Combined Analysis of thin structures: structure, microstructure, texture, stresses, phase, nanocrystals …

at once in a single approach!

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Geo-Bio Center 14th June 2012, Munchen
**Structure determination on real (textured) samples**

**Problem 1**

Structure and QTA: correlations?  
\( f(g) \) and \( |F_h|^2 \) are different!

\( f(g) \):  
- Angularly constrained: \([h_1k_1l_1]^* \) and \([h_2k_2l_2]^* \)  
  make a given angle: more determined if \( F^2 \) high  
- lot of data (spectra) needed

\( |F_h|^2 \):  
- Position, \( f_i \), and Debye-Waller constrained  
- work on the sum of all diagrams on average
Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra

Le Bail extraction + ODF: WMV, E-WIMV, Generalized spherical harmonics, components, ADC, entropy maximisation …
### Why not benefit of texture in Structure determination?

<table>
<thead>
<tr>
<th>Perfect powders:</th>
<th>Single crystals:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- overlaps (intra- and inter-(\tau))</td>
<td>- reduced overlaps</td>
</tr>
<tr>
<td>- no angular constrain</td>
<td>- max angular constrains</td>
</tr>
<tr>
<td>- anisotropy difficult to resc</td>
<td>- Perfect texture: max anisotropy</td>
</tr>
</tbody>
</table>

| Single pattern | Many individual diffracted peaks |

<table>
<thead>
<tr>
<th>Textured powders:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>- reduced overlaps</td>
<td></td>
</tr>
<tr>
<td>- angular constrain = (f(\text{texture strength}))</td>
<td></td>
</tr>
<tr>
<td>- Intermediate anisotropy</td>
<td></td>
</tr>
</tbody>
</table>

| Many patterns to measure and analyse |
Rietveld-Structure

Texture

\[ P_k(\chi, \phi) = \int f(g, \varphi) d\varphi \]

- Generalized Spherical Harmonics (Bunge):

\[ P_k(\chi, \phi) = \sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{n=-1}^{1} k_l^n(\chi, \phi) \sum_{m=-1}^{1} C_l^{mn} k_n^* m(\Theta_k \phi_k) \]

\[ f(g) = \sum_{l=0}^{\infty} \sum_{m,n=-1}^{1} C_l^{mn} T_l^{mn}(g) \]

- Components (Helming):

\[ f(g) = F + \sum_c I^c f^c(g) \]
• WIMV (William, Imhof, Matthies, Vinel) iterative process:

\[
 f^{n+1}(g) = N_n \frac{f^n(g)f^0(g)}{\left( \prod_{h=1}^{M_h} \prod_{m=1}^{n} p_h^n(y) \right)^{1/IM_n}} 
\]

\[
 f^0(g) = N_0 \left( \prod_{h=1}^{M_h} \prod_{m=1}^{1} p_h^{\text{exp}}(y) \right)^{1/IM_h} 
\]

E-WIMV (Rietveld only):

with \(0 < r_n < 1\), relaxation parameter, \(M_h\) number of division points of the integral around \(k\), \(w_h\) reflection weight

• Entropy maximisation (Schaeben):

\[
 f^{n+1}(g) = f^n(g) \prod_{m=1}^{M_h} \left( \frac{p_h(y)}{p_h^n(y)} \right)^{r_n w_h/M_h} 
\]

• arbitrarily defined cells (ADC, Pawlik): Very similar to E-WIMV, with integrals along path tubes
Residual Stresses shift peaks with $y$

Problem 2

Stress and QTA: correlations? $f(g)$ and $<C_{ijkl}>$

$f(g)$:
- Moves the $\sin^2\Psi$ law away from linear relationship
- Needs the integrated peak (full spectra)

Strains:
- Measured with pole figures
- Needs the mean peak position

Isotropic samples: triaxial, biaxial, uniaxial stress states

Textured samples: Reuss, Voigt, Hill, Bulk geometric mean approaches
Residual Stresses and Rietveld

- Macro elastic strain tensor (I kind)
- Crystal anisotropic strains (II kind)

