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Molybdenum diselenide thin films grown by ALD: An XPS analysis

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Molybdenum diselenide ($MoSe_2$) thin films were deposited on annealed titanium foils by Atomic Layer Deposition (ALD) using suitable precursors. In this work, a detailed XPS analysis of the $MoSe_2$ film is presented. Survey spectra, Mo 3d, Se 3d, Mo 3p, Se LMM, Se 3p, C 1s, Se 4s core level along with the valence band spectra were measured. Quantitative analysis indicates a surface composition of $MoSe_{1.8}$, suggesting a deficiency of selenium on the surface.

Keywords: $MoSe_2$; transition metal dichalcogenides; thin films; 2D material; XPS

Acccession#: A

Technique: XPS, XAES

Host Material: $MoSe_2$

Instrument: Scienta-Omicron ESCA 2SR

Major Elements in Spectra: Mo, Se

Minor Elements in Spectra: C

Published Spectra: 7

Spectra in Electronic Record: 7

Spectral Category: comparison

INTRODUCTION

The discovery of graphene and its subsequent success were the first step for the development and investigation of 2D materials that possess similar or even better physical, chemical, optical and/or electronic properties (Ref. 1). The most significant examples includes transition metal dichalcogenides (TMDCs). TMDCs are semiconducting 2D materials represented by the formula MX_2, where M corresponds to transition metal atom (generally from groups IV-VI) and X indicates a chalcogen atom (S, Se or Te) (Refs. 1-4). A TMDCs monolayer has a layered gap structure, where a single layer of M is sandwiched between two layers of X.The intralayer M-X bonds are predominantly covalent, while the layers interact by weak van der Waals forces, which determines the 2D nature of the crystalline phases. Unlike graphene, monolayered TMDCs have a direct band gap, which gives them great potential in optoelectronic applications (Ref. 5). $MoSe_2$ can be synthesized via top down methods such as mechanical (Ref. 6) and chemical exfoliation (Refs. 7 and 8) based on direct ultrasonication and/or ion intercalation and bottom up methods such as chemical vapor deposition (CVD) (Refs. 9-11) and atomic layer deposition (ALD) (Ref. 12 and 13) techniques. Nevertheless, ALD is the only technique that allows sub-nanometer thickness control, which is revealed as a crucial factor in the properties of 2D TMCDs materials. In this work, $MoSe_2$ thin film was synthesized by ALD and then characterized by XPS without exposition to the environment.

XPS survey spectrum shows that the deposited film was thick enough to avoid any interference from the substrate. The lack of any other signal than those corresponding to molybdenum and selenium, indicated both a complete ligand exchange reaction between the precursors and their high quality.

High resolution spectrum of Mo 3d has an overlap with the signal of Se 3s, therefore this spectrum was deconvoluted with three components, two of them corresponding to the spin-orbit splitting of Mo 3d, Mo $3d_{5/2}$ and Mo $3d_{3/2}$ centered at 228.3 and 231.4 eV, respectively and assigned to the $MoSe_2$ species (Refs. 14 and 15). On the other hand, the signal of Se 3s is at 229.3eV. For Se 3d the signal has two components corresponding to the doublet Se $3d_{5/2}$ at 53.8 eV and Se $3d_{3/2}$ at 54.6 eV attributed to $MoSe_2$.

SPECIMEN DESCRIPTION (ACCESSION # A)

Host Material: $MoSe_2$

CAS Registry #: unknown

Host Material Characteristics: homogeneous; solid; polycrystalline; semiconductor; inorganic compound; Thin Film

Chemical Name: Molybdenum diselenide

Source: Thin film prepared by Atomic Layer Deposition (ALD) on Ti foil substrate.

Host Composition: $MoSe_2$ on Ti foil

Form: Thin film

Structure: $MoSe_2$

History & Significance: $MoSe_2$ thin films were synthesized by ALD in a custom thermal ALD (Beneq, TFS 200) system using $MoCl_5$ and $(Me_3Si)_2Se$ as Mo and Se precursors, respectively on annealed titanium foil substrate. The deposition temperature and reaction chamber pressure were 300 °C and 2 mbar, respectively. One growth ALD cycle was defined by the following sequence: Se precursor (400 ms) – N_2 purge (5 s) – Mo precursor (400 ms)

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– N_2 purge (5 s). The total number of cycles was 600. All processes used N_2 (99.999%) as a carrier gas at a flow rate of 40 standard cubic centimeter per minute (sccm).

As Received Condition: As grown

Analyzed Region: same as host material

Ex Situ Preparation/Mounting: Sample was fixed in a Transfer Box using screws inside a glove box to avoid contact with the environment, then the Transfer Box was fixed in a sample holder using screws.

