The need for complementary techniques for reliable characterization of MoS_2-like layers

Aditya Deshpande[1], Koki Hojo[2], Koichi Tanaka[1], Pedro Arias[1], Hicham Zaid[1], Michael Liao[1], Mark Goorsky[1], Suneel Kodambaka[1,3*]

[1]Department of Materials Science and Engineering, University of California Los Angeles, Los Angeles, CA 90095, USA

[2]Graduate Department of Micro-Nano Mechanical Science and Engineering, Nagoya University, Nagoya, Japan

[3]Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

KEYWORDS: molybdenum disulfide, reactive sputtering, 2D materials, TMDC

* Electronic mail: kodambaka@vt.edu

ABSTRACT

The observation of characteristic A_{1g} and E^1_{2g} peaks, at around 382 cm^{-1} and 408 cm^{-1} respectively, in Raman spectroscopy is considered evidence of 2H-structured MoS_2, probably the most extensively-studied transition-metal dichalcogenide. Here, using a combination of X-ray diffraction, X-ray photoelectron spectroscopy, and resonant Raman spectroscopy, we show that detection of A_{1g} and E^1_{2g} modes in Raman spectra alone may not necessarily imply the presence of MoS_2. A series of Mo-S films, ≈ 20-nm-thick, are grown on single-crystalline Al_2O_3(0001) substrates at 1073 K as a function of H_2S partial pressure, p_{H_2S} (= 0, 0.01%, 0.1%, and 1% of total pressure) *via* ultra-high vacuum dc magnetron sputtering of a Mo target in 20 mTorr (2.67 Pa) Ar/H_2S gas mixtures. In pure Ar discharges and with p_{H_2S} up to 0.1%, i.e. $p_{H_2S} \leq 2.67 \times 10^{-3}$ Pa, we obtain body centered cubic (bcc), 110-textured films with lattice parameter a increasing from 0.3148 nm (in pure Ar), to 0.3151 nm (at $p_{H_2S} = 2.67 \times 10^{-4}$ Pa), and 0.3170 nm (at $p_{H_2S} = 2.67 \times 10^{-3}$ Pa), which we attribute to increased incorporation of S in the Mo lattice. With 1% H_2S, i.e. $p_{H_2S} = 2.67 \times 10^{-2}$ Pa, we obtain 000l oriented 2H-structured $MoS_{2.0\pm0.1}$ layers. Raman spectra of the thin films grown using 0.1% (and 1%) H_2S, show peaks at around 380 cm^{-1} (382 cm^{-1}) and 412 cm^{-1} (408 cm^{-1}), which could be interpreted as A_{1g} and E^1_{2g} Raman modes for 2H-MoS_2. By comparing the Raman spectra of $MoS_{2.0\pm0.1}$ and Mo:S thin films, we identify differences in A_{1g} and E^1_{2g} peak positions and intensities of defect-sensitive peaks relative to the A_{1g} peaks that can help distinguish pure MoS_2 from non-stoichiometric MoS_{2-x} and multiphase Mo:S materials.

I. INTRODUCTION

Transition metal dichalcogenides (TMDCs) of the form MX_2, where M is a transition metal from groups 4, 5, and 6 and X is a chalcogen (S, Se, Te), are van der Waals (vdW) bonded layers made of covalently bonded X-M-X sheets. Since the discovery of free-standing graphene, TMDCs have generated considerable interest for applications in flexible, low power consumption optoelectronics, electrocatalytic hydrogen generation, electron spin and valley based computing technologies, and DNA sequencing.[1–3] Transition-metal disulfides, such as MoS_2 and WS_2, are a subset of the TMDCs, historically well-known for their chemical properties with a variety of catalytic applications, more prominently in the processing and purification of liquid transportation fuels.[4–11] MoS_2 and WS_2 are relatively inexpensive and earth-abundant compared to more precious Ru-based compounds. MoS_2, in particular, has been extensively studied by the catalysis community[5–7,9–11] due to its attractive properties, and by the tribology community owing to its layered structure.[12–14] There are two naturally available crystalline forms of MoS_2: hexagonal structured 2H-MoS_2 ($P6_3/mmc$, with in-plane and out-of-plane lattice parameters, a = 0.316 nm and c = 1.229 nm, respectively) and rhombohedral 3R-MoS_2 (R3m, a = 0.316 nm, c = 1.837 nm). Bulk 2H-structured MoS_2 is an indirect bandgap (1.23 eV) semiconductor; in contrast, one-molecule-thick 2H-MoS_2 layer is a direct bandgap (1.9 eV) semiconductor.[15,16] It is predicted that the bandgaps of bilayer MoS_2 and other TMDCs decrease with increasing applied electric field and eventually they exhibit metallic behavior.[17] Luminescence quantum efficiency of monolayer MoS_2 is $\times 10^4$ higher than its bulk counterpart,[16,18,19] high carrier mobility,[20,21] high Seebeck coefficient,[22] high photoconductivity,[23,24] strong exciton bonding,[25] and environment sensitivity.[26,27] MoS_2 and other TMDC layers exhibit quantum spin Hall effect;[28] valley Hall effect[29] and valley polarization[1] phenomena, which helped create valleytronics, an exciting new

field of physics.[30–32] With their ability to form atomically-thin diodes,[33–36] exhibit strong size-dependent morphology and electronic structure,[37] and potentially tunable optoelectronic properties,[38,39] TMDCs are attractive as electrically switchable light sources,[40] high-performance logic devices,[41] atomically-thin electronic[21,24,42–46] and optoelectronic devices (e.g., solar cells, photodiodes),[22–24,33,35,44,47–53] flexible transistors,[54–56] chemical sensors,[57] and more.

As one may expect, properties of the 2D layers are sensitive to the layer composition, crystallinity, vacancies, substitutional dopants, and domain boundaries, number of layers (i.e. thickness), stacking sequence, and relative orientations of the layers. For example, band gaps of pseudobinary alloys (e.g., $MoS_{2-y}Se_y$, $Mo_{1-x}W_xS_2$) made by substitution of either cations (e.g., Mo, W) or anions (e.g., S, Se) vary continuously with the alloy composition.[58–61] Tunable band gaps and photocatalytic activities as well as unique electronic properties (e.g., MoS_2/WS_2) can be achieved by vertical stacking of TMDCs.[61] In polydomain (analogous to polycrystallinity in bulk crystals) TMDC layers, density and structure of domain boundaries (e.g., zigzag, twin, tilt) strongly influence the electronic and optoelectronic properties.[62–65] Doping of monolayer MoS_2 affects its structural, electronic and magnetic properties;[66] S-vacancies in TMDCs (e.g., MoS_2 and WS_2) increase conductance,[67] lead to asymmetry in electron and hole conduction characteristics,[68] and modify optical properties of the layers;[69] incorporation of O-atoms in MoS_2 affects its electronic and optoelectronic characteristics;[70–73] H-atom adsorption and point defects in MoS_2 influence its ferromagnetic properties;[74] impurities on the substrate supporting MoS_2 layers can affect the MoS_2 surface work function and its electronic conductivity;[75,76] moisture and ambient light affect MoS_2 field-effect transistor performance;[27] surface defects (e.g., step edges and step structure) dictate thermochemical stability of MoS_2 layers.[73] Placing graphene on MoS_2 can affect the MoS_2 band gap,[77] whose nature and magnitude depends on the interlayer orientation.[78] The

interlayer interaction strength in multilayer heterostructures can vary with the layer composition.[79] Therefore, accurate knowledge of, and control over the TMDC layer composition and crystallinity are critical for the realization of TMDC-based devices with optimal performance.

Several methods exist for the synthesis of TMDCs, especially MoS_2 and WS_2.[80] Here, we list a select few that have been used to grow mono/few-layer TMDCs: (i) Probably the simplest method of preparing individual sheets or hetero-layered stacks of TMDCs is *via* mechanical exfoliation followed by layer transfer onto a substrate of choice. A variant to this approach is liquid exfoliation process, using which a variety of TMDCs (e.g., MoS_2, $MoTe_2$, $TaSe_2$, etc.) are dispersed in solution and deposited as individual layers.[81] (ii) A more commonly used method for the synthesis of TMDC layers is *via* chemical vapor transport of metal-oxide and elemental S powder or H_2S gas as precursors.[63,82–86] A variant of this method uses metal-halides (e.g., $MoCl_5$, WCl_6, $NbCl_5$) instead of metal-oxides, and S precursors to grow TMDCs (MoS_2, WS_2, and NbS_2),[87–90] e.g., $MoCl_5 + S \rightarrow MoS_2$. (iii) Another method involves sulfidation of deposited metal (Mo or W) thin films using elemental S or H_2S gas to form MoS_2 or WS_2,[91–96] e.g., Mo + S or $H_2S_{(g)} \rightarrow MoS_2$. (iv) TMDC layers have also been deposited *via* decomposition of single-source precursors,[97–100] e.g., thermolysis of ammonium tetrathiomolybdate ($[NH_4]_2MoS_4 \rightarrow MoS_2$); physical vapor deposition (PVD), e.g., sputtering;[13,101–103] and evaporation/sublimation of TMDCs.[104,105] Some of these methods have been successfully used for the large-scale synthesis of TMDC layers. However, there are several aspects of the growth processes that are either unknown or not well understood. In particular, the extent of O-incorporation in TMDCs (e.g., $MoS_{2-y}O_y$) either during growth or during subsequent processing are largely unknown. This knowledge is essential because TMDCs can oxidize at fairly low temperatures in presence of moisture.[12,14] A related poorly understood aspect is the effect of deposition approach on metal-chalcogen content

in TMDC layers (e.g., thermolysis of thiomolybdates can result in excess S and sulfurization of Mo using H_2S can lead to S-vacancies).