Macro and micro stresses

Applied macro stresses

Isotropic samples: triaxial, biaxial, uniaxial stress states

Textured samples: Reuss, Voigt, Hill, Bulk geometric mean approaches
\[ \varepsilon(X) = \varepsilon^I + \varepsilon^{II}(X) + \varepsilon^{III}(X) \]

\[
\langle S \rangle^{-1}_{\text{geo}} = \exp \left[ - \sum_{m=1}^{N} \nu_m \ln S_m \right] = \exp \left[ \sum_{m=1}^{N} \nu_m \ln S_m^{-1} \right] = \langle S^{-1} \rangle_{\text{geo}} = \langle C \rangle_{\text{geo}}
\]

or

\[
\langle S \rangle^{-1}_{\text{geo}} = \left[ \prod_{m=1}^{N} S_m^{\nu_m} \right]^{-1} = \prod_{m=1}^{N} S_m^{-\nu_m} = \prod_{m=1}^{N} \left( S_m^{-1} \right)^{\nu_m} = \langle S^{-1} \rangle_{\text{geo}} = \langle C \rangle_{\text{geo}}
\]
Layered systems
Problem 3

Layer, Rietveld and QTA: correlations: f(g), thicknesses and structure

f(g):
- Pole figures need corrections for abs-vol
- Rietveld also to correct intensities

layers:
- unknown sample true absorption coefficient $\mu$
- unknown effective thickness (porosity)
Asymmetric Bragg-Brentano

Layering

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

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

Probes \( \mu T \)

\( \chi = 0^\circ \)

\( \chi > 0^\circ \)
Phase and Texture

Problem 4

Phase and QTA: correlations: $f(g)$, $S_\Phi$

$f(g)$:
- angular relationships
- plays on individual spectra
- essential to operate on textured sample

$S_\Phi$:
- plays on overall scale factor (sum diagram)
Phase analysis

- Volume fraction

\[ V_\Phi = \sum \left( \frac{S_\Phi V_{uc\Phi}^2}{S_\Phi V_{uc\Phi}} \right) \]

- Weight fraction

\[ m_\Phi = \sum \left( \frac{S_\Phi Z_\Phi M_\Phi V_{uc\Phi}^2}{S_\Phi Z_\Phi M_\Phi V_{uc\Phi}} \right) \]

- Z = number of formula units
- M = mass of the formula unit
- V = cell volume
How it works

Le Bail extraction

\[ T_{hkl}^k = T_{hkl}^{k-1} \frac{\sum_i I_i^{exp} S_{hkl}^i}{\sum_i I_i^{calc} S_{hkl}^i} \]

- Starts with nominal intensities \((T_{hkl})\)
- Computes the full pattern \((I^{calc})\)
- Uses the formula to compute next \(T_{hkl}\)
- Cycle the last two steps until convergence

- In Maud, options:
  - Only few cycles for texture (3-5) necessary
  - The range for the weighting of the profile can be reduced
  - Background subtracted or not
Structure and Residual Stresses (shift peaks with $y$)

**Problem 5**

Stress and cell parameters: correlations: peak positions and $C_{ijkl}$

**Cell parameters:**
- Measured at high angles
- Bragg law evolution

**Strains:**
- Measured precisely at high angles
- Stiffness-based variation, also with $\Psi$
Shapes, microstrains, defaults, distributions

Problem 6

Shapes .... and stress-texture-structure: correlations?

Shapes ...
- line broadening problem
- average positions modified
- if anisotropic: modification changes with y

Stress-texture-structure:
- need “true” peak positions and intensities
- need deconvoluted signals
Anisotropic sizes and microstrains

- Texture helps the "real" mean shape determination
- Determination by peak deconvolution + Popa formalism

\[
<\mathbf{R}_h> = R_0 + R_1 P_2^0(x) + R_2 P_2^1(x) \cos \varphi + R_3 P_2^1(x) \sin \varphi + R_4 P_2^2(x) \cos 2 \varphi + R_5 P_2^2(x) \sin 2 \varphi + \ldots
\]

\[
<\varepsilon_h^2> E_h^4 = E_1 h^4 + E_2 k^4 + E_3 \ell^4 + 2E_4 h^2 k^2 + 2E_5 \ell^2 k^2 + 2E_6 h^2 \ell^2 + 4E_7 h^3 k + 4E_8 h^3 \ell + 4E_9 k^3 h + 4E_{10} k^3 \ell + 4E_{11} \ell^3 h + 4E_{12} \ell^3 k + 4E_{13} h^2 k \ell + 4E_{14} k^2 h \ell + 4E_{15} \ell^2 kh
\]
\( R_0, R_1 \leq 0 \)