In Situ Preparation: None

Charge Control: Not applicable

Temp. During Analysis: 298 K

Pressure During Analysis: < 1 x 10^{-7} Pa

Pre-analysis Beam Exposure: 30 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: Scienta-Omicron ESCA 2SR

Analyzer Type: spherical sector

Detector: multichannel resistive plate

Number of Detector Elements: 128

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■*Spectrometer*

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): N=1

Excitation Source Window: Not especified.

Excitation Source: Al Ka monochromatic

Source Energy: 1486.6 eV

Source Strength: 250 W

Source Beam Size: 800 μm x 1600 μm

Signal Mode: multichannel direct

■*Geometry*

Incident Angle: 55 ˚

Source-to-Analyzer Angle: 90 ˚

Emission Angle: 0 ˚

Specimen Azimuthal Angle: Not applicable

Acceptance Angle from Analyzer Axis: 0 ˚

Analyzer Angular Acceptance Width: 8 ˚ x 8 ˚

■*Ion Gun*

Manufacturer and Model: Focus FDG 150/15

Energy: 1000 eV

Current: 70 mA

Current Measurement Method: biased stage

Sputtering Species: Ar^+

Spot Size (unrastered): 150 μm

Raster Size: 3000 μm x 3000 μm

Incident Angle: 62.8 ˚

Polar Angle: Not applicable

Azimuthal Angle: Not applicable

Comment: The specimen was analyzed as loaded. The ion gun was used to obtain the energy calibration spectra.

DATA ANALYSIS METHOD

Energy Scale Correction: The energy scale was calibrated using sputter-cleaned Au, Ag, and Cu foils, as is described in ASTM E2108 (Ref. 16).

Recommended Energy Scale Shift: 0 eV

Peak Shape and Background Method: Peak position and width were determined from fitting the spectra using a mixed Gaussian– Lorentzian function GL (70) after subtraction of a Shirley background using the CasaXPS Software. The separation between the spin-orbit splitting of Mo 3d and Se 3d, 3.13 eV and 0.86 eV (Ref. 17), respectively, were also used as a constraints for the fitting.

Quantitation Method: Peak areas were obtained from fitting the spectrums and relative sensitivity factors from the atomic photoionization cross section of each core level provided by Scienta-Omicron (Scofield factors).

ACKNOWLEDGMENTS

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SPECTRAL FEATURES TABLE							
Spectrum ID #	**Element/ Transition**	**Peak Energy (eV)**	**Peak Width FWHM (eV)**	**Peak Area (eV x cts/s)**	**Sensitivity Factor**	**Concentration (at. %)**	**Peak Assignment**
A-02[a]	Mo 3d	…	…	1.82×10^4	9.50	35.7	…
A-02	Mo $3d_{5/2}$	228.3	0.56	…	…	…	$MoSe_2$
A-02	Mo $3d_{3/2}$	231.4	0.78	…	…	…	$MoSe_2$
A-02	Se 3s	229.3	2.15	4.94×10^3	…	…	$MoSe_2$
A-03	Se 3d	…	…	8.52×10^3	2.29	64.3	…
A-03	Se $3d_{5/2}$	53.8	0.61	…	…	…	$MoSe_2$
A-03	Se $3d_{3/2}$	54.6	0.59	…	…	…	$MoSe_2$
A-04	Mo $3p_{3/2}$	394.2	2.46	2.06×10^4	…	…	$MoSe_2$
A-04	Mo $3p_{1/2}$	411.6	2.26	1.01×10^4	…	…	$MoSe_2$
A-05[b]	Se LMM	1308.0	1.97	6.11×10^4	…	…	$MoSe_2$
A-05	Se $3p_{3/2}$	160.2	1.77	7.48×10^3	…	…	$MoSe_2$
A-05	Se $3p_{1/2}$	165.8	1.59	3.62×10^3	…	…	$MoSe_2$
A-05[b]	Se LMM	1348.9	1.95	2.69×10^4	…	…	$MoSe_2$
A-06[b]	Se LMM + C1s	1202.9	2.10	1.31×10^4	…	…	$MoSe_2$ + C adventitious
A-07	Se 4s	13.4	2.07	5.21×10^2	…	…	$MoSe_2$
A-07	VB5	5.58	1.57	…	…	…	$MoSe_2$
A-07	VB4	4.30	1.07	…	…	…	$MoSe_2$
A-07	VB3	3.44	0.89	…	…	…	$MoSe_2$
A-07	VB2	2.32	1.28	…	…	…	$MoSe_2$
A-07	VB1	1.05	1.08	…	…	…	$MoSe_2$
A-07[c]	VBM	0.51	…	…	…	…	$MoSe_2$

