Thin Film Scattering: Epitaxial Layers
• Thin films. Epitaxial thin films
• What basic information we can obtain from x-ray diffraction
• Reciprocal space and epitaxial thin films
• Scan directions – reciprocal vs. real space scenarios
• Mismatch, strain, mosaicity, thickness
• How to choose right scans for your measurements
• Mosaicity vs. lateral correlation length
• SiGe(001) layers on Si(001) example
• Why we need channel analyzer
• What can we learn from reciprocal space maps
• SrRuO$_3$ and La$_{0.67}$Sr$_{0.33}$MnO$_3$ films example
• Summary
What is thin film/layer?

Material so thin that its characteristics are dominated primarily by two dimensional effects and are mostly different than its bulk properties
Source: semiconductorglossary.com

Material which dimension in the out-of-plane direction is much smaller than in the in-plane direction.

A thin layer of something on a surface
Source: encarta.msn.com
Epitaxial Layer

A single crystal layer that has been deposited or grown on a crystalline substrate having the same structural arrangement.  
*Source: photonics.com*

A crystalline layer of a particular orientation on top of another crystal, where the orientation is determined by the underlying crystal.

**Homoepitaxial layer**  
the layer and substrate are the same material and possess the same lattice parameters.

**Heteroepitaxial layer**  
the layer material is different than the substrate and usually has different lattice parameters.
## Thin films structural types

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect epitaxial</td>
<td>Single crystal in perfect registry with the substrate that is also perfect.</td>
</tr>
<tr>
<td>Nearly perfect epitaxial</td>
<td>Single crystal in nearly perfect registry with the substrate that is also nearly perfect.</td>
</tr>
<tr>
<td>Textured epitaxial</td>
<td>Layer orientation is close to registry with the substrate in both in-plane and out-of-plane directions. Layer consists of mosaic blocks.</td>
</tr>
<tr>
<td>Textured polycrystalline</td>
<td>Crystalline grains are preferentially oriented out-of-plane but random in-plane. Grain size distribution.</td>
</tr>
<tr>
<td>Perfect polycrystalline</td>
<td>Randomly oriented crystallites similar in size and shape.</td>
</tr>
<tr>
<td>Amorphous</td>
<td>Strong interatomic bonds but no long range order.</td>
</tr>
</tbody>
</table>
Thin films structural properties

- Mosaic spread
- Curvature
- Misorientation
- Relaxation
- Dislocation content
- Inhomogeneity
What we want to know about thin films?

- Crystalline state of the layers:
  - Epitaxial (coherent with the substrate, relaxed)
  - Polycrystalline (random orientation, preferred orientation)
  - Amorphous

- Crystalline quality

- Strain state (fully or partially strained, fully relaxed)

- Defect structure

- Chemical composition

- Thickness

- Surface and/or interface roughness
## Overview of structural parameters that characterize various thin films

<table>
<thead>
<tr>
<th></th>
<th>Thickness</th>
<th>Composition</th>
<th>Relaxation</th>
<th>Distortion</th>
<th>Crystalline size</th>
<th>Orientation</th>
<th>Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perfect epitaxy</strong></td>
<td>×</td>
<td>×</td>
<td></td>
<td></td>
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<td>×</td>
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</tr>
<tr>
<td><strong>Nearly perfect epitaxy</strong></td>
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<tr>
<td><strong>Textured epitaxy</strong></td>
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<td>×</td>
</tr>
<tr>
<td><strong>Textured polycrystalline</strong></td>
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<td>?</td>
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<tr>
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<td><strong>Amorphous</strong></td>
<td>×</td>
<td>×</td>
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</tr>
</tbody>
</table>
**Tetragonal Distortion**

Lattice mismatch between cubic lattice parameters:

\[
\frac{\Delta a}{a} = \frac{a_L^R - a_S}{a_S}
\]

