ANISOTROPIC CRYSTALLITE SIZE ANALYSIS OF TEXTURED NANOCRYSTALLINE SILICON THIN FILMS PROBED BY X-RAY DIFFRACTION
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Introduction

The new "combined" x-ray technique is used, which is able to characterise quantitatively:

- texture
- structure (cell parameters)
- anisotropic crystallite shapes
- film thickness

Samples are nanocrystalline silicon films, grown by reactive magnetron sputtering

Crystallographic results are correlated to refraction indexes and optical pseudo-gap
X-rays experiments

4 - circles
diffractometer
+
Curved Position
Sensitive Detector

Cu K$_\alpha$ radiation, Graphite monochromator, calibration: LaB$_6$
scans: $\omega = 14.25^\circ$ (111 Si reflection), $0 \leq \chi \leq 35^\circ$, $\Delta \chi = 5^\circ$
Samples

Silicon thin films deposition by reactive magnetron sputtering:

- power density $2 \text{W/cm}^2$
- total pressure: $p_{\text{total}} = 10^{-1} \text{Torr}$
- plasma mixture: $\text{H}_2 / \text{Ar}$, $p_{\text{H}_2} / p_{\text{total}} = 80 \%$
- temperature: $200^\circ\text{C}$
- substrates: amorphous SiO$_2$ (a-SiO$_2$) (100)-Si single-crystals
- target-substrate distance ($d$)
  - a-SiO$_2$ substrates: $d = 4, 6, 7, 8, 10, 12 \text{ cm}$
    - films A, B, C, D, E, F
  - (100)-Si: $d = 6, 12 \text{ cm}$
    - films G, H
Combined XRD analysis: MAUD

- Integrated Intensities (Le Bail extraction)
- Orientation Distribution Function
- Structural + Microstructural parameters
- Residual stresses
- Specular Reflectivity + Electronic Density Profiles
- Interface and Surface rugosities, Densities, Thicknesses

- Multiphased, layered samples:
  - Thicknesses
  - Structure,
  - Anisotropic Sizes (Popa rules)
  - $\mu$-strains,
  - Stacking faults
  - Phase ratio (amorphous + crystalline)

- Fourier analysis, $sin^2\psi$
Typical refinement

Measured: dots, simulated: lines
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 0.4</td>
<td>1.12</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 0.79</td>
<td>1.01</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 0.66</td>
<td>1.05</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 0.63</td>
<td>1.04</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 0.82</td>
<td>1.01</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 0.45</td>
<td>1.05</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 0.71</td>
<td>1.01</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 0.50</td>
<td>1.12</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> (see Table).
001 Inverse Pole Figures

a-SiO$_2$

(100)-Si
Texture evolution with $d$

Films on a-SiO$_2$ substrates:

• overall texture strength almost unaffected by $d$ ($F^2$ around 1.2 m.r.d.$^2$ at maximum), but texture components strongly influenced:
  - smallest distances (Sample A) favours $<110>$ orientation with minor $<100>$ and $<124>$ components
  - $<110>$ orientation is destabilised for larger $d$'s

• $<110>$ component removal accompanied by a slight tilt of $<100>$ and the appearance of a large $<221>$ like component

• progressive shift of $<221>$ like component towards $<111>$ for larger $d$'s (Samples B to F)

• no pure $<111>$ orientation is observed
Films on (100)-Si substrates:

• stabilisation of single <100> component for all d's

• heteroepitaxial growth:
  - [100]-film // [100]-substrate
  - native amorphous SiO$_2$ layer etched by hydrogen species of the plasma

• no <111> orientation is observed

• $a_{Si}$ in films always larger than $a_{Si}$ in bulk

• ODF maxima larger using (100)-Si substrates
### Profilometry versus XRD thickness

<table>
<thead>
<tr>
<th>Samples</th>
<th>d (cm)</th>
<th>Profilometry Thickness (nm)</th>
<th>RX thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4</td>
<td>700</td>
<td>----</td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>1350</td>
<td>711 (50)</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>1530</td>
<td>519 (60)</td>
</tr>
<tr>
<td>D</td>
<td>8</td>
<td>1465</td>
<td>1447 (66)</td>
</tr>
<tr>
<td>E</td>
<td>10</td>
<td>1470</td>
<td>1360 (80)</td>
</tr>
<tr>
<td>F</td>
<td>12</td>
<td>1208</td>
<td>1110 (57)</td>
</tr>
<tr>
<td>G</td>
<td>6</td>
<td>1350</td>
<td>1307 (50)</td>
</tr>
<tr>
<td>H</td>
<td>12</td>
<td>1200</td>
<td>1214 (18)</td>
</tr>
</tbody>
</table>

*high porosity*
Optical measurements: refractive indexes and pseudo-gap

Refractive index $n$

Pseudo-gap $E_{04}$ (eV)

$d$ spacing (cm)
µ–structure versus optical properties

- large minimum ODF values: small anisotropy expected, 60% to 20% of textured volume
- abrupt increase of the refractive index (n) for small d's then saturation
  
  reflects the film compactness

- opposite evolution of n and $E_{04}$
  
  relatively high density of microcavities inherent to the film porosity
Conclusions

• Preferred orientations, cell parameters and anisotropic crystallite sizes of nanocrystalline silicon thin films deposited on a-SiO$_2$ and (100)-Si substrates have been quantitatively determined.

• Strong texture variations are observed when the electrode distance and/or the substrate is varied.

• Texture variations are correlated to the anisotropic crystal growth

• Porosities are correlated to refractive indices