Raman spectroscopy is commonly used for the characterization of 2D layered materials including TMDCs.[106,107] In case of 2H-MoS_2, the characteristic first order Raman signatures of bulk, phase pure crystal are observed at ~32 cm^{-1}, the rigid layer mode E^2_{2g} associated with the vibration of adjacent S-Mo-S sheets against each other, at 382~383 cm^{-1}, the E^1_{2g} mode corresponding to in-plane vibration of S and Mo atoms within a sheet, and at 407~408 cm^{-1}, the A_{1g} mode due to out-of-plane vibration of S atoms within a sheet. (We note that in the back-scattering geometry, the characteristic E_{1g} mode at ~285 cm^{-1} arising from in-plane vibration of S atoms within a sheet is forbidden.[108–113]) The observation of Raman peaks characteristic of the 2D layer are generally considered as sufficient evidence for the formation/presence of that material. Here, we focus on the validity of such a conclusion.

In this report, we report on the growth and characterization of Mo-S thin films with varying S content sputter-deposited using a Mo target in 20 mTorr (2.67 Pa) Ar/H_2S gas mixtures as a function of H_2S partial pressure, p_{H_2S} at 1073 K on Al_2O_3(0001) substrates. Using X-ray diffraction (XRD), we determine that films sputter-deposited in pure Ar are body centered cubic (bcc) Mo with 110 texture and those grown using Ar + H_2S gas mixtures with $p_{H_2S} = 2.67 \times 10^{-4}$ Pa and at 2.67×10^{-3} Pa are bcc-structured Mo:S solid solutions. Using higher $p_{H_2S} = 2.67 \times 10^{-2}$ Pa, we obtain basally-oriented 2H-structured MoS_x film. Using X-ray photoelectron spectroscopy (XPS), we determine S-contents in the films grown using $p_{H_2S} = 2.67 \times 10^{-3}$ Pa and 2.67×10^{-2} Pa as ≈ 64.3 at.% and 66.7 at.%, respectively. Interestingly, resonant Raman spectra obtained using 633 nm laser from both these films show peaks due to the E^1_{2g} and A_{1g} Raman modes characteristic of

MoS_2 and peaks associated with structural defects due to longitudinal acoustic (LA) phonons at the M point, referred to as LA(M). Based on our results, we suggest that the mere observation of the E^1_{2g} and A_{1g} peaks in Raman spectra may not be sufficient to conclude the existence of phase-pure, crystalline MoS_2. We find differences in E^1_{2g} and A_{1g} peak positions and relative intensities of LA(M)/A_{1g} peaks can help determine the crystalline quality of MoS_x phase. Based on our results, we suggest that additional characterization maybe necessary to confirm the presence of MoS_2 and to accurately determine the composition and phase purity of the MoS_2-like layers.

II. EXPERIMENTAL

The Mo-S thin films are deposited on single-side polished, 10 × 2 × 0.5 mm^3, Al_2O_3(0001) substrates (miscut < 0.5°, 99.99% purity, from MTI Corp.) at temperature T_s = 1073 K in an ultra-high vacuum (UHV, base pressure < 5.0 × 10^{-9} Torr, 6.67 × 10^{-7} Pa) system, described in Refs. [114–116]. All the details of the substrate cutting, cleaning, and mounting procedures are presented in Ref. [114]. Prior to deposition, the substrates are degassed at 1273 K in the UHV chamber until the base pressure is below 8 × 10^{-7} Pa. With T_s set to1073 K, we measure up to 100 K differences in temperature along the length of the sample.

We use dc magnetron source with a 50.8 mm diameter × 3.175 mm thick Mo target (99.95% pure from ACI Alloys Inc.) for the sputter-deposition of Mo and Mo-S thin films using 2.67 Pa Ar + H_2S gas mixtures with 0, 0.01%, 0.1%, and 1% H_2S partial pressures, i.e. p_{H_2S} = 0, 2.67 × 10^{-4} Pa, 2.67 × 10^{-3} Pa, and 2.67 × 10^{-2} Pa, respectively. The deposition time is 30 min. The Mo target power is set to 50 W. The target voltages during deposition are 230 ~ 232 V, 243 ~ 248 V, 256 ~ 258 V, 292 ~ 295 V at p_{H_2S} = 0, 2.67 × 10^{-4}, 2.67 × 10^{-3}, and 2.67 × 10^{-2} Pa, respectively. Details of the Mo-S deposition procedure are presented in Ref. [114].

The as-deposited Mo-S/Al_2O_3(0001) thin films are characterized using XRD in a Bede D1 high-resolution X-ray diffractometer, resonant Raman spectroscopy with a 633 nm (1.96 eV) laser at 0.4 mW in a Renishaw In-Via Raman confocal microscope system, and XPS in a Kratos Analytical AXIS Ultra DLD following the procedures outlined in Ref. [114]. The Raman data presented here are acquired with a resolution of 2 cm^{-1}. We use Gaussian (Lorentzian) functions to extract XRD and Raman peak positions and full widths at half maxima (FWHM).[117–119] In our Raman measurements, we can access the Raman modes E^1_{2g} and A_{1g} for MoS_2 but not the low frequency E^2_{2g} mode as it is obscured due to Rayleigh scattered light. The Raman excitation energy (1.96 eV) corresponds to the direct bandgap of MoS_2, ~1.96 eV, at the K point in the Brillouin zone (BZ).[109,120] This correspondence with an optical transition can be used to enhance Raman signal intensities and probe phonon modes that are at the BZ boundary (resonant Raman scattering).[111] XPS data are obtained from the air-exposed Mo-S samples deposited with p_{H_2S} = 2.67×10^{-3} Pa and 2.67×10^{-4} Pa. The same samples are later sputter-etched with 4 keV Ar^+ ions rastered across 2 × 2 mm^2 with 50 μA extractor current. Casa XPS software package[121] was used to correct for the background based on Shirley algorithm[122] and to determine using a Gaussian function with a Lorentzian character [GL(30)] the positions and integrated intensities of Mo 3*d* and S 2*p* peaks. Using the relative sensitivity factors of 3.32 and 0.668, respectively, for Mo 3*d* and S 2*p* (from Casa XPS element library), we calculate the S/Mo contents in the films from the ratios of the integrated intensities of these peaks.

III. RESULTS AND DISCUSSION

Figure 1 is a plot of symmetric XRD 2θ-ω scans obtained from the films deposited using different p_{H_2S} values with intensities normalized to the intensity of the Al_2O_3 0006 reflection and

plotted on logarithmic scales. The two highest intensity peaks labeled **s** are Al_2O_3 0006 and 00012 reflections at 2θ values 41.68° and 90.74°, respectively, from the 0001-oriented single-crystalline α-Al_2O_3 ($R\bar{3}c$) substrate. We also find two relatively lower intensity peaks at 2θ values 20.5° and 64.5° in all the scans due to the forbidden Al_2O_3 0003 and 0009 reflections, respectively.[123]

Table I. X-ray diffraction peak positions (2θ in degrees) tabulated for data shown in Fig. 1. For comparison, $2\theta_o$ values expected for bcc-Mo,[124] bulk 2H-MoS_2,[125] and 3R-MoS_2[137] are also presented. We define $\Delta = 100\times(2\theta-2\theta_o)/2\theta_o$ as the percentage deviation between the expected and observed 2θ values for a given phase. Data in italics and within the parenthesis correspond to the 3R-MoS_2 phase.

bcc-Mo		Mo [pure Ar]	Mo:S [0.01% H_2S]	Mo:S [0.1% H_2S]	2H-MoS_2 *3R-MoS_2*	MoS_x [1% H_2S]	
hkl	$2\theta_o$	2θ Δ %	2θ Δ %	2θ Δ %	hkil	$2\theta_o$	2θ Δ %
110	40.50	40.46 -0.1	40.46 -0.1	40.2 -0.7	0002 *0003*	14.40 *14.45*	14.36 -0.3 (*-0.6*)
220	87.63	87.58 -0.06	87.52 -0.1	–	0004 *0006*	29.03 *29.14*	28.94 -0.3 (*-0.7*)
222	115.97	116.02 0.04	115.72 -0.2	–	0006 *0009*	44.16 *44.34*	44.04 -0.3 (*-0.7*)
					0008 *00012*	60.16 *60.42*	59.99 -0.3 (*-0.7*)