Lattice mismatch induces lattice strain:

\[
\varepsilon_\perp = \varepsilon_{zz} = \frac{a_L^\perp - a_L^R}{a_L^R} = \frac{d_L^\perp - d_L^R}{d_L^R}
\]
Single crystal
Polycrystalline Random
Relaxed Layer

Cubic: $a_L > a_S$

Cubic
Strained Layer

Compressive strain

Tetragonal:

\[ a_L^{II} = a_S \]
\[ a_L^\perp > a_S \]

Tetragonal distortion

Cubic
Perfect Layers: Relaxed and Strained

Reciprocal Space

(ooo) (ooo)

Cubic

Tetragonal

$\alpha_L > \alpha_S$

Cubic
Reciprocal space – Ewald sphere

$$|OC| = \frac{1}{\lambda} \sin \theta = \frac{1}{2} |d^*_{hkl}| = \frac{1}{2d_{hkl}} \rightarrow \lambda = 2d_{hkl} \sin \theta$$

$$|OB| = d^*_{hkl}$$
Reciprocal space – Scattering vector

$$\frac{s - s_0}{\lambda} = \frac{2 \sin \theta}{\lambda} = d^*_{hkl} = \frac{1}{d_{hkl}}$$

$$\lambda = 2d_{hkl} \sin \theta$$

Reciprocal Lattice Point

Diffraeted beam

Incident beam

Reciprocal space – Scattering vector

Symmetrical Scan

Asymmetrical Scan

Relaxed Layer

Strained Layer

(o0l)

(hkl)

(oo0)

(hoo)

(o0l) scan

(oo0)

(hkl)

(oo0)

(hoo) scan

(oo0)

(-hkl)
Scan Directions

Symmetrical Scan
\( \theta - 2\theta \) scan

Asymmetrical Scan
\( \omega - 2\theta \) scan

\( \alpha = \theta - \omega \)
Scan Directions

Sample Surface
Scan Directions

Symmetrical $\omega - 2\theta$ scan

Asymmetrical $\omega - 2\theta$ scan

Sample Surface
Symmetrical Scan
Grazing Incidence Diffraction
Real RLP shapes

\[ c_L > a_S \]

\[ c_L < a_S \]

Finite thickness effect

L

S

Compressive strain

Tensile strain

d-spacing variation

Mosaicity
Mismatch

True lattice mismatch is: \[ m = \frac{a_L^R - a_S}{a_S} \]

For cubic (001) oriented material the experimentally measured normal component of the mismatch:

\[ m_\perp = \frac{a_\perp - a_S}{a_S} = \left( \frac{\Delta a}{a} \right)_\perp = \left( \frac{\Delta d}{d} \right) = \frac{\sin \theta_S - \sin(\theta_S + \Delta \theta)}{\sin(\theta_S + \Delta \theta)} \]

The experimental mismatch, \( m_\perp \), can be related to the mismatch through the equation:

\[ m = \frac{a_L^R - a_S}{a_S} = \frac{1 - \nu}{1 + \nu} m_\perp \]

where \( \nu \) is Poisson ratio.
For Si, \( \nu = 0.28 \)

\[
\begin{align*}
\nu &\approx \frac{1}{3} \\
m &\approx \frac{m^*}{2}
\end{align*}
\]

The composition of the \( A_{1-x}B_x \) alloy can be calculated from Vegard’s law:

\[ a_L^R(x) = (1 - x)a_A + x a_B \]

\[ x = m \frac{a_A}{a_B - a_A} \]
**Layer Thickness**

Interference fringes observed in the scattering pattern, due to different optical paths of the x-rays, are related to the thickness of the layer:

\[
t = \frac{(n_1 - n_2) \lambda}{2(\sin \omega_1 - \sin \omega_2)}
\]

**Substrate Layer Separation**

<table>
<thead>
<tr>
<th>S-peak:</th>
<th>L-peak:</th>
<th>Separation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omega(°) 34.5649</td>
<td>Omega(°) 33.9748</td>
<td>Omega(°) 0.59017</td>
</tr>
<tr>
<td>2Theta(°) 69.1298</td>
<td>2Theta(°) 67.9495</td>
<td>2Theta(°) 1.18034</td>
</tr>
</tbody>
</table>

