Lecture 11:
Introduction to Thin Film Characterization: Structural and Morphological Characterization
Bibliography


J.C. Vickerman and D. Briggs, ToF-SIMS: Surface Analysis by Mass Spectrometry Edited, IM Publications ISBN 1 901019 03 9


Frank A. Settle, Handbook of Instrumental Techniques for Analytical Chemistry (Prentice Hall PTR, New Jersey, 1997).


Primary beam (source)
- Ions
- Electrons
- Photons

Secondary beam (spectrometers, detectors)
- Ions
- Electrons
- Photons

Vacuum
High-power lithium-ion batteries failure mechanisms

Surface films (from electrode-electrolyte interactions) and surface layers on oxide particles cause positive electrode impedance rise

- Surface films identified by XRD on the oxide particles contain polymeric compounds, LiF, Li$_2$PF$_6$, and Li$_2$PO$_4$-type compounds. Surface film compositions do not change, but surface film thickness appears to increase during aging.

- SEM images show surface films on the oxide particles that result from electrode-electrolyte interactions during aging.

TEM-EELS data:
- A LiNi$_{1/3}$O$_{2/3}$ surface layer, ~2-4 nm thick, is observed.
- The thickness of this surface layer appears to increase as oxide particles from a cell that showed 45% power fade in composition and crystal structure of this surface layer.

- O K-edge EELS data: Pre-edge observed in bulk spectra is absent in surface spectra.
- Ni L-edge EELS data: No binding energy is lower in surface than in bulk; Ni in surface and Ni in bulk.

Area selected for EELS study:
Annular DF image
60°C, 60% state of charge cycle life sample
Typical Analysis Depths for Techniques
Diffraction of x-rays by a crystal

Bragg’s Law: \( n\lambda = 2d \sin \theta \)
"Powder" Diffraction

$\omega - 2\theta \ (\theta - 2\theta)$ scan geometry
Bragg-Brentano

Glancing angle scan geometry
**X-ray analysis of polycrystalline layers and powder materials**

Bragg’s Law

\[ d_{hkl} = \frac{\lambda}{2\sin(\theta)} \]

- Bragg-Brentano or parallel beam x-ray analysis;
- Powders, polycrystalline films or nanostructures, mineralogy, cements, ceramics, pharmaceutics, polymers, biomaterials;
- Identification, quantification (w%) and structure determination of mixtures, impurities, multiple phases and amorphous fractions;
- Quantification of crystallinity, texture, twinning, grain size and strain;
- Pattern indexing, lattice parameters determination, unit cell refinement, atomic positions, bonds distances and angles;
- Pattern simulation and structure refinement (Rietveld analysis)

**Results obtained from the measured pattern:**

- Search / Match: LiNi_{0.7}Co_{0.3}O_{2}, major (minor: C graphite)
- Structure: Hexagonal R-3m (166) <1/3, 2/3, 2/3>, Z=1, hR4
- Cell (Rietveld refinement):
  - \( a = 2.86285 \text{ Å}; b = 2.86285 \text{ Å}; c = 14.17281 \text{ Å} \)
  - \( \alpha = 90^\circ; \beta = 90^\circ; \gamma = 120^\circ \)
  - Unit cell volume: 100.6 (Å)^3
  - Density: 4.8383 g cm^{-3}
  - Linear Absorption Coefficient: 385.5 cm^{-1}
- Average bond distances (Rietveld):
  - Ni-O: 1.9570 Å, Ni-Li: 2.8729 Å,
  - Ni-Ni: 2.8629 Å, Co-O: 1.9570 Å,
  - Co-Ni: 2.8629 Å, Co-Li: 2.8729 Å
  - Li-O: 2.1117 Å, Li-Li: 2.8629 Å,
  - O-O: 2.7983 Å
- Quantitative analysis: 82.9 w% LiNi_{0.7}Co_{0.3}O_{2}, 17.1 w% C
- Crystallite size: > 1000 Å
- Strain: 0.05%

**Data:** Sardela, Abraham et al
**Ta/SiO₂ vs Ts**

GA-XRD 2θ scans

XRD ω-2θ scans

**Ta/SiO₂/Si(001)**

- bcc α-Ta
- tetragonal β-Ta

**t = 500 nm**

**f_N₂ = 0**

**Ts = 100 °C**

**Intensities (a.u.)**

**θ (deg)**

**Intensity (a.u.)**

**ω (deg)**

**Intensities (a.u.)**

**Γω = 3.5**

**Γω = 4.3**
$\text{TaN}_x/\text{SiO}_2 \text{ vs } f_{N_2}$

GA-XRD 2θ scans

<table>
<thead>
<tr>
<th>$\text{TaN}_x/\text{SiO}_2/\text{Si}(001)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s = 100$ ℃</td>
</tr>
<tr>
<td>$t = 500$ nm</td>
</tr>
</tbody>
</table>

- * bct-$\text{TaN}_x$ |
- cubic $\delta$-$\text{TaN}$ |
- hexagonal $\gamma$-$\text{Ta}_2\text{N}$ |
- cubic $\text{TaN}_{0.1}$

TEM

$\delta$-$\text{TaN}_x$: $a_o = 0.443$ nm
bct-$\text{TaN}_x$: $a = 0.590$ nm, $c = 0.443$ nm

N/Ta = 1.96
Growth phase map for TaNₓ

- **Pure Ar**: tetragonal β-Ta @ Tₛ < 150 °C
  bcc α-Ta @ Tₛ > 400 °C.