Table I shows 2θ values of all the film peaks observed in the XRD data for all the Mo-S samples along with $2\theta_o$ values expected for bcc bulk Mo (a_o = 0.3147 nm)[124] and 000*l* (with l = 2, 4, 6, and 8) reflections of 2H-MoS_2 (c_o = 1.229 nm).[125] The XRD data (black curve in Figure 1) from the sample deposited using pure Ar, i.e., $p_{H_2S} = 0$, shows three peaks corresponding to 110, 220, and 222 reflections of bcc-Mo. Relative intensity of 222 peak with respect to 110 peak is 0.03, which is lower than the value expected for randomly oriented polycrystalline Mo,[124]

indicative of 110-texture. We measure lattice parameters a from each of the peak positions and determine the arithmetic average a to be 0.3148 ± 0.0002 nm. This value is 0.03% larger than the a_o of bulk bcc Mo,[124] suggestive of residual stresses in the film. For the films grown using Ar with 0.01% and 0.1% H_2S, XRD data in Figure 1, green and blue curves respectively, show three, and one peaks at slightly lower 2θ values than those expected for pure bcc-Mo (see Table I). We assign the peak positions to bcc-structured solids and determine a values as 0.3151 ± 0.0001 nm and 0.3170 ± 0.0001 nm, respectively, for the films grown using 0.01% and 0.1% H_2S. We note that these a values are 0.13% and 0.73% higher than a_o of compositionally pure bcc-Mo.[124] We attribute the larger lattice parameters to incorporation of S in the Mo lattice and refer to these films as Mo:S solid solutions.[126]

The red curve in Figure 1 is a typical XRD scan acquired from the film sputter-deposited using $p_{H_2S} = 2.67 \times 10^{-2}$ Pa, i.e. Ar + 1% H_2S gas mixture. (A portion of this data is presented in Ref. [114]) We find four peaks at 2θ values comparable to those expected for 2H-MoS_2 (see Table I), which we identify as 2H-MoS_2 000l (l = 2, 4, 6, and 8) reflections, indicative of 0001-oriented growth. We rule out the 3R-MoS_2 phase based on the differences in the peak positions observed between the expected and experimentally obtained 2θ values (see Table I). From each of the peak positions, we extract out-of-plane lattice parameters c and calculate the average c value to be 1.233 ± 0.0002 nm, which is 0.3% larger than the c_o expected for stoichiometric bulk 2H-MoS_2.[125] Full width half maximum of the 0002 peak is 0.56°. We will refer to this film as $MoS_x/Al_2O_3(0001)$.

In the following sections, we compare and contrast the Raman and XPS spectra obtained from two samples, hereto referred to as Mo:S/Al_2O_3(0001) and MoS_x/Al_2O_3(0001), sputter-deposited in Ar with 0.1% H_2S ($p_{H_2S} = 2.67 \times 10^{-3}$ Pa) and 1% H_2S ($p_{H_2S} = 2.67 \times 10^{-2}$ Pa), respectively. Figure 2 shows representative Raman spectra obtained from the Mo:S/Al_2O_3(0001)

(blue curve) and $MoS_x/Al_2O_3(0001)$ (red curve) samples using a 633 nm (1.96 eV) laser excitation. The intensities are as measured and plotted without translation on a logarithmic scale. In the Raman data of $MoS_x/Al_2O_3(0001)$, we find peaks at ~382 cm^{-1} and ~408 cm^{-1}, the characteristic E^1_{2g} and A_{1g} Raman modes, respectively for MoS_2. Interestingly, Raman spectra from $Mo:S/Al_2O_3(0001)$ show peaks at ~380 cm^{-1} and at ~412 cm^{-1}, values comparable to those expected for MoS_2. However, XRD data (Figure 1, blue curve) from the same sample does not show any peaks due to MoS_2. We note that the E^1_{2g} and A_{1g} peak intensities are approximately five-fold higher in the Raman spectra of $MoS_x/Al_2O_3(0001)$ than in the Raman spectra of $Mo:S/Al_2O_3(0001)$. For both monolayer and multilayer MoS_2, the E^1_{2g} and A_{1g} mode peak positions have been found to be sensitive to strain (both modes redshift with increasing strain) and doping (A_{1g} mode broadens and redshifts).[127–130] Defects induced by ion bombardment[128] or by electron irradiation[127] lead to an increase in the separation $\Delta\omega$ ($= A_{1g} - E^1_{2g}$) between the characteristic modes as the E^1_{2g} mode redshifts and the A_{1g} mode blueshifts, along with the activation of M-point phonons that are at the center of the BZ boundary. (For reference, $\Delta\omega$ is ~19 cm^{-1} for defect-free monoalyer MoS_2 and $\Delta\omega$ is around 25 cm^{-1} for multilayer MoS_2.[120,131]) For rf sputtered MoS_2 films that are sulfur-deficient or oxidized, larger values of $\Delta\omega$ (> 25 cm^{-1}) have been observed.[132,133] For our $MoS_x/Al_2O_3(0001)$, we measure $\Delta\omega$ as 26 ± 4 cm^{-1}, comparable to the reference value. For $Mo:S/Al_2O_3(0001)$ layers, we find $\Delta\omega$ to be considerably larger, 32 ± 4 cm^{-1}, presumably due to defects.

In addition to the characteristic modes, due to resonant Raman scattering, the curves in Figure 2 reveal several peaks at ~179 cm^{-1}, ~229 cm^{-1}, 460 cm^{-1}, ~528 cm^{-1}, ~568 cm^{-1}, ~599 cm^{-1}, ~640 cm^{-1}, and ~820 cm^{-1} for $MoS_x/Al_2O_3(0001)$; we find fewer peaks at nearly the same values, ~183 cm^{-1}, ~227 cm^{-1}, ~459 cm^{-1}, and ~641cm^{-1}, for $Mo:S/Al_2O_3(0001)$. We note that peaks at

~227 cm^{-1} and at ~820 cm^{-1} are also associated with MoO_3,[109,128] but we do not see the other Raman modes of MoO_3 at ~158 cm^{-1}, ~285 cm^{-1}, ~666 cm^{-1}, and 994 cm^{-1}. We therefore rule out the presence of MoO_3 and assign the peaks to Raman modes of MoS_2 as follows. The intense, asymmetric peak at ~459 cm^{-1} [~460 cm^{-1}] visible in the Raman spectra of Mo:S/Al_2O_3(0001) [MoS_x/Al_2O_3(0001)] is interpreted to be a convolution of two peaks – one from a second order phonon process involving the longitudinal acoustic (LA) phonon at the M point, referred to as 2LA(M) at ~454 cm^{-1} and another, a first order infrared-active optical phonon A_{2u} at ~465 cm^{-1}. The observation of the Raman inactive A_{2u} mode is attributed to resonant excitation.[111] The frequency of the LA(M) phonon based on that of the 2LA(M) phonon has been calculated to be ~227 cm^{-1} and its appearance determined to be due to confinement of phonons due to defects such as S-vacancies[127] and grain boundaries.[111] Other studies have shown that the relative intensity of the LA(M) phonon mode with respect to the characteristic peaks of MoS_2 increases with structural disorder.[128,134] Based on these previous studies,[109,111,120] we assign the peak at ~459 cm^{-1} [~460 cm^{-1}] seen in the Raman spectra of Mo:S/Al_2O_3(0001) [MoS_x/Al_2O_3(0001)] as due to 2LA(M) + A_{2u} phonons; the peaks at ~183 cm^{-1} [~179 cm^{-1}], ~227 cm^{-1} [~229 cm^{-1}], and ~641cm^{-1} [~640 cm^{-1}] to A_{1g} − LA(M), LA(M), and A_{1g} + LA(M) phonons, respectively; the peaks at ~528 cm^{-1}, ~568 cm^{-1}, ~599 cm^{-1}, and at ~820 cm^{-1} only seen in the spectrum of MoS_x/Al_2O_3(0001) can be assigned to E_{1g} + LA(M), $2E_{1g}$, E^1_{2g} + LA(M), and $2A_{1g}$ phonons, respectively. The fact that we observe overall higher intensities for all Raman peaks, relatively lower intensity LA(M) phonon peak (measured with respect to A_{1g} peak) and additional peaks in the Raman spectrum of the MoS_x/Al_2O_3(0001) sample strongly suggests the presence of highly crystalline MoS_2 phase. In contrast, the higher intensity of the LA(M) phonon peak (compared to the A_{1g} peak) and larger $\Delta\omega$ for the Mo:S/Al_2O_3(0001) sample are indicative of higher degree of structural disorder, S-

vacancies, and/or smaller size MoS_2 grains in the film. This is plausible and consistent with the absence of XRD peaks associated with MoS_2 phase in this sample.

Figure 3 shows X-ray photoelectron spectra obtained from air-exposed (a) Mo:S/Al_2O_3(0001) and (b) MoS_x/Al_2O_3(0001) samples. In the plots, we find two peaks around 162 eV associated with S 2*p* and three peaks at energies between 229 and 236 eV due to Mo 3*d* peaks. The S 2*p* peaks in the Mo:S/Al_2O_3(0001) [MoS_x/Al_2O_3(0001)] films at 162.1 eV [161.9 eV] and at 163.3 eV [163.1 eV] correspond to S $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively, as expected for S 2− species.[135] The observed Mo peaks can be attributed to the presence of Mo +4 and Mo +6 species with two sets of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ doublets: for Mo:S/ Al_2O_3(0001) [MoS_x/Al_2O_3(0001)], a Mo $3d_{5/2}$ peak at 229.3 eV [229.1 eV] and Mo $3d_{3/2}$ peak at 232.4 eV [232.2 eV] colored in dark green and another doublet with Mo $3d_{5/2}$ peak at 232.7 eV [232.5 eV], Mo $3d_{3/2}$ peak at 235.9 eV [235.6 eV] colored in brown. The Mo 3*d* doublets with peaks at lower (higher) binding energies correspond to Mo +4 (Mo +6) species.[135] The presence of Mo +4 species can be attributed to MoS_2 and MoO_2 while Mo +6 species are associated with MoO_3. From earlier studies,[136] we know that the as-deposited layers in our experiments are free of oxygen. Moreover, we do not detect MoO_3 or MoO_2 in both XRD and Raman spectra obtained from these samples. XPS data (not shown) obtained from sputter-etched samples do not show any peaks associated with Mo oxides. We therefore suggest that any detection of Mo +6 peaks in the samples is likely a result of surface oxidation upon air-exposure.