[a] The area corresponding to Se 3s was subtracted from the total area of Mo 3d

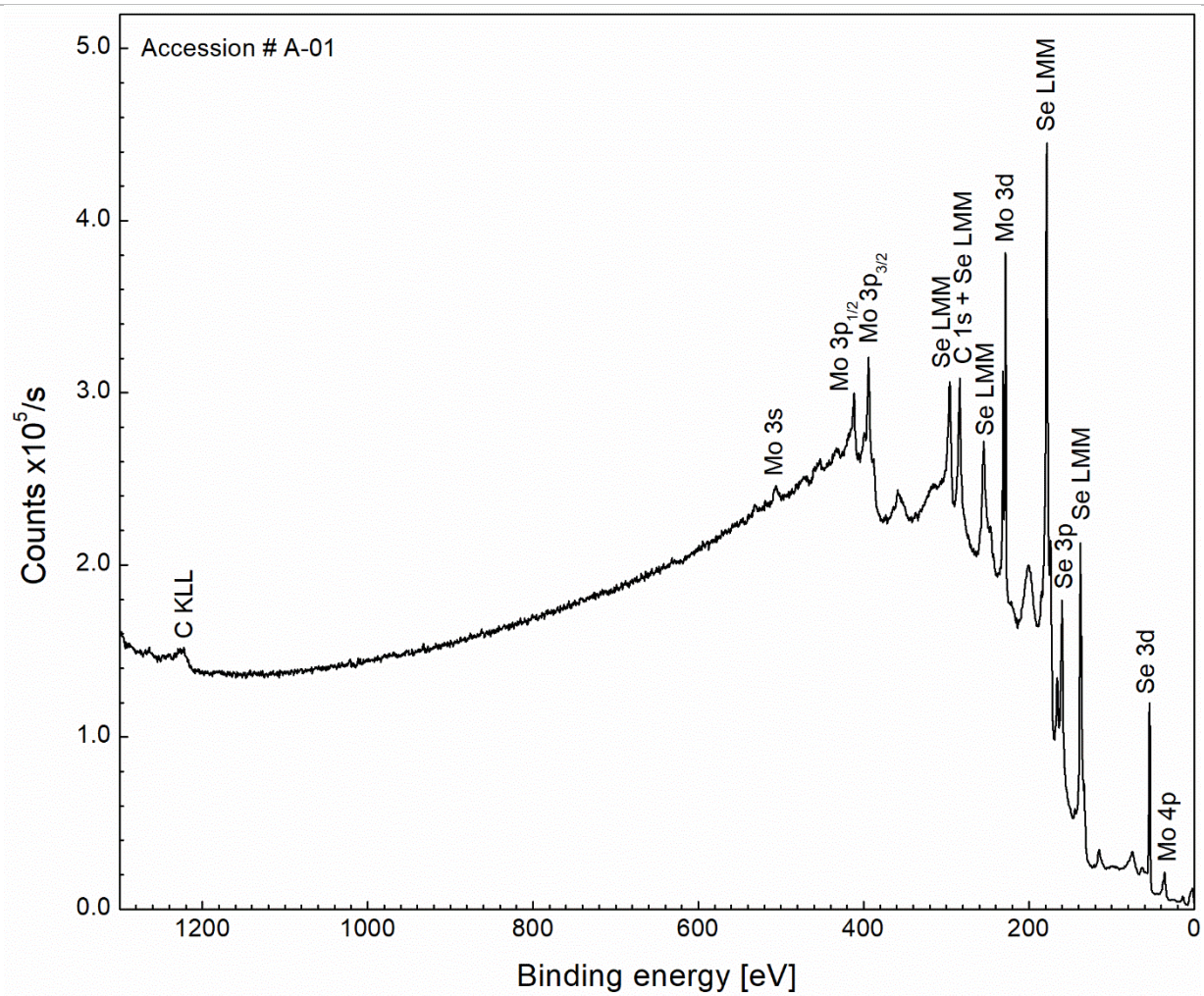
[b] Peak energy reported as kinetic energy (KE)

[c] The position of the valence band maximum (VBM) was estimated by subtracting 1/2 of the full width at half maximum (FWHM) of VB1 from the position of the maximum intensity of VB1.

