Combined Analysis for the characterisation of texture, microstructure and stresses of nanocrystalline thin layers

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ZnSe films
nano-Si films
AlN/Pt/Ni(Co) films
Irradiated FAp ceramics
Implemented codes

- 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
  - pole figures
  - inverse pole figures

- Structural parameters
  - atomic positions, substitutions, vibrations
  - cell parameters

- Multiphased, layered samples:
  - Thickness,
  - Anisotropic Sizes
  - and $\mu$-strains (Popa),
  - Stacking faults (Warren), distributions

- Phase ratio (amorphous + crystalline)
  - Le Bail
  - Rietveld

- Implemented codes
  - Voigt, Reuss,
  - Geometric mean
  - Le Bail
  - Diffractometer software
  - WIMV, E-WIMV
  - Harmonics, components, ADC

- Specular Reflectivity
  - Fresnel, Matrix (Parrat), DWBA
Rietveld

$$I_i^{calc} (\chi, \phi) = \sum_{n=1}^{Nphases} S_n \sum_{k} L_k |F_{k;n}|^2 S(2\theta_i - 2\theta_{k;n}) P_{k;n} (\chi, \phi) A + bkg_i$$

Texture

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

- ODF solved using E-WIMV, Standard functions, Harmonics, ADC or max entropy

Anisotropic sizes and microstrains

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

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

Probes \( \mu T \)

\[ \chi = 0^\circ \quad \chi > 0^\circ \]

Strain-Stress

- Using the ODF and geometric mean approach
- Fitting the macrostress tensor
Si nanocrystalline thin films

Deposition: reactive magnetron sputtering (H$_2$ / Ar)
Low temperature: 200°C
Substrates: amorphous SiO$_2$ (a-SiO$_2$) and (100)-Si single-crystals
Varying Target-substrate distance (d)

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)</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 20 27</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 20 22</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 40 52</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 22 33</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 20 25</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 22 26</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 22 28</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 22 24</td>
<td>2.77</td>
<td>0.50</td>
</tr>
</tbody>
</table>
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

a-SiO$_2$ (100)-Si
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
**AlN/Pt/TiO\(_x\)/Al\(_2\)O\(_3\)/Ni-Co-Cr-Al**

E. Derniaux, PhD

**2D Multiplot for Data 05_37P64**
- Measured data and fit

**2D difference plot for Data 05_37P64**
- Difference data - fit

\[ \text{Rw (\%)} = 24.120445 \]
\[ \text{Rexp (\%)} = 5.8517213 \]

\[ \text{T(AlN)} = 14270(3) \text{ nm} \]
\[ \text{T(Pt)} = 430(3) \text{ nm} \]
\[(\chi, \varphi)\] randomly selected diagrams

**Al_2O_3**

- \(a = 4.7562(6) \text{ Å}\)
- \(c = 12.875(3) \text{ Å}\)
- \(T = 7790(31) \text{ nm}\)
- \(<t> = 150(2) \text{ Å}\)
- \(<\varepsilon> = 0.008(3)\)

**Ni,Co**

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

\[ a = 3.11203(1) \text{ Å} \]
\[ c = 4.98252(1) \text{ Å} \]
\[ T = 14270(3) \text{ nm} \]
\[ \langle t \rangle = 2404(8) \text{ Å} \]
\[ \langle \varepsilon \rangle = 0.001853(2) \]
\[ \sigma_{11} = -1019(2) \text{ MPa} \]
\[ \sigma_{22} = -845(2) \text{ MPa} \]

Rw (%) = 33.3

\[ a = 3.91198(1) \text{ Å} \]
\[ c = 4.98252(1) \text{ Å} \]
\[ T = 1204(3) \text{ nm} \]
\[ \langle t \rangle = 2173(10) \text{ Å} \]
\[ \langle \varepsilon \rangle = 0.002410(3) \]
\[ \sigma_{11} = -196.5(8) \text{ MPa} \]
\[ \sigma_{22} = -99.6(6) \text{ MPa} \]
Substrate bias vs stress-texture evolution
Irradiated FluorApatite (FAp) ceramics

S. Miro, PhD

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
texture corrected, $10^{13} \text{ Kr cm}^{-2}$

Virgin, with texture correction

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/a(_0) (%)</th>
<th>Δc/c(_0) (%)</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>(10^{11}) Kr</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(10^{12})</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(5.10^{12}) Kr</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>(10^{13}) Kr</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>(5.10^{13}) Kr</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>(10^{11}) I</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(5.10^{11}) I</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>(10^{12})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(3.10^{12})</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>
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<tr>
<td>(5.10^{12})</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>(10^{13})</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 $F_d = V_a / V$) as determined by x-ray diffraction

### Fitting parameters

<table>
<thead>
<tr>
<th></th>
<th>Krypton</th>
<th></th>
<th>Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single impact</td>
<td>Double impact</td>
<td>Single 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>
<td>$3.3 \pm 0.15 \times 10^{-13}$</td>
</tr>
<tr>
<td>Radius $R$ (nm)</td>
<td>$2.4 \pm 0.2$</td>
<td>$3.6$</td>
<td>$3.2$</td>
</tr>
<tr>
<td>$B$ (Max. damage rate)</td>
<td>$0.87$</td>
<td>$0.85 \pm 0.2$</td>
<td>$0.92 \pm 0.2$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>$0.013$</td>
<td>$0.0006$</td>
<td>$0.0004$</td>
</tr>
</tbody>
</table>
ZnSe:Cr\(^{2+}\) films
N. Vivet, PhD

**conditions:**
- \(20 \leq T_d \leq 385^\circ\text{C}\)
- \(P_{\text{RF}} = 50\text{-}200\text{W}\)
- \(P_{\text{Ar}} = 0.5\text{ Pa and } 2\text{ Pa}\)
- \(d = 7\text{ and } 10\text{ cm}\)

- Large emission band centred at 2200nm: \(^5\text{E} \rightarrow ^5\text{T}_2\) transition (Cr\(^{2+}\))
- Single crystals and thin films: similar spectra

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![Graph showing PL Intensity vs. Wavelength with notable peak at 2200nm for Cr\(^{2+}\):ZnSe film compared to bulk ZnSe.](image_url)
Residual stresses and/or stacking faults

Anisotropic sizes

$\chi = 5^\circ$

$\chi = 20^\circ$

$\chi = 40^\circ$

$\chi = 60^\circ$

111 Peak shifts

100 h

101 h

103 h
Fibre Texture + 2 polytypes (6H and 3C) + anisotropic sizes + residual stresses and/or stacking faults + layering

Hard to model even with E-WIMV

Sum diagram: $\omega = 13.65^\circ$, $P_{RF} = 200W$
Conclusions

a) Texture affects phase ratio and structure determination

b) Microstructure (crystallite size) affects texture (go to a)

c) Stresses shift peaks then affects structure and texture determination

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: local probes ...

g) www.ecole.ensicaen.fr/~chateign/texture/combined.pdf