We note that the XPS of Mo:S/Al_2O_3(0001) film shows a higher integrated intensity for Mo +6 species than the XPS data from MoS_x/Al_2O_3(0001) film suggestive of a higher degree of oxidation in the Mo:S/Al_2O_3(0001) sample. The XPS of the sputter etched Mo:S/Al_2O_3(0001) [MoS_x/Al_2O_3(0001)] film near the Mo 3*d* binding energy shows an asymmetric Mo 3*d* doublet

with peaks at ~228.2 eV [~227.9 eV] (Mo $3d_{5/2}$), ~231.4 eV [~231.1 eV] (Mo $3d_{3/2}$) that we identify as due to metallic Mo (0) species. For Mo:S/Al_2O_3(0001), we are unable to resolve the fairly broad and noisy signal at energies associated with S 2*p* peaks; for MoS_x/Al_2O_3(0001), a S $2p_{3/2}$ (S $2p_{1/2}$) peak was resolved at ~162 eV (~163.2 eV). Based on these results, we suggest that the entire Mo +4 peak intensity is due to MoS_2 and attribute the Mo +6 peaks to surface oxidation of metallic Mo and/or Mo:S solid solution. From the peak areas of S and Mo +4, we determine the effective *sulfide* composition of Mo:S/Al_2O_3(0001) as $MoS_{1.8\pm0.1}$ and that of MoS_x/Al_2O_3(0001) as $MoS_{2.0\pm0.1}$. We note that this quantification approach does not account for metallic Mo present in the films and therefore the overall composition of Mo:S/Al_2O_3(0001) film is likely a combination of Mo + $MoS_{1.8\pm0.1}$. The fact that we do not see in Fig. 1 any XRD peaks associated with MoS_2 but only a weak bcc-Mo reflection in the Mo:S/Al_2O_3(0001) films is consistent with our conclusion.

IV. CONCLUSIONS

In summary, using a combination of materials characterization techniques, we show that the detection of A_{1g} and E^1_{2g} Raman modes does not necessarily imply that the material is 2H-MoS_2. To this purpose, we deposited a series of Mo-S thin films with varying S-contents by reactive sputtering of a Mo target in 2.67 Pa Ar/H_2S gas mixtures on Al_2O_3(0001) substrates at 1073 K. XRD and XPS measurements indicate the formation of bcc-structured Mo films at p_{H_2S} = 0 Pa, 2.67×10^{-4} Pa, a bcc Mo:S solid solution with 64 at.% S at $p_{H_2S} = 2.67 \times 10^{-3}$ Pa, and a 000*l* oriented 2H-MoS_2 film at $p_{H_2S} = 2.67 \times 10^{-2}$ Pa. Raman spectroscopy results of the films deposited at $p_{H_2S} = 2.67 \times 10^{-3}$ Pa and 2.67×10^{-2} Pa show characteristic A_{1g} and E^1_{2g} peaks, commonly attributed to 2H-MoS_2, however, with noticeable differences in the peak separations ($\Delta\omega = A_{1g} - E^1_{2g}$) and peak intensities of the A_{1g}, E^1_{2g}, and the defect sensitive LA(M) phonon modes. Based on

these results, we suggest that careful interpretation of Raman spectra along with complementary characterization data are highly desirable not only for identification of MoS_2 and other TMDCs but also for accurate determination of the composition and crystallinity of non-stoichiometric compounds.

ACKNOWLEDGEMENTS

We gratefully acknowledge support from the Air Force Office of Scientific Research (AFOSR, Dr. Ali Sayir) under Grant # FA9550-18-1-0050 and FA9550-20-1-0184. SK thanks the National Science Foundation (NSF) for DMR Award 2211350 (Dr. James Edgar). AD is partially supported by UCLA Department of Materials Science and Engineering (MSE). KT is supported by the Japanese Student Service Organization (L16111111026) and the UCLA MSE for his doctoral study in the United States. KH is supported by the Japan US Advanced Collaborative Education Program (JUACEP).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Declarations

Conflict of interest: The authors have no conflicts to disclose.

REFERENCES

[1] H.L. Zeng, J.F. Dai, W. Yao, D. Xiao, and X.D. Cui, "Valley polarization in MoS2 monolayers by optical pumping," Nat Nanotechnol **7**(8), 490–493 (2012).
[2] A.B. Farimani, K. Min, and N.R. Aluru, "DNA Base Detection Using a Single-Layer MoS2," ACS Nano **8**(8), 7914–7922 (2014).
[3] H. Li, Y. Shi, M.-H. Chiu, and L.-J. Li, "Emerging energy applications of two-dimensional layered transition metal dichalcogenides," Nano Energy **18**, 293–305 (2015).
[4] C.N.R. Rao, and K.P.R. Pisharody, "Transition metal sulfides," Progress in Solid State Chemistry **10, Part 4**(0), 207–270 (1976).
[5] K.I. Tanaka, and T. Okuhara, "Regulation of Intermediates on Sulfided Nickel and MoS2 Catalysts," Catalysis Reviews-Science and Engineering **15**(2), 249–292 (1977).
[6] E. Furimsky, "Role of MoS2 and WS2 in Hydrodesulfurization," Catalysis Reviews-Science and Engineering **22**(3), 371–400 (1980).
[7] M.D. Curtis, in *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, edited by E.I. Stiefel and K. Matsumoto (Amer Chemical Soc, Washington, 1996), pp. 154–175.
[8] I. Mochida, and K.H. Choi, "An overview of hydrodesulfurization and hydrodenitrogenation," Journal of the Japan Petroleum Institute **47**(3), 145–163 (2004).
[9] R.R. Chianelli, M.H. Siadati, M.P. De la Rosa, G. Berhault, J.P. Wilcoxon, R. Bearden, and B.L. Abrams, "Catalytic properties of single layers of transition metal sulfide catalytic materials," Catalysis Reviews-Science and Engineering **48**(1), 1–41 (2006).
[10] P.M. Mortensen, J.D. Grunwaldt, P.A. Jensen, K.G. Knudsen, and A.D. Jensen, "A review of catalytic upgrading of bio-oil to engine fuels," Applied Catalysis A-General **407**(1–2), 1–19 (2011).
[11] S. Zaman, and K.J. Smith, "A Review of Molybdenum Catalysts for Synthesis Gas Conversion to Alcohols: Catalysts, Mechanisms and Kinetics," Catalysis Reviews-Science and Engineering **54**(1), 41–132 (2012).
[12] J.K. Lancaster, "A Review of the Influence of Environmental Humidity and Water on Friction, Lubrication, and Wear," Tribol Int **23**(6), 371–389 (1990).
[13] C. Muratore, and A.A. Voevodin, "Chameleon Coatings: Adaptive Surfaces to Reduce Friction and Wear in Extreme Environments," Annu Rev Mater Res **39**, 297–324 (2009).
[14] W.O. Winer, "Molybdenum Disulpide As a Lurricant: a Review of Fundamental Knowledge," Wear **10**, 422–452 (1967).
[15] K.K. Kam, and B.A. Parkinson, "Detailed photocurrent spectroscopy of the semiconducting group VI transition metal dichalcogenides," Journal of Physical Chemistry **86**(4), 463–467 (1982).
[16] K.F. Mak, C. Lee, J. Hone, J. Shan, and T.F. Heinz, "Atomically Thin MoS2: A New Direct-Gap Semiconductor," Phys Rev Lett **105**(13), 2–5 (2010).
[17] A. Ramasubramaniam, D. Naveh, and E. Towe, "Tunable band gaps in bilayer transition-metal dichalcogenides," Phys Rev B **84**(20), 205325 (2011).
[18] A. Splendiani, L. Sun, Y.B. Zhang, T.S. Li, J. Kim, C.-Y.Y. Chim, G. Galli, and F. Wang, "Emerging Photoluminescence in Monolayer MoS2," Nano Lett **10**(4), 1271–1275 (2010).
[19] R.S. Sundaram, M. Engel, A. Lombardo, R. Krupke, A.C. Ferrari, P. Avouris, and M. Steiner, "Electroluminescence in Single Layer MoS 2," Nano Lett **13**(4), 1416–1421 (2013).
[20] Y. Zhang, J. Ye, Y. Matsuhashi, and Y. Iwasa, "Ambipolar MoS 2 Thin Flake Transistors," Nano Lett **12**(3), 1136–1140 (2012).