ANALYZER CALIBRATION TABLE							
Spectrum ID #	**Element/ Transition**	**Peak Energy (eV)**	**Peak Width FWHM (eV)**	**Peak Area (eV x cts/s)**	**Sensitivity Factor**	**Concentration (at. %)**	**Peak Assignment**
…	Ag $3d_{5/2}$	368.3	0.54	9.22×10^4	...	...	...
…	Au $4f_{7/2}$	83.9	0.64	6.81×10^4	…	…	…
…	Cu $2p_{3/2}$	932.6	0.84	1.43×10^5	…	…	…

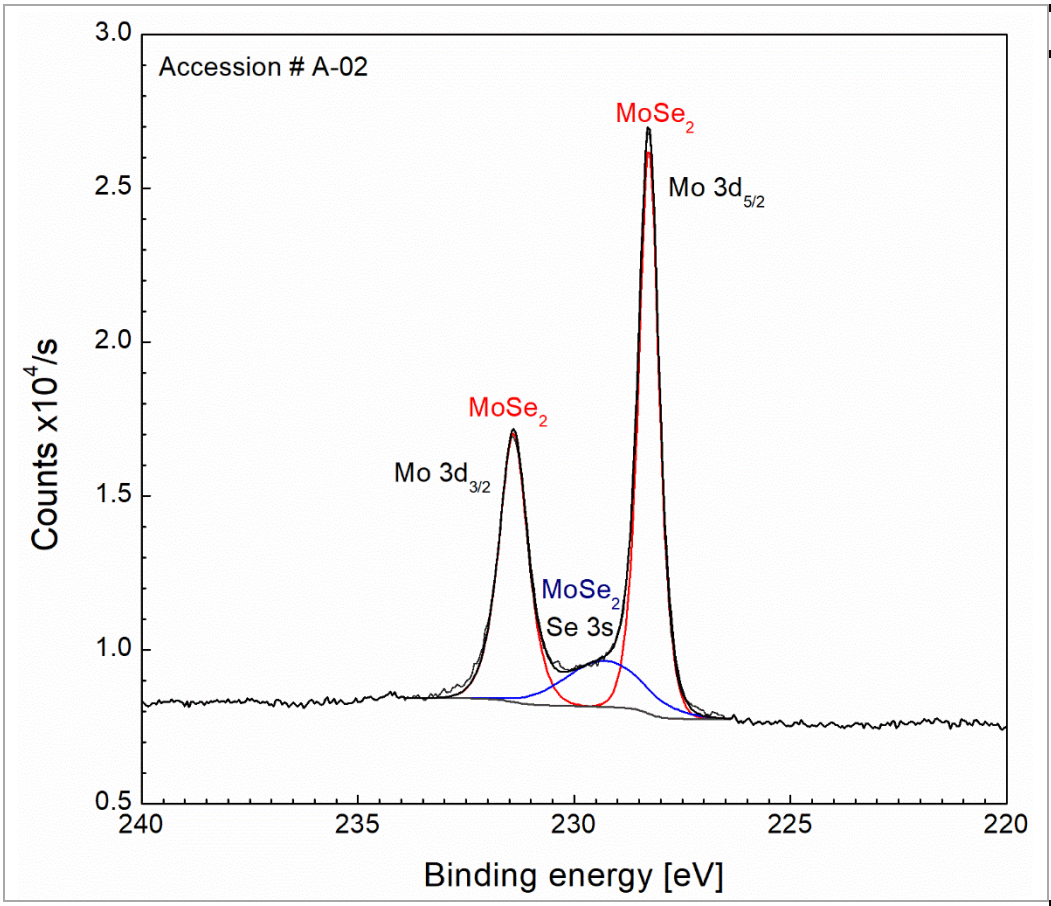
GUIDE TO FIGURES					
Spectrum (Accession) #	**Spectral Region**	**Voltage Shift***	**Multiplier**	**Baseline**	**Comment #**
A-01	Survey	0	1	0	1
A-02	Mo 3d, Se 3s	0	1	0	1
A-03	Se 3d	0	1	0	1
A-04	Mo 3p	0	1	0	1
A-05	Se LMM, Se 3p	0	1	0	1
A-06	C 1s, Se LMM	0	1	0	1
A-07	Se 4s, VB	0	1	0	1

1, refers to as received $MoSe_2$ thin film



Publish in *Surface Science Spectra*: Yes ☒ No ☐

Accession #	**A-01**
Host Material	$MoSe_2$
Technique	XPS
Spectral Region	survey
Instrument	Scienta-Omicron ESCA 2SR
Excitation Source	Al Ka monochromatic
Source Energy	1486.7 eV
Source Strength	250 W
Source Size	0.8 mm x 1.6 mm
Analyzer Type	spherical sector analyzer
Incident Angle	55˚
Emission Angle	0˚
Analyzer Pass Energy	150 eV
Analyzer Resolution	1.67 eV
Total Signal Accumulation Time	298 s
Total Elapsed Time	307 s
Number of Scans	1
Effective Detector Width	21.75 eV