\( R_0, R_1 > 0 \)

\( R_0, R_6 > 0 \)

\( R_0, R_2 \) and \( R_6 > 0 \)

\( R_0, R_6 < 0 \)

\( 6/m \)

\( R_0, R_4 > 0 \)

\( R_0, R_1 > 0 \)

\( R_0, R_1 < 0 \)

\( m3m \)
## Gold thin films

<table>
<thead>
<tr>
<th>Crystallite size (Å) along</th>
<th>10nm</th>
<th>15nm</th>
<th>20nm</th>
<th>25nm</th>
<th>35nm</th>
<th>40nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[111]</td>
<td>176</td>
<td>153</td>
<td>725</td>
<td>254</td>
<td>343</td>
<td>379</td>
</tr>
<tr>
<td>[200]</td>
<td>64</td>
<td>103</td>
<td>457</td>
<td>173</td>
<td>321</td>
<td>386</td>
</tr>
<tr>
<td>[202]</td>
<td>148</td>
<td>140</td>
<td>658</td>
<td>234</td>
<td>337</td>
<td>381</td>
</tr>
</tbody>
</table>

**10 nm**

**15 nm**

**20 nm**

**25 nm**

**35 nm**

**40 nm**
EMT nanocrystalline zeolite

Ng, Chateigner, Valtchev, Mintova: *Science* **335** (2012) 70
**Combined Analysis approach**

- **Extracted Intensities**
  - WIMV, E-WIMV
  - Harmonics, components, ADC
- **Orientation Distribution Function**
  - Rietveld
  - Structure +
  - Microstructure +
  - phase %
  - Popa-Balzar, $\sin^2\psi$
  - Residual stresses
  - Strain Distribution Function

- **Specular Reflectivity**
  - Roughness, electron Density & EDP, Thickness
  - Structural parameters: atomic positions, substitutions, vibrations, cell parameters
  - Multiphased, layered samples: Thickness, Anisotropic Sizes and $\mu$-strains (Popa), Stacking faults (Warren), Distributions, Turbostratism (Ufer)
  - Phase ratio (amorphous + crystalline)
  - XRF, PDF

- **Fresnel, Matrix (Parrat), DWBA**
- **Voigt, Reuss, Geometric mean**
Grinding to powderise another problem!

Grinding: removes angular relationship, adds correlations

Texture:
- not measured
- removed? hope to get a perfect powder

Strains, defaults, anisotropy ... :
- some removed, some added

Same sample?
Rare samples?
Minimum experimental requirements

1D or 2D Detector + 4-circle diffractometer
(X-rays and neutrons)
CRISMAT, ILL

+ 

~1000 experiments (2θ diagrams)
in as many sample orientations

+ 

Instrument calibration
(peaks widths and shapes, misalignments, defocusing …)
2D Curved Area Position Sensitive Detector

D19 - ILL

~100 experiments (2D Debye-Scherrer diagrams) in as many sample orientations
Calibration

\[ \omega = 20^\circ \]

\[ \omega = 40^\circ \]

KCl, LaB\textsubscript{6} ...

FWHM (\(\omega, \chi, 2\theta, \eta \ldots\))

2\theta shift

gaussianity

asymmetry

misalignments ...
Minimization algorithms

- Can be fully used in the method (everywhere)

- **Marquardt Least Squares** (based on steepest decrease and Gauss-Newton)
  - Efficient, best with few parameters, near the solution

- **Evolutionary computation** (or genetic algorithm)
  - Slow, not efficient, requires a lot of resources
  - Unlimited number of parameters
  - Can start far from the solution

- **Simulated annealing** (the solution proceed like a random walk, but the walking step decreases as temperature decreases)
  - In between the Marquardt and evolutionary algorithms

- **Simplex** (generates n+1 starting solutions as vertices of a polygon, n number of parameters, and contract/expand the polygon around the minima)
  - Slow on convergence
  - Remains close to the solution, but explore more minima with respect to the Marquardt
Ca$_3$Co$_4$O$_9$ thermoelectrics