[21] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS2 transistors," Nat Nano **6**(3), 147–150 (2011).
[22] M. Buscema, M. Barkelid, V. Zwiller, H.S.J. Van Der Zant, G.A. Steele, and A. Castellanos-Gomez, "Large and tunable photothermoelectric effect in single-layer MoS 2," Nano Lett **13**(2), 358–363 (2013).
[23] H.S. Lee, S.-W.W. Min, Y.-G.G. Chang, M.K. Park, T. Nam, H. Kim, J.H. Kim, S. Ryu, and S. Im, "MoS2 Nanosheet Phototransistors with Thickness-Modulated Optical Energy Gap," Nano Lett **12**(7), 3695–3700 (2012).
[24] Z.Y. Yin, H.H. Li, H.H. Li, L. Jiang, Y.M. Shi, Y.H. Sun, G. Lu, Q. Zhang, X.D. Chen, and H. Zhang, "Single-Layer MoS2 Phototransistors," ACS Nano **6**(1), 74–80 (2012).
[25] A. Ramasubramaniam, "Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides," Phys Rev B **86**(11), 115409 (2012).
[26] H. Qiu, L. Pan, Z. Yao, J. Li, Y. Shi, and X. Wang, "Electrical characterization of back-gated bi-layer MoS2 field-effect transistors and the effect of ambient on their performances," Appl Phys Lett **100**(12), (2012).
[27] D.J. Late, B. Liu, H.S.S.R. Matte, V.P. Dravid, and C.N.R. Rao, "Hysteresis in single-layer MoS2 field effect transistors," ACS Nano **6**(6), 5635–5641 (2012).
[28] M.A. Cazalilla, H. Ochoa, and F. Guinea, "Quantum Spin Hall Effect in Two-Dimensional Crystals of Transition-Metal Dichalcogenides," Phys Rev Lett **113**(7), 077201 (2014).
[29] K.F. Mak, K.L. McGill, J. Park, and P.L. McEuen, "The valley Hall effect in MoS2 transistors," Science (1979) **344**(6191), 1489–1492 (2014).
[30] S.Z. Butler, S.M. Hollen, L.Y. Cao, Y. Cui, J.A. Gupta, H.R. Gutiérrez, T.F. Heinz, S.S. Hong, J.X. Huang, A.F. Ismach, H.R. Gutierrez, T.F. Heinz, S.S. Hong, J.X. Huang, A.F. Ismach, E. Johnston-Halperin, M. Kuno, V. V Plashnitsa, R.D. Robinson, R.S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M.G. Spencer, M. Terrones, W. Windl, and J.E. Goldberger, "Progress, challenges, and opportunities in two-dimensional materials beyond graphene," ACS Nano **7**(4), 2898–2926 (2013).
[31] T. Cao, G. Wang, W.P. Han, H.Q. Ye, C.R. Zhu, J.R. Shi, Q. Niu, P.H. Tan, E. Wang, B.L. Liu, and J. Feng, "Valley-selective circular dichroism of monolayer molybdenum disulphide," Nat Commun **3**, (2012).
[32] D. Xiao, G. Bin Liu, W.X. Feng, X.D. Xu, and W. Yao, "Coupled Spin and Valley Physics in Monolayers of MoS2 and Other Group-VI Dichalcogenides," Phys Rev Lett **108**(19), 1–5 (2012).
[33] B.W.H. Baugher, H.O.H. Churchill, Y.F. Yang, and P. Jarillo-Herrero, "Optoelectronic devices based on electrically tunable p-n diodes in a monolayer dichalcogenide," Nat Nanotechnol **9**(4), 262–267 (2014).
[34] C.-H.H. Lee, G.-H.H. Lee, A.M. van der Zande, W.C. Chen, Y.L. Li, M.Y. Han, X. Cui, G. Arefe, C. Nuckolls, T.F. Heinz, J. Guo, J. Hone, and P. Kim, "Atomically thin p–n junctions with van der Waals heterointerfaces," Nat Nanotechnol **9**(9), 676–681 (2014).
[35] A. Pospischil, M.M. Furchi, and T. Mueller, "Solar-energy conversion and light emission in an atomic monolayer p-n diode," Nat Nanotechnol **9**(4), 257–261 (2014).
[36] J.S. Ross, P. Klement, A.M. Jones, N.J. Ghimire, J.Q. Yan, D.G. Mandrus, T. Taniguchi, K. Watanabe, K. Kitamura, W. Yao, D.H. Cobden, and X.D. Xu, "Electrically tunable excitonic light-emitting diodes based on monolayer WSe2 p-n junctions," Nat Nanotechnol **9**(4), 268–272 (2014).

[37] J. V Lauritsen, J. Kibsgaard, S. Helveg, H. Topsoe, B.S. Clausen, E. Laegsgaard, and F. Besenbacher, "Size-dependent structure of MoS2 nanocrystals," Nat Nanotechnol **2**(1), 53–58 (2007).
[38] H. Fang, C. Battaglia, C. Carraro, S. Nemsak, B. Ozdol, J.S. Kang, H.A. Bechtel, S.B. Desai, F. Kronast, A.A. Unal, G. Conti, C. Conlon, G.K. Palsson, M.C. Martin, A.M. Minor, C.S. Fadley, E. Yablonovitch, R. Maboudian, and A. Javey, "Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides," Proc Natl Acad Sci U S A **111**(17), 6198–6202 (2014).
[39] M.-H.H. Chiu, M.-Y.Y. Li, W.J. Zhang, W.-T.T. Hsu, W.-H.H. Chang, M. Terrones, H. Terrones, and L.-J.J. Li, "Spectroscopic Signatures for Interlayer Coupling in MoS2–WSe2 van der Waals Stacking," ACS Nano **8**(9), 9649–9656 (2014).
[40] Y.J. Zhang, T. Oka, R. Suzuki, J.T. Ye, and Y. Iwasa, "Electrically Switchable Chiral Light-Emitting Transistor," Science (1979) **344**(6185), 725–728 (2014).
[41] W.J. Yu, Z. Li, H.L. Zhou, Y. Chen, Y. Wang, Y. Huang, and X.F. Duan, "Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters," Nat Mater **12**(3), 246–252 (2013).
[42] Y. Zhang, J. Ye, Y. Matsuhashi, and Y. Iwasa, "Ambipolar MoS2 Thin Flake Transistors," Nano Lett **12**(3), 1136–1140 (2012).
[43] B. Radisavljevic, M.B. Whitwick, and A. Kis, "Integrated Circuits and Logic Operations Based on Single-Layer MoS2," ACS Nano **5**(12), 9934–9938 (2011).
[44] H. Wang, L.L. Yu, Y.H. Lee, Y.M. Shi, A. Hsu, M.L. Chin, L.J. Li, M. Dubey, J. Kong, and T. Palacios, "Integrated Circuits Based on Bilayer MoS2 Transistors," Nano Lett **12**(9), 4674–4680 (2012).
[45] S. Kim, A. Konar, W.S. Hwang, J.H. Lee, J.H. Lee, J. Yang, C. Jung, H. Kim, J.B. Yoo, J.Y. Choi, Y.W. Jin, S.Y. Lee, D. Jena, W. Choi, and K. Kim, "High-mobility and low-power thin-film transistors based on multilayer MoS2 crystals," Nat Commun **3**, (2012).
[46] T. Roy, M. Tosun, J.S. Kang, A.B. Sachid, S.B. Desai, M. Hettick, C.M.C. Hu, and A. Javey, "Field-Effect Transistors Built from All Two-Dimensional Material Components," ACS Nano **8**(6), 6259–6264 (2014).
[47] L. Britnell, R.M. Ribeiro, A. Eckmann, R. Jalil, B.D. Belle, A. Mishchenko, Y.J. Kim, R. V Gorbachev, T. Georgiou, S. V Morozov, A.N. Grigorenko, A.K. Geim, C. Casiraghi, A.H. Castro Neto, and K.S. Novoselov, "Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films," Science (1979) **340**(6138), 1311–1314 (2013).
[48] M. Bernardi, M. Palummo, and J.C. Grossman, "Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials," Nano Lett **13**(8), 3664–3670 (2013).
[49] K. Roy, M. Padmanabhan, S. Goswami, T.P. Sai, G. Ramalingam, S. Raghavan, and A. Ghosh, "Graphene-MoS2 hybrid structures for multifunctional photoresponsive memory devices," Nat Nanotechnol **8**(11), 826–830 (2013).
[50] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, and A. Kis, "Ultrasensitive photodetectors based on monolayer MoS2," Nat Nanotechnol **8**(7), 497–501 (2013).
[51] W.J. Zhang, C.P. Chuu, J.K. Huang, C.H. Chen, M.L. Tsai, Y.H. Chang, C.T. Liang, Y.Z. Chen, Y.L. Chueh, J.H. He, M.Y. Chou, and L.J. Li, "Ultrahigh-Gain Photodetectors Based on Atomically Thin Graphene-MoS2 Heterostructures," Sci Rep **4**, (2014).

