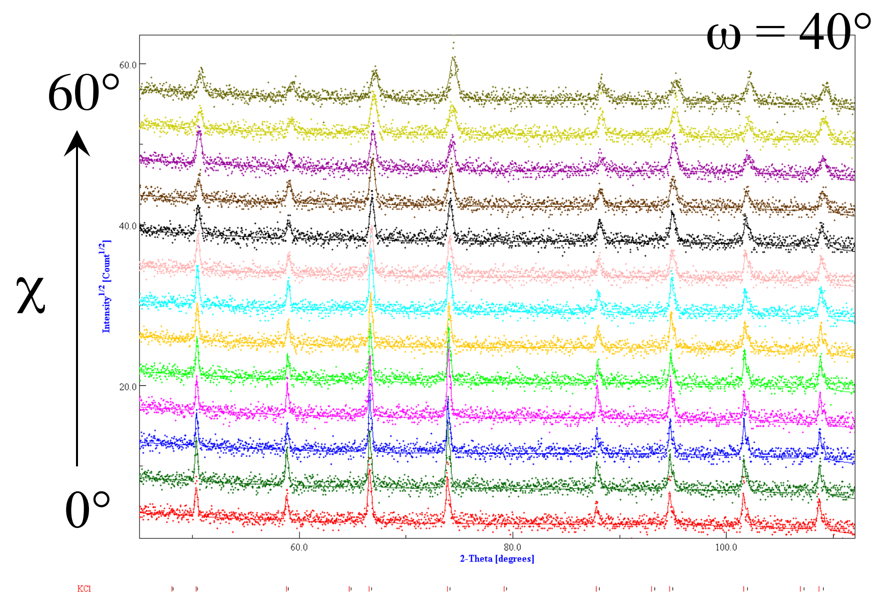
Experimental needs



Mapping Spectrometer space for correction of:

- instrumental resolution
- instrumental misalignments

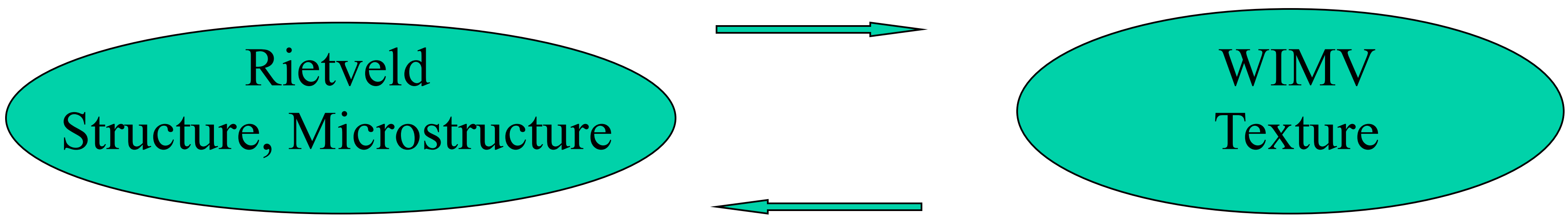




Methodology-Algorithm

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): $P_{hkl}(\chi,\varphi)$

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

Ultrastructure implementation

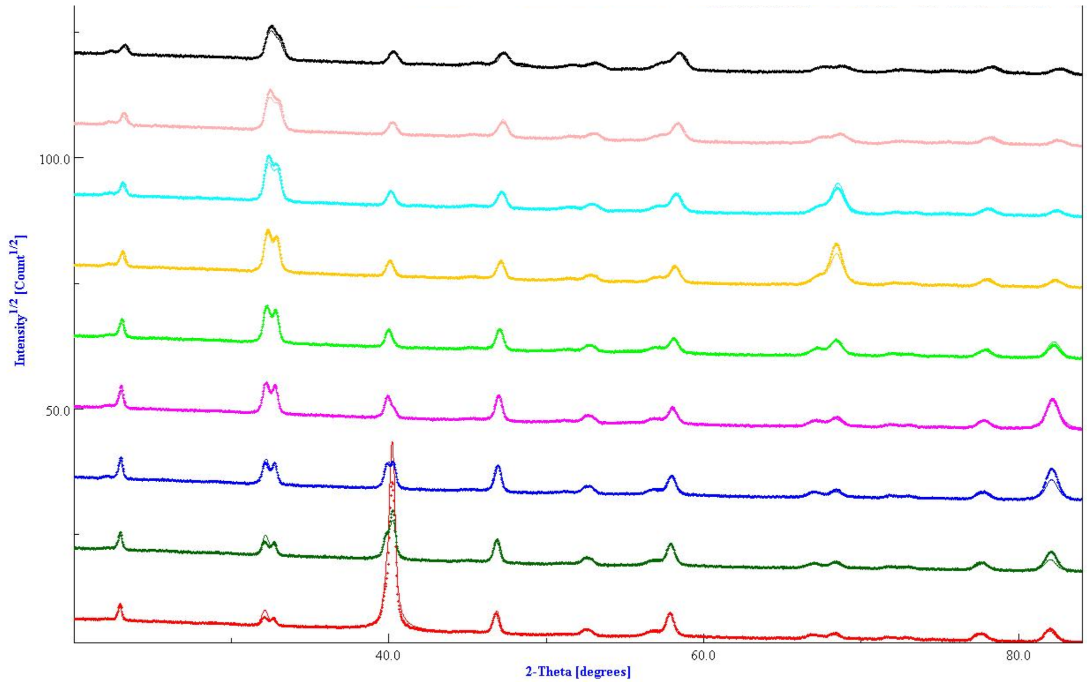
Corrections are needed for volumic/absorption changes when the samples are rotated. With a CPS detector, these correction factors are:

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

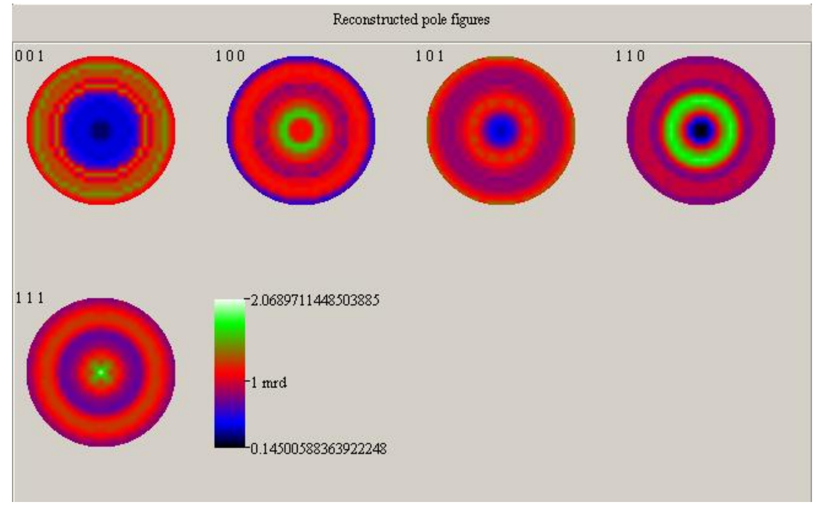
$$C_\chi^{\text{cov. layer}} = C_\chi^{\text{top film}}\left(\exp\left(-g_2\sum \mu_i' T_i' / \cos\chi\right)\right)/\left(\exp\left(-2\sum \mu_i' T_i' / \sin\omega\cos\chi\right)\right)$$