Ca$_3$Co$_4$O$_9$: Misfit lamellar and modulated Structure, with high thermopower

Two monoclinic sub-systems:
S1 with $a \sim 4.8\,\text{Å}$, $b_1 \sim 4.5\,\text{Å}$, $c \sim 10.8\,\text{Å}$ et $\beta \sim 98^\circ$ (NaCl-type)
S2 with $a \sim 4.8\,\text{Å}$, $b_2 \sim 2.8\,\text{Å}$, $c \sim 10.8\,\text{Å}$ et $\beta \sim 98^\circ$ (CdI$_2$-type)

$\Gamma = \sigma_{ab}/\sigma_c \sim 10$

Texture
Supercell

\[ \chi = 0^\circ \]

\[ \Delta \chi = 5^\circ \]

\[ \chi = 90^\circ \]

**RP=19.7%**, **Rw=11.9%**
Bi2223 compounds
E. Guilmeau, PhD

Grain alignment $\Rightarrow J_c$
(00\ell) Texture

Intensity (a. u.) vs. 2-Theta Angle (°)

- (0010)-Bi2223
- (0010)-2212
- (0014)-2223
- (0012)-2212
- (008)-Bi2212
Combined Analysis

- Neutrons
- Sample: ~70 mm³
- 2θ patterns for χ=0° to 90°
- No φ rotation (fibre texture).
### Effect of the sinter-forging treatment on the texture development, crystal growth, transport properties

<table>
<thead>
<tr>
<th>Sinter-forging dwell time (h)</th>
<th>Orientation Distribution Max (m.r.d.)</th>
<th>% Bi2223</th>
<th>Cell parameters (Å)</th>
<th>Crystallite size Bi2223 (nm)</th>
<th>Rb (%)</th>
<th>Rw (%)</th>
<th>Rexp (%)</th>
<th>RP0 (%)</th>
<th>RP1 (%)</th>
<th>$J_c$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Bi2212: 21.8, Bi2223: 20.7</td>
<td>59.9±1.3</td>
<td>Bi2223: a=5.419(3) b=5.391(3) c=37.168(3)</td>
<td>Bi2212: a=5.414(3) b=5.393(3) c=30.800(3)</td>
<td>205±7</td>
<td>7.56</td>
<td>11.1</td>
<td>4.55</td>
<td>17.74</td>
<td>10.56</td>
</tr>
<tr>
<td>50</td>
<td>Bi2212: 24.1, Bi2223: 24.4</td>
<td>72.9±2.9</td>
<td>Bi2223: a=5.419(3) b=5.408(3) c=37.192(3)</td>
<td>Bi2212: a=5.416(3) b=5.396(3) c=30.806(3)</td>
<td>273±10</td>
<td>7.54</td>
<td>11.37</td>
<td>4.58</td>
<td>17.05</td>
<td>11.04</td>
</tr>
<tr>
<td>100</td>
<td>Bi2212: 31.5, Bi2223: 25.2</td>
<td>84.4±4.6</td>
<td>Bi2223: a=5.410(3) b=5.405(3) c=37.144(3)</td>
<td>Bi2212: a=5.412(3) b=5.403(3) c=30.752(3)</td>
<td>303±10</td>
<td>5.4</td>
<td>8.04</td>
<td>3.69</td>
<td>13.54</td>
<td>9.31</td>
</tr>
<tr>
<td>150</td>
<td>Bi2212: 65.4, Bi2223: 27.2</td>
<td>87.0±4.1</td>
<td>Bi2223: a=5.417(3) b=5.403(3) c=37.199(3)</td>
<td>Bi2212: a=5.413(3) b=5.407(3) c=30.792(3)</td>
<td>383±13</td>
<td>6.13</td>
<td>9.12</td>
<td>4.8</td>
<td>16.24</td>
<td>12.25</td>
</tr>
</tbody>
</table>

**Texture strength**

- **% Bi2223**
- **Crystallite Size**

*E. Guilmeau et al., JAC*
**Ferroelectric PCT films**

J. Ricote, Madrid

**Thin films:**

\((\text{Ca}_{0.24}\text{Pb}_{0.76})\text{TiO}_3\) sol-gel synthesised solutions deposited by spin coating on a substrate of \(\text{Pt/TiO}_2/\text{Si}\), with and without a treatment at 650°C for 30 min.