**Layer Thickness**

Mean fringe period (°): 0.09368
Mean thickness (um): 0.113 ± 0.003

<table>
<thead>
<tr>
<th>2Theta/Omega (°)</th>
<th>Fringe Period (°)</th>
<th>Thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.22698 - 66.32140</td>
<td>0.09442</td>
<td>0.111637</td>
</tr>
<tr>
<td>66.32140 - 66.41430</td>
<td>0.09290</td>
<td>0.113528</td>
</tr>
<tr>
<td>66.41430 - 66.50568</td>
<td>0.09138</td>
<td>0.115481</td>
</tr>
<tr>
<td>66.50568 - 66.59858</td>
<td>0.09290</td>
<td>0.113648</td>
</tr>
<tr>
<td>66.59858 - 66.69300</td>
<td>0.09442</td>
<td>0.111878</td>
</tr>
<tr>
<td>66.69300 - 66.78327</td>
<td>0.09027</td>
<td>0.117079</td>
</tr>
</tbody>
</table>
Partially Relaxed + Thin

Partially Relaxed + Mosaicity
Symmetrical scan

ω-2θ direction

Defined by receiving optics (e.g. slits)

Defined by incident optics – monochromator

Mosaicity

(oool)

S

L

(ooo)
Symmetrical Scan

ω direction

ω-2θ direction

(ool)

(ooo)

d-spacing variation

mosaicity

receiving slit

analyzer crystal

analyzer crystal

receiving slit
Triple axis diffractometry

Ge content: 50% 40% 30% 20% 10%

Open detector

Triple axis

[Graphs and diagrams showing data and analysis related to Ge content and triple axis diffractometry]
Symmetrical Scan

Asymmetrical Scan

ω-scan

ω-2θ scan

h-scan

l-scan

(ool)

(hkl)

(ooo)

(hoo)

(ool)

(hkl)

(ooo)

(hoo)
Relaxed SiGe on Si(001)

Shape of the RLP might provide much more information
Relaxed SiGe on Si(001)
$\omega$-scan

$\omega$-2$\theta$ scan

(004)

(113)
Relaxation

The relaxation is defined as:

$$R = \frac{a_L - a_S}{a_L - a_S} \times 100$$

To separate the layer tilt from the true splitting we can make grazing incidence and grazing exit measurements:

- The effect of tilt on the peak splitting is reversed if the specimen is rotated by $180^\circ$ about its surface normal.
- The splitting due to mismatch will not be affected by such rotation

$$\Delta \theta_{gi} = \Delta \theta + \Delta \varphi \quad - \quad \text{grazing incidence}$$
$$\Delta \theta_{ge} = \Delta \theta - \Delta \varphi \quad - \quad \text{grazing exit}$$
Analysis of Laterally Inhomogeneous Layers

The Mosaic Spread and Lateral Correlation Length functionality derives information from the shape of a layer peak in a diffraction space map recorded using an asymmetrical reflection

\[
L_3 = \sqrt{\Delta q_x^2 + \Delta q_z^2}
\]

and

\[
\varphi = \frac{1}{\tan \left( \frac{q_x}{q_z} \right)}
\]

\[
\xi = \frac{1}{\tan \left( \frac{\Delta q_x}{\Delta q_z} \right)}
\]

\[
\frac{L_1}{L_2} = -\frac{\cos \xi}{\cos (\varphi + \xi)}
\]

\[
\frac{L_3}{L_2} = -\frac{\sin \varphi}{\cos \xi}
\]

Lateral correlation length \( = \frac{1}{L_1} \)

Microscopic tilt \( = \frac{L_2}{\sqrt{q_x^2 + q_z^2}} \)
Superlattices and Multilayers

