Raman spectroscopy probing grain orientation of synthesized MoS$_2$

Characterization and metrology for 3D CMOS
20 April 2018

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Key properties of $\text{MoS}_2$ for nano-electronics

- Layered material $\rightarrow$ VdWaals
- Stable electr. properties in nm regime
  - Band gap: 1.3 eV ($>1$ ML)
  - Fair mobility
- “Synthesis” $\rightarrow$ Mechanical exfoliation

2D transistor

Nano-electronics $\rightarrow$ scalable synthesis
- Atomic-Layer Deposition (ALD) & Texture synthesized MoS$_2$
- Typical Raman response MoS$_2$
- Mapping Raman response onto angular grain distribution
- Test cases:
  - Sulfidized MoO$_x$
  - PE-ALD MoS$_2$ thickness series
- Impact measurement imperfections
What is atomic layer deposition?

- Thin-film deposition
- Cyclic process
- Sequential self-limiting reactions

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Merits of (PE-) ALD

- Low temperature
- Sub-nm thickness control
- Large scale / wafer size
- Excellent uniformity

Texture synthesized MoS$_2$: TEM analysis

1 Layer of MoS$_2$ [ALD + sulfidation]
- Domain size 10 … 100 nm
- Arbitrary rotation around $c$-axis
Texture synthesized MoS$_2$ : TEM analysis

Different textures:
- Exfoliated $\rightarrow c \parallel n$ single crystal
- Sulfidized MoS$_2$ $\rightarrow c \parallel n$ patches
- Thick PE-ALD $\rightarrow$ fins $\rightarrow$ angular distribution $c$ axis

Need to characterize angular grain orientation
- Synthesized MoS$_2$: Atomic-Layer Deposition (ALD)
- Typical Raman response MoS$_2$
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Raman response MoS$_2$

**Tight focus**
- Better light collection $\rightarrow$ greater sensitivity

**Raman response MoS$_2$**
- Dominated by A$_{1g}$ & E$_{2g}$

**Thick exfoliated flake**

![Diagram of Raman response MoS$_2$ with grating, laser, and CCD](image)

$I_{A_{1g}}/I_{E_{2g}} : 1.688$

<table>
<thead>
<tr>
<th>Raman shift (cm$^{-1}$)</th>
<th>Intensity (a.u.)</th>
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</thead>
<tbody>
<tr>
<td>360</td>
<td>0</td>
</tr>
<tr>
<td>380</td>
<td>300</td>
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<tr>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>420</td>
<td>0</td>
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</table>
Polarized Raman of MoS$_2$
Determining grain orientation
Create mapping of
- reliably measurable quantity
- parameterization grain orientation

Angular grain orientation with Raman
Raman response of nc material?

Cross: $I_{A1g}/I_{E2g} : 0.135$

$\theta_p = 20$
$\alpha = 10$

Single crystal
Nanocrystalline c-aligned
Nanocrystalline angular distribution
Nanocrystalline uniform

Raman response of nc material?
Response 1 crystal MoS$_2$
- \( I = |E_{\text{out}} R E_{\text{in}}|^2 \)

\[
A_{1g} = \text{Calculate response for each grain} \quad \& \quad \text{Add up / Sum}
\]

\[
E_{2gx} = \begin{pmatrix} 0 & -c & d \\ 0 & d & 0 \end{pmatrix}
\]

Response nc MoS$_2$
- We know: Raman response 1 crystal for arbitrary rotation

Microcrystalline c-aligned
Modeling angular distributions

Nanocrystalline uniform

Nanocrystalline angular distribution

Top down view

Rotation $\theta$

Rotation $\Psi$
Mapping A1g/E2g ratio Gaussian distr.
● Synthesized MoS$_2$: Atomic-Layer Deposition (ALD)

● Typical Raman response MoS$_2$

● Mapping Raman response onto angular grain distribution

● Test cases:
  ○ Sulfidized MoO$_x$
  ○ PE-ALD MoS$_2$ thickness series

● Impact measurement imperfections
Angular distribution thermally sulf. MoS$_2$

- Spectrum similar to exfoliated response

Angular distribution from A$_{1g}$/E$_{2g}$ ratio

- Par: $I_{A_{1g}}/I_{E_{2g}} : 2.422$
- Cross: $I_{A_{1g}}/I_{E_{2g}} : 0.221$
Angular distribution from $A_{1g}/E_{2g}$ ratio

- 2 ratios → 2 lines → same FWHM + theta
- Lines nearly intersect at FWHM → 0
  - Dominated by c-aligned
Sulphurized MoOx $\rightarrow$ MoS$_2$

- Mainly 2D layers parallel to surface
- High temperature process $\rightarrow$ relaxation / anneal

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Thickness</th>
<th>NA=0.7 (50x) Par</th>
<th>Cross</th>
<th>COP (%)</th>
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</thead>
<tbody>
<tr>
<td>Exfoliated</td>
<td>$&gt;&gt;$ 1ML</td>
<td>2.63±0.05</td>
<td>0.14±0.05</td>
<td>0±2</td>
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<tr>
<td>Sulph. MoOx</td>
<td>8.0</td>
<td>2.42</td>
<td>0.22</td>
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<tr>
<td>ALD 450°C</td>
<td>8.0</td>
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<td>ALD 450°C</td>
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<td>ALD 450°C</td>
<td>1.6</td>
<td>1.58</td>
<td>0.48</td>
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</tbody>
</table>
Grain orientation with Raman

- Modeled Raman response nano-crystalline material
- For MoS\textsubscript{2}: Mapping A1g/E2g ratio \rightarrow grain orientation

- **Polarized** Raman allows unique determination grain orientation

- Successfully applied to thickness series PE-ALD MoS\textsubscript{2}: annealing effect
Validity:
- Calculation → general (any materials, In2O3, ZnO…)
- Analysis → depends on symmetry material

Influence sample non-idealities:
- Strain / Stress
  - Peak shift
- Grain size
  - Broadening
- Tilt of sample
- Focus error

Influence "grain size" on Raman

- 2 nm radius
- 7 nm
- ∞ nm radius
Modeling Raman response & NA objective

Excitation by laser light

\[ I = \iiint vduudvdu \psi \iiint d\theta' d\psi' d\phi' \iiint d\theta'' d\psi'' d\phi'' \left| \vec{E}_{\text{out}}(\theta', \psi', \phi') \cdot \Phi(\theta'' \psi'' d\phi'') \right| \left( \hat{x} \vec{\Phi}(\theta'' \psi'' d\phi'') \cdot \vec{E}_{\text{in}}(u, v, \psi) \right)^2 \]