All films are crystallised at 700°C for 50 s by Rapid Thermal Processing (RTP; 30°C/s). A series is also recrystallised at 650°C for 1 to 3 h.

Refinement of individual spectra
$a = 3.9156(1) \text{ Å}$
$c = 4.0497(3) \text{ Å}$
$T = 2525(13) \text{ Å}$
$t_{iso} = 390(7) \text{ Å}$
$\varepsilon = 0.0067(1) \text{ rms}$

$R_W = 13\%$; $R_B = 12\%$; $R_{exp} = 22\%$ (Rietveld)
$R_W = 5\%$; $R_B = 6\%$ (E-WIMV)
<table>
<thead>
<tr>
<th>Atom</th>
<th>Occupancy</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.76</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ca</td>
<td>0.24</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.477(2)</td>
</tr>
<tr>
<td>O1</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.060(2)</td>
</tr>
<tr>
<td>O2</td>
<td>1.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.631(1)</td>
</tr>
</tbody>
</table>

**Diagram:**
- **PTL/Pt/TiO$_2$/Si**
- **PTL/Ti/Pt/Ti/Si**

**Color Legend:**
- 0.01 to 1 m.r.d.
- 111, 115 colors indicate specific orientations or intensities.
<table>
<thead>
<tr>
<th>Compliance coefficients [10^{-3} GPa^{-1}]</th>
<th>PbTiO_3 single crystal (data set A)</th>
<th>Film random orientation</th>
<th>PCT-Si (&lt;001&gt;) contrib. \approx 17%</th>
<th>PLT (&lt;001&gt;) contrib. \approx 49%</th>
<th>PCT-Mg (&lt;001&gt;) contrib. \approx 68%</th>
</tr>
</thead>
<tbody>
<tr>
<td>s_{11}</td>
<td>6.5</td>
<td>10.1</td>
<td>10.5</td>
<td>10.0</td>
<td>9.7</td>
</tr>
<tr>
<td>s_{22}</td>
<td>6.5</td>
<td>10.0</td>
<td>10.5</td>
<td>10.0</td>
<td>9.7</td>
</tr>
<tr>
<td>s_{33}</td>
<td>33.3</td>
<td>9.8</td>
<td>9.0</td>
<td>10.3</td>
<td>11.3</td>
</tr>
<tr>
<td>s_{44}</td>
<td>14.5</td>
<td>13.2</td>
<td>12.8</td>
<td>12.9</td>
<td>13.1</td>
</tr>
<tr>
<td>s_{55}</td>
<td>14.5</td>
<td>13.2</td>
<td>12.8</td>
<td>13.0</td>
<td>13.1</td>
</tr>
<tr>
<td>s_{66}</td>
<td>9.6</td>
<td>13.4</td>
<td>14.0</td>
<td>13.5</td>
<td>12.7</td>
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<tr>
<td>s_{12}</td>
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<td>-3.3</td>
<td>-3.5</td>
<td>-3.2</td>
<td>-3.0</td>
</tr>
<tr>
<td>s_{21}</td>
<td>-0.35</td>
<td>-3.3</td>
<td>-3.5</td>
<td>-3.2</td>
<td>-3.0</td>
</tr>
<tr>
<td>s_{13}</td>
<td>-7.1</td>
<td>-3.2</td>
<td>-3.1</td>
<td>-3.4</td>
<td>-3.6</td>
</tr>
<tr>
<td>s_{31}</td>
<td>-7.1</td>
<td>-3.2</td>
<td>-3.1</td>
<td>-3.4</td>
<td>-3.6</td>
</tr>
<tr>
<td>s_{23}</td>
<td>-7.1</td>
<td>-3.2</td>
<td>-3.1</td>
<td>-3.4</td>
<td>-3.6</td>
</tr>
<tr>
<td>s_{32}</td>
<td>-7.1</td>
<td>-3.2</td>
<td>-3.1</td>
<td>-3.4</td>
<td>-3.6</td>
</tr>
<tr>
<td>s_{33}/s_{11}</td>
<td>5.1</td>
<td>0.97</td>
<td>0.86</td>
<td>1.03</td>
<td>1.16</td>
</tr>
<tr>
<td>s_{13}/s_{12}</td>
<td>20.3</td>
<td>0.97</td>
<td>0.89</td>
<td>1.06</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Geometric mean average + biaxial stress state
Ferroelectric PMN-PT films
J. Ricote, DMF-Madrid

