Characterization of 2D Materials using XPS, SIMS, & Raman

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Outline

- Intro to 2D materials and their synthesis
- Introduction to TOF SIMS and utility in 2D materials
- XPS & UPS basic principles and instrumentation
- Characterization of advanced materials with XPS and UPS
- Raman on 2D materials including Polarized Raman and TERS
2D materials: Literature Overview

88 TMDs have been explored since 1960s

Metals: ScTe₂, TaS₂, etc.

Semiconductors: WSe₂, MoS₂, WS₂, MoSe₂, etc.

Insulators: PtSe₂, PdS₂, etc.

Superconductors: VS₂, NbSe₂, etc.
Synthesis of 2D materials

CVD

MOCVD

Nano Lett. 2012, 12, 1538–1544
ACS Nano, 2014, 8, 6902–6910
Adv. Mater. 2020, 32, 1904302
Characterization in 2D limit: Challenging!
SIMS for Elemental analysis of 2D materials
Thickness mapping via SIMS
Versatility of Elemental Mapping

h-BN

WS₂
Mapping on heterostructures

Chem. Mater. 2018, 30, 1718−1728
Thickness mapping via Depth Profiles
TOF SIMS: THE M6

ToF-SIMS uses a pulsed primary ion beam (Bin+, Cs+, Ar+, etc.) to impact on a sample surface and induce a fragmentation cascade. The result is the desorption of neutrals, secondary ions (+/-) and electrons from the first few monolayers of the sample. The secondary ions can then be accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector.

1. High lateral resolution (< 50 nm) with the new Nanoprobe 50
2. Mass resolution > 30,000
3. Unique delayed extraction mode for high transmission with high lateral and high mass resolution simultaneously
4. Unmatched dynamic range and detection limits
5. TOF MS/MS with CID fragmentation for molecular structure elucidation
6. New flexible, push-button, closed-loop sample heating and cooling system for long-term operation without user interaction
7. Sophisticated SurfaceLab 7 software including fully integrated Multivariate Statistical Analysis (MVSA) software package

https://www.iontof.com/m6-tof-sims-technology-mass-resolution-secondary-ion-mass-spectrometry.html
XPS & UPS: An overview

Surface electron spectroscopies

**XPS**
- Core electrons ejected
- Gives elemental composition
- Provides some info about "environment" of atoms

**UPS**
- Valence electrons ejected
- Provides estimates for "density of states", frontier orbital energies (HOMO), work function

Equal electron detected in experiment
UPS: An overview

UPS spectrum of Au surface

Schematic energy diagram of a metal.

Schematic energy diagram of a semiconductor.

Work function = 21.21 - 15.9 = 5.31 eV

Literature value 5.3 eV

KE = hν - BE - Ø

BE = hν - KE - Ø
XPS and UPS: FeCoP$_2$S$_6$ & MnCoP$_2$S$_6$

XPS indicates distinct suppression of Fe and Co 2p$_{1/2}$ and 2p$_{3/2}$ peaks in both Fe and Co-rich samples. UPS indicates two distinct work functions with both Fe and Co-rich systems exhibiting a higher work function shift.
XPS of 2D materials on different substrates

On Sapphire

Cu$_2$S

Cu$_2$Se

On Tungsten

Cu

Cu$_2$S

Cu$_2$Se

Cu$_2$Te

Te
Depth Profiling

**Destructive depth profiling**

1. Acquire XPS spectrum
2. Ar ion sputtering
3. Acquire XPS spectrum
4. Ar ion sputtering
5. Acquire XPS spectrum

![Diagram of Sputtering](image)

![Graph of Wavenumber vs. Intensity](image)
Example: Depth Profile of TiO$_x$-Si
RAMAN for 2D materials

Different types of grown structures

Strain induced Raman

Defects

Ferrari et al. PRB (2000) 61, 20
Thickness dependent Raman
Examples of Raman

**Fe-CoP₂S₆**

**Cu₂Te**

**Mn-CoP₂S₆**
Polarization dependent Raman

Anisotropy in Mo$_2$C
Polarization dependent Raman: NiP$_2$Se$_6$

Anisotropy in vibrational modes

Anisotropy in NiPS
ERS overcomes these limitations as the Raman spectrum obtained originates primarily from the molecules within a few tens of nanometers of the tip.

Nanoscale TER imaging of carbon nanotubes see structural heterogeneity, characterize defect sites, chirality variations, and electronic behavior.
Conclusions

- XPS can be used to determine elemental composition of layered 2D materials
- UPS can be used to determine work function of layered structures
- TOF SIMS is an important tool to determine thickness dependence mapping and elemental composition map
- Polarized Raman can determine the anisotropy in the layered system.
THANK YOU!

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Would you please share information on the characterization of 2D materials heterostructures? Particularly, can Raman, XPS, or other surface analysis tools give us information on the twist angle between adjacent 2D layers, for example, the twist angle between graphene layers in bilayer graphene? Thank you!

Application of XPS and Raman in identifying cement hydration mechanism.

Quantitative techniques for Raman and SIMS