→ Gives access to individual Thicknesses in the refinement

Case study on $Pb_{0.76}Ca_{0.24}TiO_3$

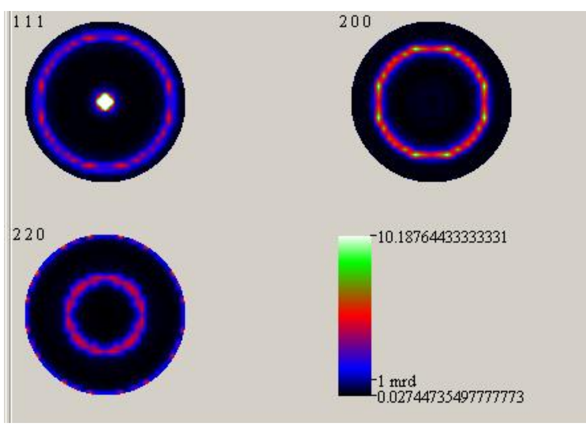


PTC



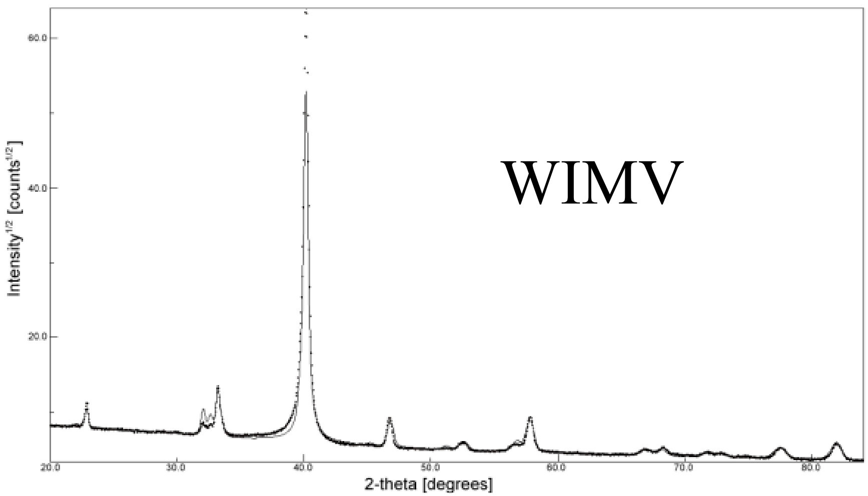
$a = 3.945(1)$ Å
$c = 4.080(1)$ Å
$T = 4080(10)$ Å
$t_{iso} = 390(7)$ Å
$\varepsilon = 0.0067(1)$

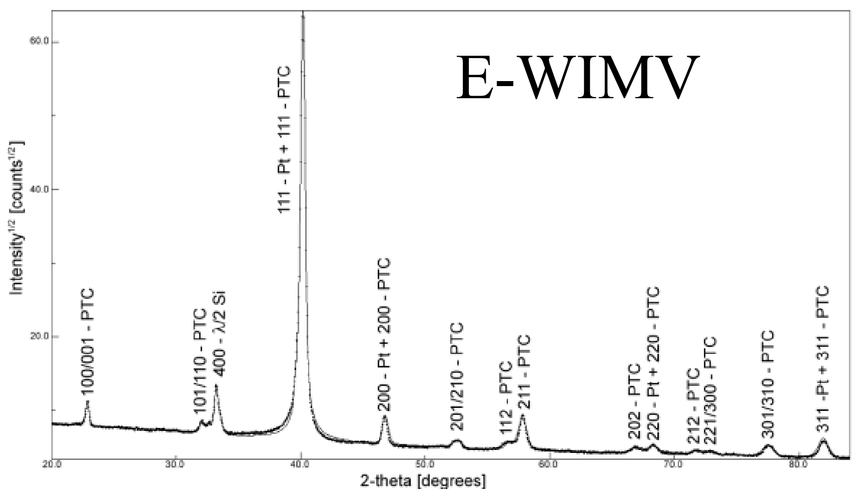
Pt



$a = 3.955(1)$ Å
$T' = 462(4)$ Å
$t'_{iso} = 458(3)$ 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

Texture	Pt Texture Index (m.r.d.^{2})	PTC Texture Index (m.r.d.^{2})	Pt RP_0 (%)	PTC RP_0 (%)	Rw (%)	R_{Bragg} (%)
WIMV	48.1	1.3	18.4	11.4	12.4	7.7
EWIMV	40.8	2	13.7	11.2	7	4.7