Pt
\[ a = 3.91172(1) \, \text{Å} \]
\[ T = 583(5) \, \text{Å} \]
\[ t_{iso} = 960(1) \, \text{Å} \]
\[ \varepsilon = 0.0032(1) \, \text{rms} \]
\[ \sigma_{11} = 0.639(1) \, \text{GPa} \]
\[ \sigma_{22} = 0.651(1) \, \text{GPa} \]
\[ \sigma_{12} = -0.009(1) \, \text{GPa} \]

Pb\(_{0.7}\) (Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-Pb\(_{0.3}\)TiO\(_3\) /TiO\(_2\)/Pt/Si-(100)

\[ a = 5.67858(9) \, \text{Å} \]
\[ b = 5.69038(9) \, \text{Å} \]
\[ c = 3.99558(4) \, \text{Å} \]
\[ \beta = 90.392(1) \, \text{Å} \]
\[ T = 1322(9) \, \text{Å} \]
\[ t_{iso} = 1338(2) \, \text{Å} \]
\[ \varepsilon = 0.0067(1) \, \text{rms} \]
AlN/Pt/TiO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}/Ni-Co-Cr-Al

Rw (%) = 24.120445
Rexp (%) = 5.8517213
T(AlN) = 14270(3) nm
T(Pt) = 430(3) nm
\[(\chi, \varphi)\] randomly selected diagrams

**\(\text{Al}_2\text{O}_3\)**

\[a = 4.7562(6) \text{ Å}\]
\[c = 12.875(3) \text{ Å}\]
\[T = 7790(31) \text{ nm}\]
\[\langle t \rangle = 150(2) \text{ Å}\]
\[\langle \varepsilon \rangle = 0.008(3)\]

**\(\text{Ni}, \text{Co}\)**

\[a = 3.569377(5) \text{ Å}\]
\[\langle t \rangle = 7600(1900) \text{ Å}\]
\[\langle \varepsilon \rangle = 0.00236(3)\]
\[\sigma_{11} = -328(8) \text{ MPa}\]
\[\sigma_{22} = -411(9) \text{ MPa}\]
Rw (%) = 4.1

a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<t> = 2404(8) Å
<ε> = 0.001853(2)
σ_{11} = -1019(2) MPa
σ_{22} = -845(2) MPa

Rw (%) = 33.3

a = 3.91198(1) Å
T = 1204(3) nm
<t> = 2173(10) Å
<ε> = 0.002410(3)
σ_{11} = -196.5(8)
σ_{22} = -99.6(6)
Substrate bias vs stress-texture evolution
Si nanocrystalline thin films

M. Morales, Caen

Silicon thin films deposition by reactive magnetron sputtering:
- power density 2W/cm²
- total pressure: \( p_{\text{total}} = 10^{-1} \) Torr
- plasma mixture: \( \text{H}_2 / \text{Ar}, \frac{\text{pH}_2}{p_{\text{total}}} = 80 \% \)
- temperature: 200°C
- substrates: amorphous SiO\(_2\) (a-SiO\(_2\))
  - (100)-Si single-crystals
- target-substrate distance (d)
  - a-SiO\(_2\) substrates: \( d = 4, 6, 7, 8, 10, 12 \) cm
    - films A, B, C, D, E, F
  - (100)-Si:
    - d = 6, 12 cm
    - films G, H