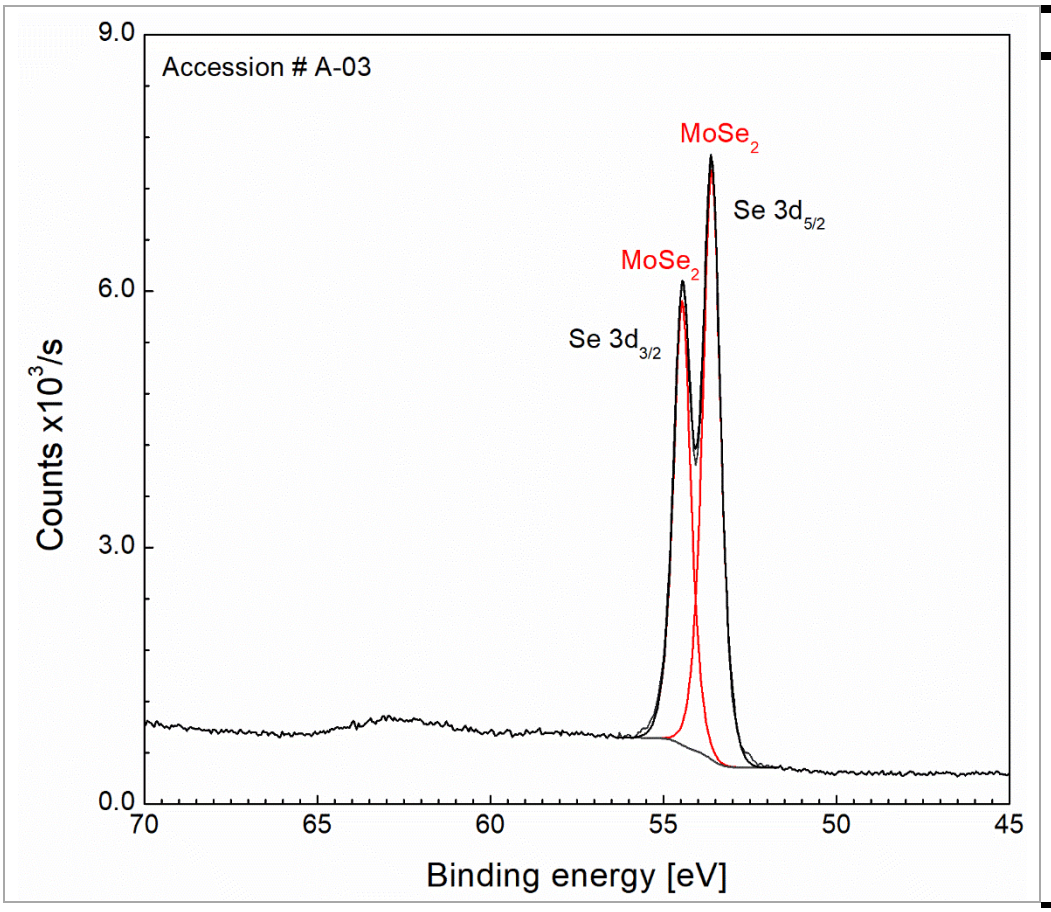


Publish in *SSS*: Yes ☒ No ☐

- **Accession #: A-02**
- **Host Material:** $MoSe_2$
- **Technique:** XPS
- **Spectral Region:** Mo 3d

Instrument: Scienta-Omicron ESCA 2SR
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: 0.8 mm x 1.6 mm
Analyzer Type: spherical sector
Incident Angle: 55 ˚
Emission Angle: 0 ˚
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.5 eV
Total Signal Accumulation Time: 632 s
Total Elapsed Time: 702 s