[52] D.S. Tsai, D.H. Lien, M.L. Tsai, S.H. Su, K.M. Chen, J.J. Ke, Y.C. Yu, L.J. Li, and J.H. He, "Trilayered MoS2 Metal-Semiconductor-Metal Photodetectors: Photogain and Radiation Resistance," IEEE Journal of Selected Topics in Quantum Electronics **20**(1), (2014).
[53] M.L. Tsai, S.H. Su, J.K. Chang, D.S. Tsai, C.H. Chen, C.I. Wu, L.J. Li, L.J. Chen, and J.H. He, "Monolayer MoS2 Heterojunction Solar Cells," ACS Nano **8**(8), 8317–8322 (2014).
[54] S. Das, R. Gulotty, A. V Sumant, and A. Roelofs, "All Two-Dimensional, Flexible, Transparent, and Thinnest Thin Film Transistor," Nano Lett **14**(5), 2861–2866 (2014).
[55] G.-H.H. Lee, Y.-J.J. Yu, X. Cui, N. Petrone, C.C.-H.C.C.H. Lee, M.S. Choi, D.-Y.Y. Lee, C.C.-H.C.C.H. Lee, W.J. Yoo, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, and J. Hone, "Flexible and Transparent MoS2 Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures," ACS Nano **7**(9), 7931–7936 (2013).
[56] J. Yoon, W. Park, G.Y. Bae, Y. Kim, H.S. Jang, Y. Hyun, S.K. Lim, Y.H. Kahng, W.K. Hong, B.H. Lee, and H.C. Ko, "Highly Flexible and Transparent Multilayer MoS2 Transistors with Graphene Electrodes," Small **9**(19), 3295–3300 (2013).
[57] F.K. Perkins, A.L. Friedman, E. Cobas, P.M. Campbell, G.G. Jernigan, and B.T. Jonker, "Chemical Vapor Sensing with Mono layer MoS2," Nano Lett **13**(2), 668–673 (2013).
[58] H.P. Komsa, and A. V Krasheninnikov, "Two-Dimensional Transition Metal Dichalcogenide Alloys: Stability and Electronic Properties," Journal of Physical Chemistry Letters **3**(23), 3652–3656 (2012).
[59] Y.F. Chen, J.Y. Xi, D.O. Dumcenco, Z. Liu, K. Suenaga, D. Wang, Z.G. Shuai, Y.-S.S. Huang, and L.M. Xie, "Tunable band gap photoluminescence from atomically thin transition-metal dichalcogenide alloys," ACS Nano **7**(5), 4610–4616 (2013).
[60] Y.J. Gong, Z. Liu, A.R. Lupini, G. Shi, J.H. Lin, S. Najmaei, Z. Lin, A.L. Elias, A. Berkdemir, G. You, H. Terrones, M. Terrones, R. Vajtai, S.T. Pantelides, S.J. Pennycook, J. Lou, W. Zhou, P.M. Ajayan, A.L. Elías, A. Berkdemir, and G. You, "Band gap engineering and layer-by-layer mapping of selenium-doped molybdenum disulfide," Nano Lett **14**(2), 442–449 (2014).
[61] X.L. Wei, H. Zhang, G.C. Guo, X.B. Li, W.M. Lau, and L.M. Liu, "Modulating the atomic and electronic structures through alloying and heterostructure of single-layer MoS2," J Mater Chem A Mater **2**(7), 2101–2109 (2014).
[62] Y.N. Liu, R. Ghosh, D. Wu, A. Ismach, R. Ruoff, and K.J. Lai, "Mesoscale Imperfections in MoS2 Atomic Layers Grown by a Vapor Transport Technique," Nano Lett **14**(8), 4682–4686 (2014).
[63] A.M. van der Zande, P.Y. Huang, D.A. Chenet, T.C. Berkelbach, Y.M. You, G.H. Lee, T.F. Heinz, D.R. Reichman, D.A. Muller, and J.C. Hone, "Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide," Nat Mater **12**(6), 554–561 (2013).
[64] X.L. Zou, Y.Y. Liu, and B.I. Yakobson, "Predicting Dislocations and Grain Boundaries in Two-Dimensional Metal-Disulfides from the First Principles," Nano Lett **13**(1), 253–258 (2013).
[65] S. Najmaei, M. Amani, M.L. Chin, Z. Liu, A.G. Birdwell, T.P. O'Regan, P.M. Ajayan, M. Dubey, and J. Lou, "Electrical Transport Properties of Polycrystalline Monolayer Molybdenum Disulfide," ACS Nano **8**(8), 7930–7937 (2014).
[66] Q. Yue, S.L. Chang, S.Q. Qin, and J.B. Li, "Functionalization of monolayer MoS2 by substitutional doping: A first-principles study," Phys Lett A **377**(19–20), 1362–1367 (2013).
[67] B.H. Kim, M. Park, M. Lee, S.J. Baek, H.Y. Jeong, M. Choi, S.J. Chang, W.G. Hong, T.K. Kim, H.R. Moon, Y.W. Park, N. Park, and Y. Jun, "Effect of sulphur vacancy on geometric and electronic structure of MoS2 induced by molecular hydrogen treatment at room temperature," RSC Adv **3**(40), 18424–18429 (2013).

[68] J.Y. Tan, A. Avsar, J. Balakrishnan, G.K.W. Koon, T. Taychatanapat, E.C.T. O'Farrell, K. Watanabe, T. Taniguchi, G. Eda, A.H.C. Neto, and B. Ozyilmaz, "Electronic transport in graphene-based heterostructures," Appl Phys Lett **104**(18), (2014).
[69] S.J. Yuan, R. Roldan, M.I. Katsnelson, and F. Guinea, "Effect of point defects on the optical and transport properties of MoS2 and WS2," Phys Rev B **90**(4), (2014).
[70] S.J. Wi, M.K. Chen, H. Nam, A.C. Liu, E. Meyhofer, and X.G. Liang, "High blue-near ultraviolet photodiode response of vertically stacked graphene-MoS2-metal heterostructures," Appl Phys Lett **104**(23), (2014).
[71] I.S. Kim, V.K. Sangwan, D. Jariwala, J.D. Wood, S. Park, K.-S.S. Chen, F. Shi, F. Ruiz-Zepeda, A. Ponce, M. Jose-Yacaman, V.P. Dravid, T.J. Marks, M.C. Hersam, and L.J. Lauhon, "Influence of Stoichiometry on the Optical and Electrical Properties of Chemical Vapor Deposition Derived MoS2," ACS Nano **8**(10), 10551–10558 (2014).
[72] M.R. Islam, N. Kang, U. Bhanu, H.P. Paudel, M. Erementchouk, L. Tetard, M.N. Leuenberger, and S.I. Khondaker, "Tuning the electrical property via defect engineering of single layer MoS2 by oxygen plasma," Nanoscale **6**(17), 10033–10039 (2014).
[73] M. Yamamoto, T.L. Einstein, M.S. Fuhrer, and W.G. Cullen, "Anisotropic Etching of Atomically Thin MoS2," The Journal of Physical Chemistry C **117**(48), 25643–25649 (2013).
[74] S.W. Han, Y.H. Hwang, S.-H.H. Kim, W.S. Yun, J.D. Lee, M.G. Park, S. Ryu, J.S. Park, D.-H.H. Yoo, S.-P.P. Yoon, S.C. Hong, K.S. Kim, and Y.S. Park, "Controlling Ferromagnetic Easy Axis in a Layered MoS2 Single Crystal," Phys Rev Lett **110**(24), 247201 (2013).
[75] O. Ochedowski, K. Marinov, N. Scheuschner, A. Poloczek, B.K. Bussmann, J. Maultzsch, and M. Schleberger, "Effect of contaminations and surface preparation on the work function of single layer MoS2," Beilstein Journal of Nanotechnology **5**, 291–297 (2014).
[76] K. Dolui, I. Rungger, and S. Sanvito, "Origin of the n-type and p-type conductivity of MoS2 monolayers on a SiO2 substrate," Phys Rev B **87**(16), 165402 (2013).
[77] H.C. Diaz, R. Addou, and M. Batzill, "Interface properties of CVD grown graphene transferred onto MoS2(0001)," Nanoscale **6**(2), 1071–1078 (2014).
[78] A. Ebnonnasir, B. Narayanan, S. Kodambaka, and C. V Ciobanu, "Tunable MoS2 bandgap in MoS2-graphene heterostructures," Appl Phys Lett **105**(3), 31603 (2014).
[79] X.D. Li, S. Yu, S.Q. Wu, Y.H. Wen, S. Zhou, and Z.Z. Zhu, "Structural and Electronic Properties of Superlattice Composed of Graphene and Monolayer MoS2," Journal of Physical Chemistry C **117**(29), 15347–15353 (2013).
[80] P. Afanasiev, "Synthetic approaches to the molybdenum sulfide materials," Comptes Rendus Chimie **11**(1–2), 159–182 (2008).
[81] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I. V Shvets, S.K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G.T. Kim, G.S. Duesberg, T. Hallam, J.J. Boland, J.J. Wang, J.F. Donegan, J.C. Grunlan, G. Moriarty, A. Shmeliov, R.J. Nicholls, J.M. Perkins, E.M. Grieveson, K. Theuwissen, D.W. McComb, P.D. Nellist, and V. Nicolosi, "Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials," Science (1979) **331**(6017), 568–571 (2011).
[82] J. Xia, X. Huang, L.Z. Liu, M. Wang, L. Wang, B. Huang, D.D. Zhu, J.J. Li, C.Z. Gu, and X.M. Meng, "CVD synthesis of large-area, highly crystalline MoSe2 atomic layers on diverse substrates and application to photodetectors," Nanoscale **6**(15), 8949–8955 (2014).
[83] X. Ling, Y.H. Lee, Y.X. Lin, W.J. Fang, L.L. Yu, M.S. Dresselhaus, and J. Kong, "Role of the Seeding Promoter in MoS2 Growth by Chemical Vapor Deposition," Nano Lett **14**(2), 464–472 (2014).