Aim: quantum confinement, photoluminescence properties
Typical refinement

broad, anisotropic diffracted lines, textured samples
## Refinement Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>d (cm)</th>
<th>a (Å)</th>
<th>RX thickness (nm)</th>
<th>Anisotropic sizes (Å) &lt;111&gt;</th>
<th>Texture parameters</th>
<th>Reliability factors (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum (m.r.d.)</td>
<td>minimum (m.r.d.)</td>
</tr>
<tr>
<td>A</td>
<td>4</td>
<td>5.4466 (3)</td>
<td>---</td>
<td>94</td>
<td>1.95</td>
<td>0.4</td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>5.4439 (2)</td>
<td>711 (50)</td>
<td>101</td>
<td>1.39</td>
<td>0.79</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>5.4346 (4)</td>
<td>519 (60)</td>
<td>99</td>
<td>1.72</td>
<td>0.66</td>
</tr>
<tr>
<td>D</td>
<td>8</td>
<td>5.4461 (2)</td>
<td>1447 (66)</td>
<td>100</td>
<td>1.57</td>
<td>0.63</td>
</tr>
<tr>
<td>E</td>
<td>10</td>
<td>5.4462 (2)</td>
<td>1360 (80)</td>
<td>98</td>
<td>1.22</td>
<td>0.82</td>
</tr>
<tr>
<td>F</td>
<td>12</td>
<td>5.4452 (3)</td>
<td>1110 (57)</td>
<td>85</td>
<td>1.59</td>
<td>0.45</td>
</tr>
<tr>
<td>G</td>
<td>6</td>
<td>5.4387 (3)</td>
<td>1307 (50)</td>
<td>89</td>
<td>1.84</td>
<td>0.71</td>
</tr>
<tr>
<td>H</td>
<td>12</td>
<td>5.4434 (2)</td>
<td>1214 (18)</td>
<td>88</td>
<td>2.77</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Mean anisotropic shape

Schematic of the mean crystallite shape for Sample D represented in a cubic cell, as refined using the Popa approach and exhibiting a strong elongation along $<111>$, and TEM image.
001 Inverse Pole Figures

a-SiO$_2$

(100)-Si

min

max
Sample B (d = 6 cm)

XRR:
Roughness governed

AFM:
homogeneous roughness
Refractive index linked to film porosities:
Larger target-sample distances: increased compacity due to lower nanopowder filling
Irradiated FluorApatite (FAp) ceramics

Self-recrystallisation under irradiation, depending on SiO$_4$/PO$_4$ ratio (FAp / Nd-Britholite) and on irradiating species

TEM of FAp irradiated with 70 MeV, $10^{12}$ Kr cm$^{-2}$ ions
Virgin, with texture correction

$10^{13}$ Kr cm$^{-2}$

Virgin, no texture correction
<table>
<thead>
<tr>
<th>Fluence (ions.cm⁻²)</th>
<th>Vc/V (%)</th>
<th>A (Å)</th>
<th>c (Å)</th>
<th>&lt;t&gt; (nm)</th>
<th>Δa/a₀ (%)</th>
<th>Δc/c₀ (%)</th>
<th>R_w (%)</th>
<th>R_B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>9.3365(3)</td>
<td>6.8560(5)</td>
<td>294(22)</td>
<td>-</td>
<td>-</td>
<td>14.6</td>
<td>9.1</td>
</tr>
<tr>
<td>10¹¹</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10¹²</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.10¹²</td>
<td>49(1)</td>
<td>9.3775(9)</td>
<td>6.8912(8)</td>
<td>294(20)</td>
<td>0.44</td>
<td>0.53</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>10¹³</td>
<td>20(1)</td>
<td>9.4236(5)</td>
<td>6.9105(5)</td>
<td>291(20)</td>
<td>0.94</td>
<td>0.82</td>
<td>9.9</td>
<td>6</td>
</tr>
<tr>
<td>5.10¹³</td>
<td>14(1)</td>
<td>9.3160(4)</td>
<td>6.8402(5)</td>
<td>294(22)</td>
<td>-0.21</td>
<td>-0.22</td>
<td>10.5</td>
<td>5.9</td>
</tr>
<tr>
<td>10¹¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.10¹¹</td>
<td>86(2)</td>
<td>9.3603(3)</td>
<td>6.8790(5)</td>
<td>90(10)</td>
<td>0.26</td>
<td>0.35</td>
<td>23.9</td>
<td>15.1</td>
</tr>
<tr>
<td>10¹²</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.10¹²</td>
<td>47(2)</td>
<td>9.3645(3)</td>
<td>6.8840(5)</td>
<td>91(6)</td>
<td>0.30</td>
<td>0.42</td>
<td>13.3</td>
<td>9</td>
</tr>
<tr>
<td>5.10¹²</td>
<td>29.2(5)</td>
<td>9.3765(5)</td>
<td>6.8881(6)</td>
<td>77(11)</td>
<td>0.44</td>
<td>0.48</td>
<td>10.4</td>
<td>7.3</td>
</tr>
<tr>
<td>10¹³</td>
<td>13.2(2)</td>
<td>9.3719(4)</td>
<td>6.8857(6)</td>
<td>82(9)</td>
<td>0.38</td>
<td>0.45</td>
<td>6.7</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Single impact model associated to crystal size reduction