Substrate

\[ \Lambda \]

\[ t \]

\[ d_{hkl} \]
Superlattices and Multilayers
Structure of SrRuO₃

- **Orthorhombic**:
  - $a = 5.586\ \text{Å}$
  - $b = 5.555\ \text{Å}$
  - $c = 7.865\ \text{Å}$
  - Temperature range: 275-550 °C

- **Tetragonal**:
  - $a = 5.578\ \text{Å}$
  - $c = 7.908\ \text{Å}$
  - Temperature range: 510-702 °C

- **Cubic**:
  - $a = 3.956\ \text{Å}$
Samples:

$\text{SrRuO}_3$ on SrTiO$_3$ and DyScO$_3$

$\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ on NdGaO$_3$, LSAT, SrTiO$_3$ and DyScO$_3$

Pseudo-cubic lattice parameters:
Finite thickness fringes around the Bragg peak indicate very good structural quality throughout the film.
X-ray diffraction scan types for [110] growth

Q scan

ω – 2θ scan

Reciprocal Space Map

Orthorhombic SrRuO$_3$

Tetragonal SrRuO$_3$

(0 0 2) SrTiO$_3$

(2 0 4) SrRuO$_3$

(6 2 0)

(4 4 -4)
Compressive Stress $\rightarrow$ Unit cell is orthorhombic

$a \neq b$
Tensile Stress

Unit cell is tetragonal

\[ a = b \]
Twinning in SrRuO$_3$/SrTiO$_3$
High-Resolution Reciprocal Area Mapping

Orthorhombic to Tetragonal Transition

Orthorhombic SrRuO$_3$
O–T Structural Transition, (620) & (260) reflections

Transition Orthorhombic to Tetragonal ~ 350 °C

O – T Structural Transition, (221) reflection

Transition Orthorhombic to Tetragonal ~ 310 °C

<table>
<thead>
<tr>
<th>(221) Peak</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthorhombic</td>
<td>Present</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>Absent</td>
</tr>
</tbody>
</table>

Literature: 510-702 °C

\[ \gamma \text{ angle accommodates the stress along [1-10]} \]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(ab) (Å)</th>
<th>(c) (Å)</th>
<th>Layer</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(ab) (Å)</th>
<th>(c) (Å)</th>
<th>(\gamma) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdGaO(_3)</td>
<td>5.428</td>
<td>5.498</td>
<td>7.726</td>
<td>7.708</td>
<td>LSMO/NGO</td>
<td>5.477</td>
<td>5.513</td>
<td>7.725</td>
<td>7.707</td>
<td>89.32</td>
</tr>
<tr>
<td>LSAT</td>
<td>5.476</td>
<td>5.476</td>
<td>7.744</td>
<td>7.740</td>
<td>LSMO/LSAT</td>
<td>5.471</td>
<td>5.507</td>
<td>7.744</td>
<td>7.740</td>
<td>89.72</td>
</tr>
<tr>
<td>SrTiO(_3)</td>
<td>3.905</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DyScO(_3)</td>
<td>5.444</td>
<td>5.721</td>
<td>7.897</td>
<td>7.904</td>
<td>LSMO/DSO</td>
<td>5.478</td>
<td>5.483</td>
<td>7.895</td>
<td>7.902</td>
<td>92.16</td>
</tr>
<tr>
<td>LSMO (O)</td>
<td>5.488</td>
<td>5.524</td>
<td>7.762</td>
<td>7.787</td>
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</table>

<table>
<thead>
<tr>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdGaO(_3)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>LSAT</td>
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</tr>
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<td></td>
</tr>
<tr>
<td>DyScO(_3)</td>
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<td></td>
</tr>
</tbody>
</table>
Summary

- Reciprocal space for epitaxial thin films is very rich.

- Shape and positions of reciprocal lattice points with respect to the substrate reveal information about:
  - Mismatch
  - Strain state
  - Relaxation
  - Mosaicity
  - Composition
  - Thickness ....

- Diffractometer instrumental resolution has to be understood before measurements are performed.
Polycrystalline
Preferred orientation
Single crystal
Polycrystalline