Number of Scans: 10 Enter source energy.
Effective Detector Width: 2.90 eV



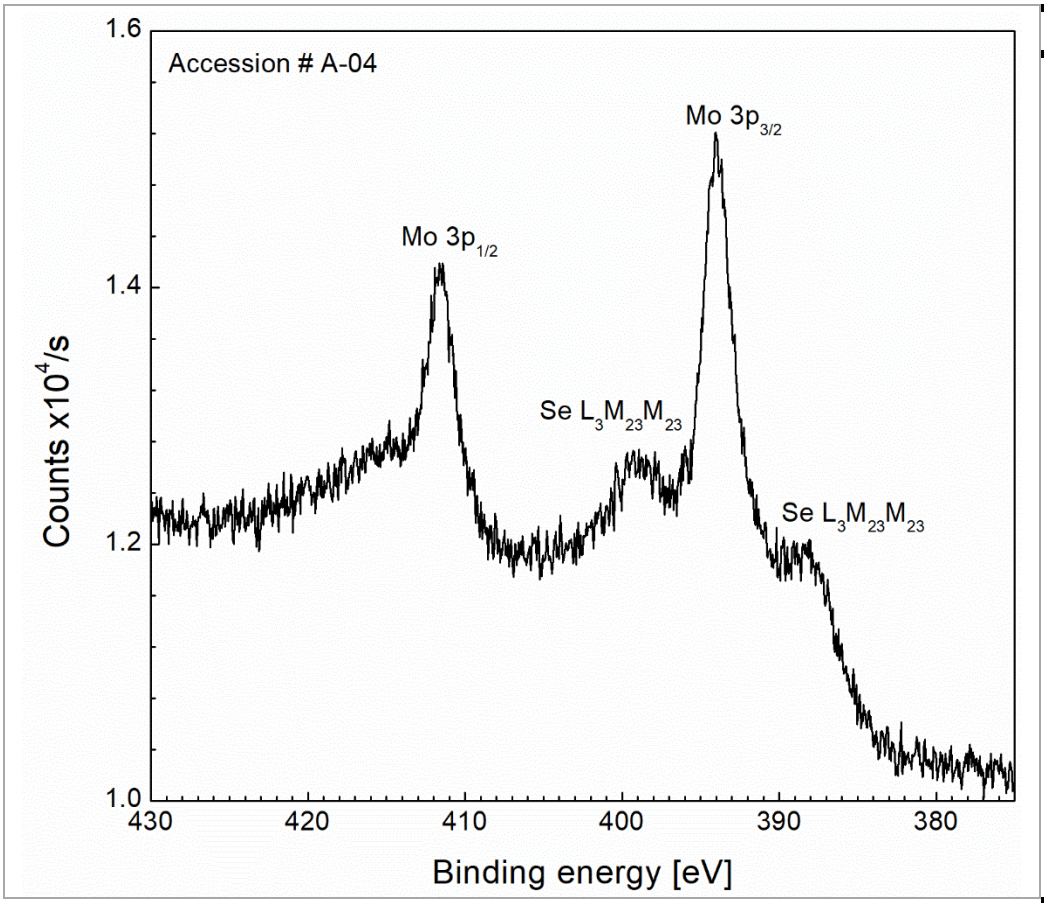
Publish in *SSS*: Yes ☒ No ☐

- **Accession #: A-03**
- **Host Material:** $MoSe_2$
- **Technique:** XPS
- **Spectral Region:** Se 3d

Instrument: Scienta-Omicron ESCA 2SR
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: 0.8 mm x 1.6 mm
Analyzer Type: spherical sector
Incident Angle: 55 ˚
Emission Angle: 0 ˚
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.5 eV
Total Signal Accumulation Time: 832 s
Total Elapsed Time: 924 s