- **fₓN₂ < 0.1**: three consecutive narrow lower nitride regions, defined by tilted boundaries toward higher fₓN₂ with increasing Tₛ.

- **0.1 < fₓN₂ < 0.3 and Tₛ ≤ 650 °C**: single-phase δ-TaNₓ.

- **0.1 < fₓN₂ < 0.3 and Tₛ > 650 °C**: hexagonal ε-TaNₓ + δ-TaNₓ.

- **Pure N₂**: δ-TaNₓ + bct-TaNₓ.
Stress measurements (\(\sin^2\psi\) method)

\[
\varepsilon_\psi = \frac{a_\psi - a_0}{a_0} = \frac{1 + \nu}{E} \sigma_\phi \sin^2 \psi - \frac{2\nu}{E} \sigma_\phi
\]

\[
a_\psi = \frac{a_0 \sigma_\phi}{E} [(1 + \nu) \sin^2 \psi - 2\nu] + a_0 = \delta \sin^2 \psi + \xi
\]

\(a_\psi\) is expected to depend linearly on \(\sin^2\psi\).
Stress measurement (sin\(^2\)\(\psi\) method)

\[
\epsilon_\psi = \frac{a_\psi - a_0}{a_0} = \frac{1 + v}{E} \sigma_\phi \sin^2 \psi - \frac{2v}{E} \sigma_\phi
\]

\[
a_\psi = \frac{a_0 \sigma_\phi}{E} [(1 + v) \sin^2 \psi - 2v] + a_0 = \frac{a_0 \sigma_\phi (1 + v)}{E} \sin^2 \psi + a_0 \left(1 - \frac{2 \sigma_\phi v}{E}\right)
\]

\(a_\psi\) is expected to depend linearly on \(\sin^2 \psi\).
Stress measurement using XRD

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<th>( 20 )</th>
<th>( \sin^2 \psi )</th>
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<td>57.601</td>
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</table>

\[
a_0 = \xi + \frac{2\delta\nu}{1 + \nu} = 4.5280 \text{ Å}
\]

\[
\sigma_\phi = \frac{E\delta}{2\delta\nu + (1 + \nu)\xi} = -757.9 \text{ MPa (compressive stress)}
\]

\( \delta = -0.01751 \)

\( \xi = 4.53503 \)
Stress and $a_0$ of HfN$_x$/SiO$_2$

- $X \leq 1.17$ : (111) preferred orientation, tensile stress
- $X \geq 1.18$ : (200) preferred orientation, compressive stress
- $X \uparrow \Rightarrow a_0 \uparrow$
X-ray analysis of textured materials

- Texture orientation and quantification
- Volume fraction of textured grains, twinning and random distributions
- Texture strength and sharpness
- Crystallographic orientation
- Crystallographic relationship between layers and substrate

Texture results from a rolled Cu foil

Data: Sardela et al

Orientation distribution function (ODF)
X-ray analysis of lattice mismatched epitaxial films

- **High resolution reciprocal lattice mapping** requires multi-reflection monochromator and analyzer crystal in order to separate strain from mosaicity
  - Sensitive to lattice distortions within $10^{-5}$
  - Accurate lattice parameter determination *(in and out of plane)*
  - Determination of strain and composition variations, strain relaxation, mosaic size and rotation, misfit dislocation density, nanostructure dimensions, lattice disorder and diffuse scattering

No strain relaxation:

- $a_{//} = a_s$

Strain relaxation:

- $a_{//} \neq a_s$

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Data: Sardela et al
HR-XRD and TEM: CeN /MgO(001):

f_{N_2} = 0.25, J_i/J_Me = 15, E_i = 30 eV

Cube on cube epitaxial relationship:
(001)_{CeN}||(001)_{MgO} with [100]_{CeN}||(100)_{MgO}

\( a_{CeN} = 5.021 \text{ Å}, \quad a_{TiN} = 4.242 \text{ Å} \)
Relaxed lattice constant:

\[
a_o = a_\perp \left(1 - \frac{2v(a_\perp - a_\parallel)}{a_\perp(1 + v)}\right)
\]

\[
a_\parallel = \sqrt{2/k_\parallel} \quad \text{for 113 reflection}
\]

\[
a_\perp = 3/k_\perp
\]

The degree of in-plane layer relaxation:

\[
R_L = \frac{a_\parallel - a_s}{a_o - a_s}
\]

\[
R_L = 94\pm4\% \quad \text{for } \delta-\text{TaN}_x \quad (1.0 \leq x \leq 1.37)
\]
X-ray reflectometry of thin films