Future trends

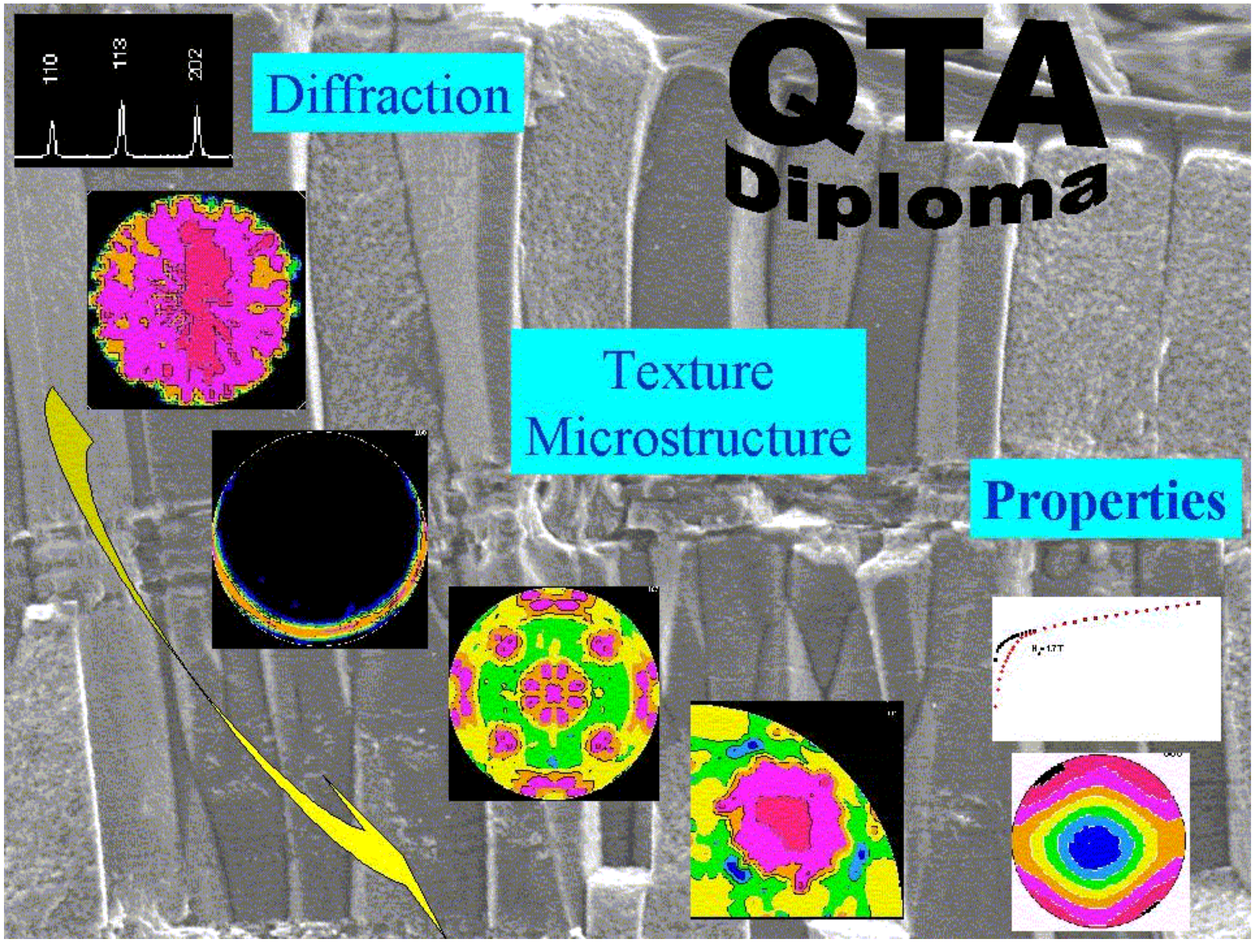
- Combining with reflectivity measurements: independently measured and refined thicknesses, electron densities and roughnesses
- Adding residual stress determinations

- 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.

Quantitative Texture Analysis Internet Course



http://lpec.univ-lemans.fr/qta