Number of Scans: 12

Effective Detector Width: 2.90 eV



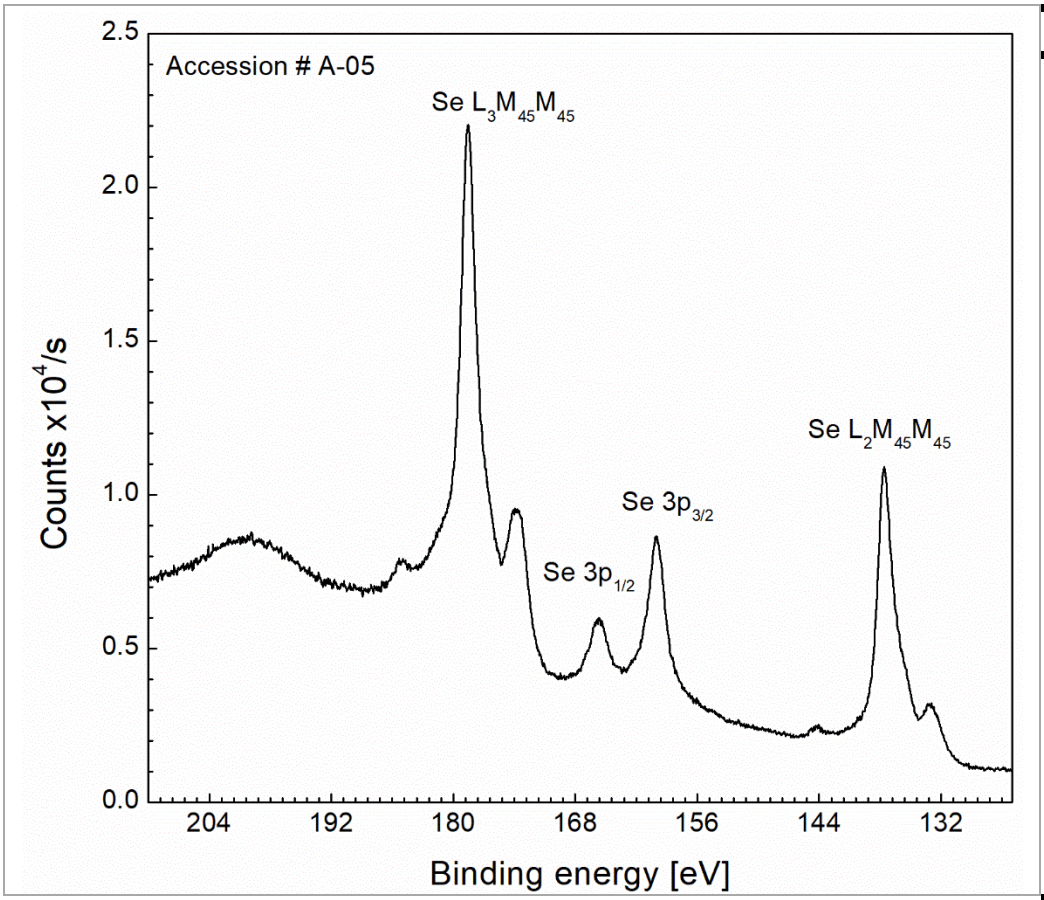
Publish in *SSS*: Yes ☒ No ☐

- **Accession #: A-04**
- **Host Material:** $MoSe_2$
- **Technique:** XPS, XAES
- **Spectral Region:** Mo 3p

Instrument: Scienta-Omicron ESCA 2SR
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: 0.8 mm x 1.6 mm
Analyzer Type: spherical sector
Incident Angle: 55 ˚
Emission Angle: 0 ˚
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.5 eV
Total Signal Accumulation Time: 1305 s
Total Elapsed Time: 1450 s

Number of Scans: 8

Effective Detector Width: 2.90 eV



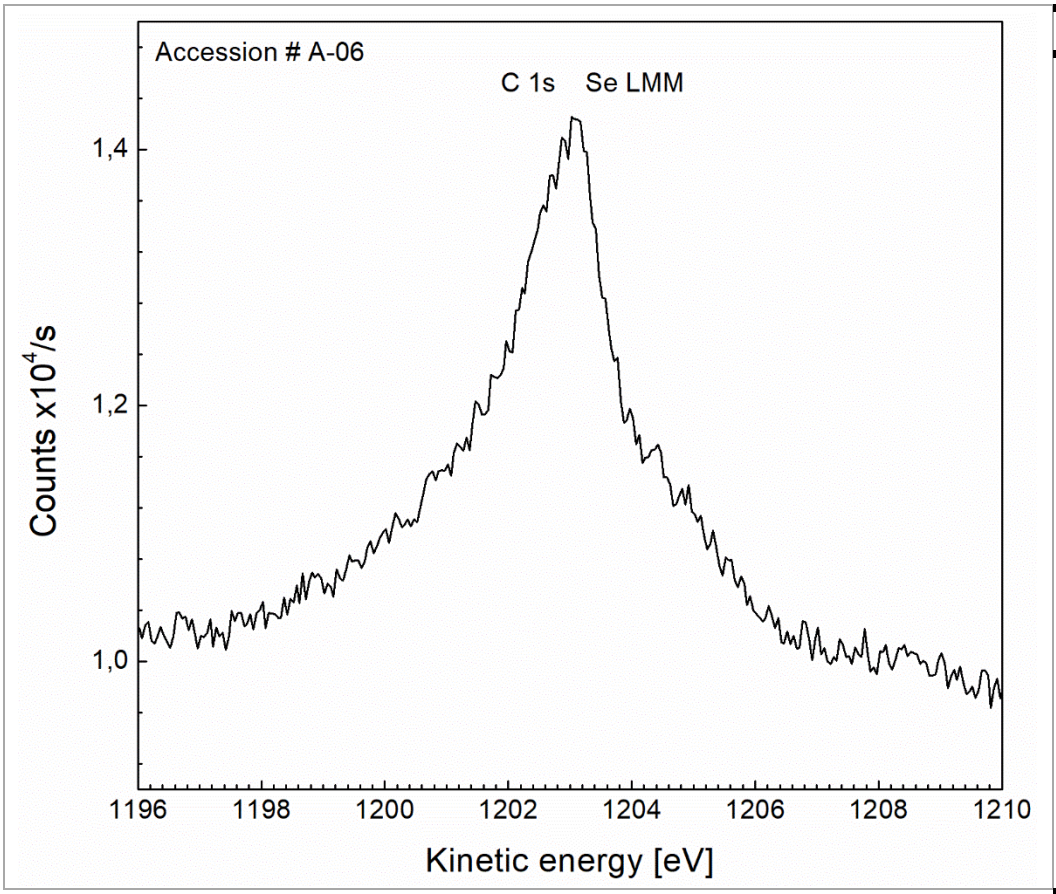
Publish in *SSS*: Yes ☒ No ☐

- **Accession #: A-05**
- **Host Material:** $MoSe_2$
- **Technique:** XPS, XAES
- **Spectral Region:** Se LMM, Se 3p