- Film thickness measurements: 2 – 300 nm
- Applicable to ultra-thin films, amorphous or crystalline materials, multilayers and liquids
- Simulation and fitting: determination of interface roughness (rms) at each interface, and roughness correlation.
- Very sensitive to density variations
- Determination of critical angle, refractive index and density

Log Reflectivity $R$

One sharp surface (density $\rho_e$ variation: step function at surface)

One rough interface ("broad" $\rho_e$ variation at surface)

Two interfaces

2.3 nm thick polymer on Si

Metallic multilayer

Amorphous PZT film

Data: Heitzman et al

Data: Sardela, Auoadi et al

Data: Mikalsen et al

$R \sim \theta^{-4}$

Thickness fringes

\[ \Delta \theta = \frac{\lambda}{2 \cdot \text{thickness}} \]

\[ \Delta I \sim \Delta \rho_e \]

Critical angle $\theta_c$
Atomic Force Microscopy

AFM is a technique which uses a small tip to physically scan the sample surface topography on a sub-nm scale and produce a quantitative map of height vs location.
Atomic Force Microscopy
AFM: Surface morphology evolution during Ge MBE
**Surface Morphological Evolution of TM Nitrides**

- (a) $t = 250$
- (b) $t = 500$
- (c) $t = 1000$
- (d) $t = 2300$

**Universal Scaling Theory**

\[
\langle w \rangle \propto t^\beta, \quad \beta = \text{roughening exponent}
\]

\[
\langle d \rangle \propto t^\gamma, \quad \gamma = \text{coarsening exponent}
\]

\[
\xi = \frac{\langle w \rangle}{\langle d \rangle}, \quad \xi = \text{aspect ratio}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge*</td>
<td>1</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe**</td>
<td>0.16</td>
<td>0.16</td>
<td>0.1</td>
</tr>
<tr>
<td>TiN</td>
<td>0.25</td>
<td>0.25</td>
<td>0.006</td>
</tr>
</tbody>
</table>

\[
G(\rho) = \left\langle (h_i - h_j)^2 \right\rangle
\]
$\textit{Ti}_{1-x}\textit{Ce}_x\textit{N}/\textit{SiO}_2$, $x = 0 - 0.25$

$J_i/J_{Me} \approx 16$, $E_i \approx 14\text{eV}$, $T_S = 350 \, ^\circ\text{C}$
**Ti$_{1-x}$Ce$_x$N/SiO$_2$ (x = 0 - 0.23), T$_S$ = 350 °C, J$_i$/J$_{Me}$ = 15, E$_i$ = 14 eV**

### x < 0.1:
- $a_0$ increases linearly with x.
- $\Gamma_{2\theta}$ (FWHM) remains small.
- $\rho$ increases linearly with x.

### x > 0.1:
- extensive CeN segregation
- 2 phases (TiN-rich / CeN-rich)
- $\Gamma_{2\theta}$ jumps and then increases linearly with x.
- $\rho$ increases faster than x < 0.1.

---

**Mathematical Expression**

\[
D_v = \frac{K \cdot \lambda}{\Gamma_{2\theta} \cdot \cos \theta}
\]

- $D_v$ = Volume weighted crystallite size,
- $K$ = Scherrer constant (0.87-1.0),
- $\lambda$ = The wavelength of the radiation,
- $\Gamma_{2\theta}$ = The integral breadth of a reflection (in radians $2\theta$) located at $2\theta$. 

---
Ti\textsubscript{1-x}Ce\textsubscript{x}N (14 eV) surface morphology f(x)

x = 0
w = 6.82 nm

x = 0.1
w = 4.57 nm

x = 0.15
w = 1.31 nm

x = 0.2
w = 0.32 nm

w = surface width (RMS roughness)

x > 0.1:
- CeN segregation.
- 2 phases (TiN-rich & CeN-rich).
- w drops below 2 nm.
- w reaches 0.32 nm when x = 0.2.
XTEM as \( f(x) \) at \( E_i = 14 \text{ eV} \)

**Kinetic roughening:**
- Low adatom mobility in the presence of Ehrlich barriers* \( E_b \).
- Local epitaxial growth in individual columns \( \bigodot \) facets
  - atomic shadowing
  - underdense structure.

Polycrystalline ScN/MgO(001)

ScN layers on MgO(001) are polycrystalline with 111- and 002-oriented grains, as observed by x-ray diffraction θ-2θ scans.

MgO(001)

ScN

7% mismatch
12-fold symmetry is due to 4-different azimuthal orientations of the ScN three-fold 111-grains on MgO(001)
Nucleation of 111- and 002-oriented ScN grains

ScN(002)/MgO(001)

MgO

ScN

0.425 nm

ScN(111)/MgO(001)

MgO

ScN

0.425 nm

MgO(010)

ScN(010)

ScN(100)

ScN(110)

MgO(100)

7% compression

8% tension

7% compression
Initially both 111- and 002-oriented grains nucleate. However the 111-grains overgrow the 002-grains in a competitive growth mode.