Cell parameters and volume increase, then relax

Amorphisation / recrystallisation competition: single or double impact
Amorphous/crystalline volume fraction (damaged fraction $F_d = \frac{V_a}{V}$) as determined by x-ray diffraction

<table>
<thead>
<tr>
<th>Fitting parameters</th>
<th>Krypton</th>
<th>Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single impact</td>
<td>Double impact</td>
</tr>
<tr>
<td>$A = \pi R^2 \text{ (cm}^2\text{)}$</td>
<td>$1.85 \pm 0.15 \times 10^{-13}$</td>
<td>$4.1 \pm 0.15 \times 10^{-13}$</td>
</tr>
<tr>
<td>Radius $R \text{ (nm)}$</td>
<td>$2.4 \pm 0.2$</td>
<td>$3.6$</td>
</tr>
<tr>
<td>$B \text{ (Max. damage rate)}$</td>
<td>$0.87$</td>
<td>$0.85 \pm 0.2$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>$0.013$</td>
<td>$0.0006$</td>
</tr>
</tbody>
</table>
Mullite-silica composites

ODF: $R_w = 4.87 \%$, $R_B = 4.01 \%$
Rietveld: $R_w = 12.90 \%$, GoF = 1.77
Mullite: $a = 7.56486(5) \text{ Å}$; $b = 7.71048(5) \text{ Å}$; $c = 2.89059(1)\text{ Å}$
Uniaxially pressed

Centrifugated
for all $(\chi, \varphi)$ sample orientations

refined experiments

GoF: 1.72
Rw: 28.0%
Rexp: 21.3%
IRC layer of *Charonia lampas lampas* for selected \((\chi,\varphi)\) sample orientations
Turbostratic phyllosilicate aggregates

GoF = 3.3

V%
1.45(2)
6.6(1)
0.19(1)
91.8(3)
Specular reflectivity: \( q=(0,0,z) \)

- **Fresnel:**
  \[
  R(q) = \frac{q_z - \sqrt{q_z^2 - q_e^2 + \frac{32i\pi^2\beta}{\lambda^2}}}{q_z + \sqrt{q_z^2 - q_e^2 + \frac{32i\pi^2\beta}{\lambda^2}}} \delta q_x \delta q
  \]

- **matrix:**
  \[
  R_{flat} = \frac{r_{0,1}^2 + r_{1,2}^2 + 2r_{0,1} r_{1,2} \cos 2k_{Z,1} h}{1 + r_{0,1}^2 r_{1,2}^2 + 2r_{0,1} r_{1,2} \cos 2k_{Z,1} h}
  \]

- **Born approximation:**
  Electron Density Profile
  \[
  R(q_z) = r_0 r^* = R_F(q_z) \left| \frac{1}{\rho_s} \int_{-\infty}^{+\infty} d\rho(z) e^{iq_z z} dz \right|^2
  \]

- **Roughness:**
  \[
  R^{\text{rough}}(q_z) = R(q_z) \exp(-q_{z,0} q_{z,1} \sigma^2) \quad \text{Low-angles (reflectivity)}
  \]
  \[
  S_R = 1 - p \exp(-q) + p \exp\left(\frac{-q}{\sin\theta}\right) \quad \text{high-angle (Suortti)}
  \]
CPS scans

20 = w + w_c

Useful for having both specular and off-specular signals in one scan
Microstructure of nanocrystalline materials: TiO$_2$ rutile \(^{(1)}\)

- *quantitative analysis of electron diffraction ring pattern* ?
Why not more?
Conclusions

a) A lot of dilemma are only apparent

b) Texture helps to resolve them: good for real samples

c) Anisotropy favours higher resolutions

d) Combined analysis may be a solution, unless you can destroy your sample or are not interested in macroscopic anisotropy ... 

e) If you think you can destroy it, perhaps think twice

f) more information is always needed: why not more?

g) Combined Analysis (D. Chateigner Ed), Wiley-ISTE 2010