[84] Y.H. Lee, L.L. Yu, H. Wang, W.J. Fang, X. Ling, Y.M. Shi, C.T. Lin, J.K. Huang, M.T. Chang, C.S. Chang, M. Dresselhaus, T. Palacios, L.J. Li, and J. Kong, "Synthesis and Transfer of Single-Layer Transition Metal Disulfides on Diverse Surfaces," Nano Lett **13**(4), 1852–1857 (2013).
[85] Y.F. Zhang, Y.F. Zhang, Q.Q. Ji, J. Ju, H.T. Yuan, J.P. Shi, T. Gao, D.L. Ma, M.X. Liu, Y.B. Chen, X.J. Song, H.Y. Hwang, Y. Cui, and Z.F. Liu, "Controlled Growth of High-Quality Monolayer WS2 Layers on Sapphire and Imaging Its Grain Boundary," ACS Nano **7**(10), 8963–8971 (2013).
[86] S. Najmaei, Z. Liu, W. Zhou, X.L. Zou, G. Shi, S.D. Lei, B.I. Yakobson, J.C. Idrobo, P.M. Ajayan, and J. Lou, "Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers," Nat Mater **12**(8), 754–759 (2013).
[87] N. Imanishi, K. Kanamura, and Z. Takehara, "Synthesis of MoS2 Thin Film by Chemical Vapor Deposition Method and Discharge Characteristics as a Cathode of the Lithium Secondary Battery," J Electrochem Soc **139**(8), 2082–2087 (1992).
[88] W.Y. Ge, K. Kawahara, M. Tsuji, and H. Ago, "Large-scale synthesis of NbS2 nanosheets with controlled orientation on graphene by ambient pressure CVD," Nanoscale **5**(13), 5773–5778 (2013).
[89] M.Y. Lin, C.E. Chang, C.H. Wang, C.F. Su, C. Chen, S.C. Lee, and S.Y. Lin, "Toward epitaxially grown two-dimensional crystal hetero-structures: Single and double MoS2/graphene hetero-structures by chemical vapor depositions," Appl Phys Lett **105**(7), (2014).
[90] M. Okada, T. Sawazaki, K. Watanabe, T. Taniguch, H. Hibino, H. Shinohara, and R. Kitaura, "Direct Chemical Vapor Deposition Growth of WS 2 Atomic Layers on Hexagonal Boron Nitride," ACS Nano **8**(8), 8273–8277 (2014).
[91] M. Genut, L. Margulis, R. Tenne, and G. Hodes, "Effect of substrate on growth of WS2 thin films," Thin Solid Films **219**(1–2), 30–36 (1992).
[92] S. Helveg, J. V Lauritsen, E. Laegsgaard, I. Stensgaard, J.K. Norskov, B.S. Clausen, H. Topsoe, and F. Besenbacher, "Atomic-scale structure of single-layer MoS2 nanoclusters," Phys Rev Lett **84**(5), 951–954 (2000).
[93] Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan, and J. Lou, "Large-Area Vapor-Phase Growth and Characterization of MoS 2 Atomic Layers on a SiO 2 Substrate," Small **8**(7), 966–971 (2012).
[94] M.R. Laskar, L. Ma, S. Kannappan, P. Sung Park, S. Krishnamoorthy, D.N. Nath, W. Lu, Y. Wu, and S. Rajan, "Large area single crystal (0001) oriented MoS 2," Appl Phys Lett **102**(25), 252108 (2013).
[95] R. Gatensby, N. McEvoy, K. Lee, T. Hallam, N.C. Berner, E. Rezvani, S. Winters, M. O'Brien, and G.S. Duesberg, "Controlled synthesis of transition metal dichalcogenide thin films for electronic applications," Appl Surf Sci **297**, 139–146 (2014).
[96] I. Song, C. Park, M. Hong, J. Baik, H.J. Shin, and H.C. Choi, "Patternable Large-Scale Molybdenium Disulfide Atomic Layers Grown by Gold-Assisted Chemical Vapor Deposition," Angewandte Chemie-International Edition **53**(5), 1266–1269 (2014).
[97] T.P. Prasad, E. Diemann, and A. Müller, "Thermal decomposition of (NH4)2MoO2S2, (NH4)2MoS4, (NH4)2WO2S2 and (NH4)2WS4," Journal of Inorganic and Nuclear Chemistry **35**(6), 1895–1904 (1973).
[98] A. Adeogun, M. Afzaal, and P. O'Brien, "Studies of Molybdenum Disulfide Nanostructures Prepared by AACVD Using Single-Source Precursors," Chemical Vapor Deposition **12**(10), 597–599 (2006).

[99] K.-K.K. Liu, W.J. Zhang, Y.-H.H. Lee, Y.-C.C. Lin, M.-T.T. Chang, C.-Y. Su, C.-S.S. Chang, H. Li, Y.M. Shi, H. Zhang, C.S. Lai, and L.J. Li, "Growth of large-area and highly crystalline MoS2 thin layers on insulating substrates," Nano Lett **12**(3), 1538–1544 (2012).
[100] Y. Shi, W. Zhou, A.-Y. Lu, W. Fang, Y.-H. Lee, A.L. Hsu, S.M. Kim, K.K. Kim, H.Y. Yang, L.-J. Li, J.-C. Idrobo, and J. Kong, "van der Waals Epitaxy of MoS 2 Layers Using Graphene As Growth Templates," Nano Lett **12**(6), 2784–2791 (2012).
[101] J.R. Lince, and P.D. Fleischauer, "Crystallinity of rf-sputtered MoS 2 films," J Mater Res **2**(6), 827–838 (1987).
[102] C. Müller, C. Menoud, M. Maillat, and H.E. Hintermann, "Thick compact MoS2 coatings," Surf Coat Technol **36**(1–2), 351–359 (1988).
[103] C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M.L. Jespersen, P.J. Shamberger, M.E. McConney, R.D. Naguy, and A.A. Voevodin, "Continuous ultra-thin MoS 2 films grown by low-temperature physical vapor deposition," Appl Phys Lett **104**(26), 261604 (2014).
[104] S. Wu, C. Huang, G. Aivazian, J.S. Ross, D.H. Cobden, and X. Xu, "Vapor–Solid Growth of High Optical Quality MoS 2 Monolayers with Near-Unity Valley Polarization," ACS Nano **7**(3), 2768–2772 (2013).
[105] W.K. Hsu, B.H. Chang, Y.Q. Zhu, W.Q. Han, H. Terrones, M. Terrones, N. Grobert, A.K. Cheetham, H.W. Kroto, and D.R.M. Walton, "An Alternative Route to Molybdenum Disulfide Nanotubes," J Am Chem Soc **122**(41), 10155–10158 (2000).
[106] B.R. Carvalho, and M.A. Pimenta, "Resonance Raman spectroscopy in semiconducting transition-metal dichalcogenides: Basic properties and perspectives," 2d Mater **7**(4), (2020).
[107] M.A. Pimenta, E. del Corro, B.R. Carvalho, C. Fantini, and L.M. Malard, "Comparative Study of Raman Spectroscopy in Graphene and MoS 2 -type Transition Metal Dichalcogenides," Acc Chem Res **48**(1), 41–47 (2015).
[108] J.U. Lee, K. Kim, S. Han, G.H. Ryu, Z. Lee, and H. Cheong, "Raman Signatures of Polytypism in Molybdenum Disulfide," ACS Nano **10**(2), 1948–1953 (2016).
[109] B.C. Windom, W.G. Sawyer, and D.W. Hahn, "A raman spectroscopic study of MoS 2 and MoO 3: Applications to tribological systems," Tribol Lett **42**(3), 301–310 (2011).
[110] J.L. Verble, and T.J. Wieting, "Lattice mode degeneracy in MoS2 and other layer compounds," Phys Rev Lett **25**(6), 362–365 (1970).
[111] G.L. Frey, R. Tenne, M.J. Matthews, M.S. Dresselhaus, and G. Dresselhaus, "Raman and resonance Raman investigation of MoS2 nanoparticles," Phys Rev B Condens Matter Mater Phys **60**(4), 2883–2892 (1999).
[112] T.J. Wieting, "Long-wavelength lattice vibrations of MoS2 and GaSe," Solid State Commun **12**(9), 931–935 (1973).
[113] S. Najmaei, Z. Liu, P.M. Ajayan, and J. Lou, "Thermal effects on the characteristic Raman spectrum of molybdenum disulfide (MoS 2) of varying thicknesses," Appl Phys Lett **100**(1), 013106 (2012).
[114] A. Aleman, C. Li, H. Zaid, H. Kindlund, J. Fankhauser, S. V. Prikhodko, M.S. Goorsky, and S. Kodambaka, " Ultrahigh vacuum dc magnetron sputter-deposition of epitaxial Pd(111)/Al 2 O 3 (0001) thin films ," Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **36**(3), 030602 (2018).
[115] K. Tanaka, J. Fankhauser, H. Zaid, A. Aleman, M. Sato, D. Yu, A. Ebnonnasir, C. Li, M. Kobashi, M.S. Goorsky, and S. Kodambaka, "Kinetics of Zr-Al intermetallic compound formation during ultra-high vacuum magnetron sputter-deposition of Zr/Al2O3(0001) thin films," Acta Mater **152**, 34–40 (2018).