Instrument: Scienta-Omicron ESCA 2SR
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: 0.8 mm x 1.6 mm
Analyzer Type: spherical sector
Incident Angle: 55 ˚
Emission Angle: 0 ˚
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.5 eV
Total Signal Accumulation Time: 1681 s
Total Elapsed Time: 1868 s

Number of Scans: 8

Effective Detector Width: 2.90 eV



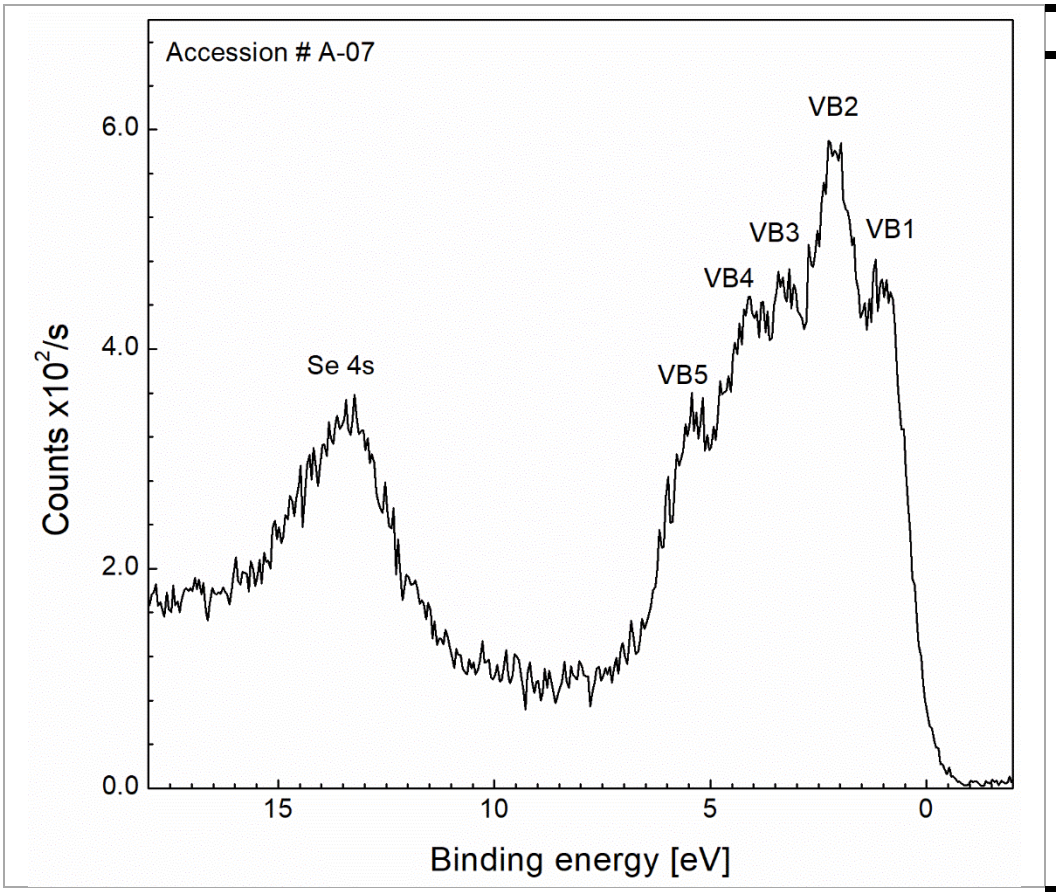
Publish in *SSS*: Yes ☒ No ☐

- **Accession #: A-06**
- **Host Material:** $MoSe_2$
- **Technique:** XPS, XAES
- **Spectral Region:** C 1s, Se LMM

Instrument: Scienta-Omicron ESCA 2SR
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: 0.8 mm x 1.6 mm
Analyzer Type: spherical sector
Incident Angle: 55 ˚
Emission Angle: 0 ˚
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.5 eV
Total Signal Accumulation Time: 473 s
Total Elapsed Time: 526 s

Number of Scans: 8

Effective Detector Width: 2.90 eV



Publish in *SSS*: Yes ☒ No ☐

- **Accession #: A-07**
- **Host Material:** $MoSe_2$
- **Technique:** XPS
- **Spectral Region:** Se 4s, VB

Instrument: Scienta-Omicron ESCA 2SR
Excitation Source: Al Ka monochromatic
Source Energy: 1486.6 eV
Source Strength: 250 W
Source Size: 0.8 mm x 1.6 mm
Analyzer Type: spherical sector
Incident Angle: 55 ˚
Emission Angle: 0 ˚
Analyzer Pass Energy 20 eV
Analyzer Resolution: 0.5 eV
Total Signal Accumulation Time: 701 s
Total Elapsed Time: 779 s

Number of Scans: 8

Effective Detector Width: 2.90 eV