[116] K. Tanaka, A. Aleman, M.E. Liao, Y. Wang, M.S. Goorsky, and S. Kodambaka, "Effects of ultra-low ethylene partial pressure on microstructure and composition of reactively sputter-deposited Ta–C thin films," Thin Solid Films **688**(July), 137440 (2019).
[117] R. Yan, J.R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. Wu, A. Kis, T. Luo, A.R. Hight Walker, and H.G. Xing, "Thermal Conductivity of Monolayer Molybdenum Disulfide Obtained from Temperature-Dependent Raman Spectroscopy," ACS Nano **8**(1), 986–993 (2014).
[118] Y. Wang, C. Cong, C. Qiu, and T. Yu, "Raman Spectroscopy Study of Lattice Vibration and Crystallographic Orientation of Monolayer MoS 2 under Uniaxial Strain," Small **9**(17), 2857–2861 (2013).
[119] B. Chakraborty, H.S.S.R. Matte, A.K. Sood, and C.N.R. Rao, "Layer-dependent resonant Raman scattering of a few layer MoS 2," Journal of Raman Spectroscopy **44**(1), 92–96 (2013).
[120] H. Li, Q. Zhang, C.C.R. Yap, B.K. Tay, T.H.T. Edwin, A. Olivier, and D. Baillargeat, "From bulk to monolayer MoS 2: Evolution of Raman scattering," Adv Funct Mater **22**(7), 1385–1390 (2012).
[121] N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton, E. Smith, D. Flahaut, M. Greiner, M. Biesinger, S. Tougaard, D. Morgan, and J. Baltrusaitis, "Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy," Applied Surface Science Advances **5**, 100112 (2021).
[122] D.A. Shirley, "High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold," Phys Rev B **5**(12), 4709–4714 (1972).
[123] K. Tanaka, A. Aleman, H. Zaid, M.E. Liao, K. Hojo, Y. Wang, M.S. Goorsky, and S. Kodambaka, "Ultra-high vacuum dc magnetron sputter-deposition of 0001-textured trigonal α-Ta2C/Al2O3(0001) thin films," Materialia (Oxf) **13**, 100838 (2020).
[124] M.E. Straumanis, and R.P. Shodhan, "Lattice Constants, Thermal Expansion Coefficients and Densities of Molybdenum and the Solubility of Sulphur, Selenium and Tellurium in it at 1100°C," International Journal of Materials Research **59**(6), 490–493 (1968).
[125] K.D. Bronsema, J.L. De Boer, and F. Jellinek, "On the structure of molybdenum diselenide and disulfide," ZAAC - Journal of Inorganic and General Chemistry **540**(9–10), 15–17 (1986).
[126] L. Brewer, and R.H. Lamoreaux, "The Mo-S system (Molybdenum-Sulfur)," Bulletin of Alloy Phase Diagrams **1**(2), 93–95 (1980).
[127] W.M. Parkin, A. Balan, L. Liang, P.M. Das, M. Lamparski, C.H. Naylor, J.A. Rodríguez-Manzo, A.T.C. Johnson, V. Meunier, and M. Drndić, "Raman Shifts in Electron-Irradiated Monolayer MoS 2," ACS Nano **10**(4), 4134–4142 (2016).
[128] S. Mignuzzi, A.J. Pollard, N. Bonini, B. Brennan, I.S. Gilmore, M.A. Pimenta, D. Richards, and D. Roy, "Effect of disorder on Raman scattering of single-layer Mo S2," Phys Rev B Condens Matter Mater Phys **91**(19), 1–7 (2015).
[129] C. Rice, R.J. Young, R. Zan, U. Bangert, D. Wolverson, T. Georgiou, R. Jalil, and K.S. Novoselov, "Raman-scattering measurements and first-principles calculations of strain-induced phonon shifts in monolayer MoS2," Phys Rev B Condens Matter Mater Phys **87**(8), 1–5 (2013).
[130] B. Chakraborty, A. Bera, D.V.S. Muthu, S. Bhowmick, U. V Waghmare, and A.K. Sood, "Symmetry-dependent phonon renormalization in monolayer MoS 2 transistor," Phys Rev B **85**(16), 161403 (2012).
[131] C. Lee, H. Yan, L.E. Brus, T.F. Heinz, J. Hone, and S. Ryu, "Anomalous lattice vibrations of single- and few-layer MoS2," ACS Nano **4**(5), 2695–2700 (2010).
[132] S. Ishihara, K. Suda, Y. Hibino, N. Sawamoto, T. Ohashi, S. Yamaguchi, K. Matsuura, H. Machida, M. Ishikawa, H. Sudoh, H. Wakabayashi, and A. Ogura, "Evaluation of Sputtering

Deposited 2-Dimensional MoS 2 Film by Raman Spectroscopy," MRS Proceedings **1781**(100), 11–16 (2015).
[133] S. Ishihara, Y. Hibino, N. Sawamoto, K. Suda, T. Ohashi, K. Matsuura, H. Machida, M. Ishikawa, H. Sudoh, H. Wakabayashi, and A. Ogura, "Improving crystalline quality of sputtering-deposited MoS2 thin film by postdeposition sulfurization annealing using (t-C4H9)2S2," Jpn J Appl Phys **55**(4S), 04EJ07 (2016).
[134] N.T. McDevitt, J.S. Zabinski, M.S. Donley, and J.E. Bultman, " Disorder-Induced Low-Frequency Raman Band Observed in Deposited MoS 2 Films ," Appl Spectrosc **48**(6), 733–736 (1994).
[135]"NIST X-ray Photoelectron Spectroscopy Database, Version 4.1 (National Institute of Standards and Technology, Gaithersburg, 2012)," (n.d.).
[136] A. Deshpande, K. Hojo, K. Tanaka, P. Arias, H. Zaid, M. Liao, M. Goorsky, and S.K. Kodambaka, "hBN-Layer-Promoted Heteroepitaxy in Reactively Sputter-Deposited MoSx≈2(0001)/Al2O3(0001) Thin Films: Implications for Nanoelectronics," ACS Appl Nano Mater, (2023).
[137] B. Schönfeld, J.J. Huang, and S.C. Moss, "Anisotropic mean-square displacements (MSD) in single-crystals of 2H- and 3R-MoS2," Acta Crystallographica Section B **39**(4), 404–407 (1983).

FIGURES

Figure 1. Symmetric 2θ:ω X-ray diffraction (XRD) data plotted on a logarithmic scale, obtained from samples sputter deposited in Ar + H_2S atmosphere on Al_2O_3(0001) substrates, with p_{H_2S} (partial pressure of H_2S during sputter deposition) = 0%, 0.01%, 0.1%, and 1% (black, green, blue, and red curves) of total gas pressure (2.67 Pa). Film reflections from Mo and MoS_x are labeled as shown while substrate reflections are denoted by **s**. A portion of the red curve is adapted with permission from A. Deshpande, K. Hojo, K. Tanaka, P. Arias, H. Zaid, M. Liao, M. Goorsky, and S.K. Kodambaka, ACS Appl Nano Mater, (2023). Copyright (2023) American Chemical Society.

Figure 2. Raman spectra obtained from MoS_x samples sputter deposited with $p_{H_2S} = 2.67 \times 10^{-3}$ Pa (blue) and 2.67×10^{-2} Pa (red), acquired with a 633 nm wavelength laser and plotted on a logarithmic scale. The first order modes – E^1_{2g} (~382 cm^{-1}, red curve; ~380 cm^{-1} blue curve) and A_{1g} (~408 cm^{-1}, red curve; ~412 cm^{-1}, blue curve) are visible in both curves along with second order modes excited due to resonant Raman scattering – $A_{1g} \pm$ LA(M), 2LA(M) + A_{2u}. The LA(M) mode at (~227 cm^{-1}, blue curve; ~229 cm^{-1}, red curve) associated with defects, is observed in both curves but with a reduced relative intensity (with respect to the characteristic A_{1g} peak) for the red curve. The difference in the peak positions $\Delta\omega = E^1_{2g} - A_{1g}$ for both samples is also labeled. Red curve is reprinted with permission from A. Deshpande, K. Hojo, K. Tanaka, P. Arias, H. Zaid, M. Liao, M. Goorsky, and S.K. Kodambaka, ACS Appl Nano Mater, (2023). Copyright (2023) American Chemical Society.

Figure 3. X-ray photoelectron spectra (XPS) obtained from air-exposed Mo-S films deposited with p_{H_2S} = (a) 2.67×10^{-3} Pa (blue) and (b) 2.67×10^{-2} Pa (red). Open symbols are raw data while Gaussian-Lorentzian (GL (30)) fits to the data, carried out after a Shirley background (green dashes) subtraction are shown in solid lines – dark green for Mo +4 (MoS_x) and brown for Mo +6 (MoO_3). For $p_{H_2S} = 2.67 \times 10^{-3}$ Pa, we determine the film S-content as ~64 at.% and it is more oxidized in comparison to the sample sputter-deposited using $p_{H_2S} = 2.67 \times 10^{-2}$ Pa, whose composition is $MoS_{2.0\pm0.1}$. Red curve is reprinted with permission from A. Deshpande, K. Hojo, K. Tanaka, P. Arias, H. Zaid, M. Liao, M. Goorsky, and S.K. Kodambaka, ACS Appl Nano Mater, (2023). Copyright (2023) American Chemical Society.